College Chemistry
Instructor Guide

PASCO®

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College Chemistry

Instructor Guide
21^{st} Century Science

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Contents

This lab guide contains both PASCO activities and *ODYSSEY* molecular simulations, which supplement the activities of selected topics.

PASCO Activities

Introduction

PASCO scientific's probeware and laboratory investigations move students from the low-level task of memorization of science facts to higher-level tasks of data analysis, concept construction, and application. For science to be learned at a deep level, it is essential to combine the teaching of abstract science concepts with "real-world" science investigations. Hands-on, technology-based, laboratory experiences serve to bridge the gap between the theoretical and the concrete, driving students toward a greater understanding of natural phenomenon. Students also gain important science process skills that include: developing and using models, carrying out investigations, interpreting data, and using mathematics.

At the foundation of teaching science are a set of science standards that clearly define the science content and concepts, the instructional approach, and connections among the science disciplines. The Next Generation Science Standards (2012)© are a good example of a robust set of science standards.

The Next Generation Science Standards (NGSS) position student inquiry at the forefront. The standards integrate and enhance science, technology, engineering, and math (STEM) concepts and teaching practices. Three components comprise these standards: Science and Engineering Practices, Disciplinary Core Ideas, and Crosscutting Concepts. The lab activities in PASCO’s 21st Century Science Guides are all correlated to the NGSS (see http://pasco.com).

- The *Science and Engineering Practices* help students to develop a systematic approach to problem solving that builds in complexity from kindergarten to their final year in high school. The practices integrate organization, mathematics and interpretive skills so that students can make data-based arguments and decisions.
- *Disciplinary Core Ideas* are for the physical sciences, life sciences, and earth and space sciences. The standards are focused on a limited set of core ideas to allow for deep exploration of important concepts. The core ideas are an organizing structure to support acquiring new knowledge over time and to help students build capacity to develop a more flexible and coherent understanding of science.
- *Crosscutting Concepts* are the themes that connect all of the sciences, mathematics and engineering. As students advance through school, rather than experiencing science as discrete, disconnected topics, they are challenged to identify and practice concepts that cut across disciplines, such as "cause and effect". Practice with these concepts that have broad application helps enrich students' understanding of discipline-specific concepts.

PASCO’s lab activities are designed so that students complete guided investigations that help them learn the scientific process and explore a core topic of science, and then are able to design and conduct extended inquiry investigations. The use of electronic sensors reduces the time for data collection, and increases the accuracy of results, providing more time in the classroom for independent investigations.

In addition to supporting the scientific inquiry process, the lab activities fulfill STEM education requirements by bringing together science, technology, engineering, and math. An integration of these areas promotes student understanding of each of these fields and develops their abilities to become self-reliant researchers and innovators. When faced with an idea or problem, students learn to develop, analyze, and evaluate possible solutions. Then collaborate with others to construct and test a procedure or product.

Information and computer tools are essential to modern lab activities and meeting the challenge of rigorous science standards, such as NGSS. The use of sensors, data analysis and graphing tools, models and simulations, and work with instruments, all support the science and engineering practices as implemented in a STEM-focused curriculum, and are explicitly cited in NGSS. PASCO's lab activities provide students with hands-on and minds-on learning experiences, making it possible for them to master the scientific process and the tools to conduct extended scientific investigations.

About the College Science Lab Manual

This manual presents teacher-developed laboratory activities using current technologies to help you and your students explore topics, develop scientific inquiry skills. Using electronic-sensor data collection, display and analysis devices in your classroom fulfills STEM requirements and provides several benefits. Sensor data collection allows students to:

- observe phenomena that occur too quickly or are too small, occur over too long a time span, or are beyond the range of observation by unaided human senses
- perform measurements with equipment that can be used repeatedly over the years
- collect accurate data with time and/or location stamps
- rapidly collect, graphically display, and analyze data so classroom time is used effectively
- practice using equipment and interpreting data produced by equipment that is similar to what they might use in their college courses and adult careers

The Data Collection System

"Data collection system" refers to PASCO's DataStudio®, the Xplorer GLX™, SPARKvue™, and SPARK Science Learning System™ and PASCO Capstone™. Each of these can be used to collect, display, and analyze data in the various lab activities.

Activities are designed so that any PASCO data collection system can be used to carry out the procedure. The DataStudio, Xplorer GLX, SPARKvue, or SPARK Science Learning System Tech Tips provide the steps on how to use the data collection system and are available on the storage device that came with your manual. For assistance in using PASCO Capstone, refer to its help system.

Getting Started with Your Data Collection System

To help you and your students become familiar with the many features of your data collection system, start with the tutorials and instructional videos that are available on PASCO's website (www.pasco.com).

Included on the storage device accompanying your manual is a Scientific Inquiry activity that acts as a tutorial for your data collection system. Each data collection system (except for PASCO Capstone) has its own custom Scientific Inquiry activity. The activity introduces students to the process of conducting science investigations, the scientific method, and introduces instructors and students to the commonly used features of their data collection system. Start with this activity to become familiar with the data collection system.

Instructor and Student Guide Contents

All the instructor and student materials are included on the storage device accompanying the instructor's lab manual.

Lab Experiment Components

Each activity has two components: Instructor Information and Student Inquiry Worksheets.

Instructor Information is in the instructor's version of the lab manual. It contains information on selecting, planning, and implementing a lab, as well as the complete student version with answer keys. Instructor Information includes all sections of a lab activity, including objectives, procedural overview, time requirements, and materials and equipment at-a-glance.

Student Inquiry Worksheets begin with a driving question, providing students with a consistent scientific format that starts with formulating a question to be answered in the process of conducting a scientific investigation.

This table identifies the sections in each of these two activity components.

INSTRUCTOR INFORMATION	STUDENT INQUIRY WORKSHEET
Objectives	Driving Questions
Procedural Overview	Background
Time Requirement	Pre-Lab Activity
Materials and Equipment	Materials and Equipment
Concepts Students Should Already Know	
Related Labs in This Guide	
Using Your Data Collection System	
Background	
Pre-Lab Activity	
Lab Preparation	
Safety	Safety
Sequencing Challenge	Sequencing Challenge
Procedure With Inquiry	Procedure (+ conceptual questions)
Data Analysis	Data Analysis
Analysis Questions	Analysis Questions
Synthesis Questions	Synthesis Questions
Multiple Choice Questions	Multiple Choice Questions
Extended Inquiry Suggestions	

Electronic Materials

The storage device accompanying this manual contains the following:

- Complete instructor and student versions of the lab manual (with Student Inquiry Worksheets in PDF format).
- The Scientific Inquiry activity for SPARK™, SPARKvue™, Xplorer GLX®, and DataStudio® and the Student Inquiry Worksheets for the laboratory activities are in an editable Microsoft™ Word format. PASCO provides editable files of the student lab activities so that instructors can customize activities to their needs.
- Tech Tips for the SPARK, SPARKvue, Xplorer GLX, DataStudio, and individual sensor technologies in PDF format.
- User guides for SPARKvue and GLX.
- DataStudio and PASCO Capstone® Help is available in the software application itself.

Using ODYSSEY Molecular Labs

Wavefunction's ODYSSEY is a unique software program for use in chemistry classes. With ODYSSEY students can use scientifically based simulations to experiment with core chemistry topics from a molecular perspective. The software enhances and complements the hands-on, experiential PASCO activities in this manual.

ODYSSEY includes a collection of ready-to-use chemistry experiments called “Molecular Labs” and student worksheets. A number of the Molecular Labs applicable to the PASCO activities are identified under selected topic areas in the table of contents. The student worksheets for these labs are provided in the ODYSSEY Molecular Labs section of this manual and the answer key can be found on the accompanying storage device. A fully functional 60-day licensed version of the ODYSSEY Instructor Edition, containing the complete set of ODYSSEY’s Molecular Labs, is included with this manual.

In addition to the Molecular Labs, ODYSSEY provides:

Prelabs which serve as tutorials – ideal learning about how to use the program

Applied Chemistry – a collection of chemistry samples commonly encountered in modern society

Molecular Stockroom – the electronic equivalent of your chemistry stockroom with more than a thousand pre-constructed samples spanning the periodic table

To successfully get started with ODYSSEY, check the system requirements and install the software that is on the accompanying ODYSSEY storage device; use the activation code provided to access the software for 60 days. Contact PASCO (www.pasco.com) for information on instructor and student licensing.

About Correlations to Science Standards

The lab activities in this manual are correlated to a number of standards, including United States National Science Education Standards, the Next Generation Science Standards, and all State Science Standards. See http://pasco.com for the correlations.

Global Number Formats and Standard Units

Throughout this guide, the International System of Units (SI) or metric units is used unless specific measurements, such as air pressure, are conventionally expressed otherwise. In some instances, such as weather parameters, it may be necessary to alter the units used to adapt the material to conventions typically used and widely understood by the students.

Reference

NGSS Lead States. 2013. Next Generation Science Standards: For States, By States. Washington, DC: The National Academies Press.

Normal Laboratory Safety Procedures

Overview

PASCO is concerned with your safety and because of that, we are providing a few guidelines and precautions to use when exploring the labs in our Chemistry guide. This is a list of general guidelines only; it is by no means all-inclusive or exhaustive. Of course, common sense and standard laboratory safety practices should be followed.

Regarding chemical safety, some of the substances and chemicals referred to in this manual are regulated under various safety laws (local, state, national, or international). Always read and comply with the safety information available for each substance or chemical to determine its proper storage, use and disposal.

Since handling and disposal procedures vary, our safety precautions and disposal comments are generic. Depending on your lab, instruct students on proper disposal methods. Each of the lab activities also has a Safety section for procedures necessary for that experiment.

General Lab Safety Procedures and Precautions

- Follow all standard laboratory procedures.
- Absolutely no food, drink, or chewing gum is allowed in the lab.
- Keep water away from electrical outlets.
- Wear eye protection (splash-proof goggles), lab apron, and protective gloves.
- Do not touch your face with gloved hands. If you need to sneeze or scratch, take off your gloves, wash your hands, and then take care of the situation. Do not leave the lab with gloves on.
- Wash your hands after handling chemicals, glassware, and equipment.
- Know the safety features of your lab such as eye-wash stations, fire extinguisher, first-aid equipment or emergency phone use.
- Insure that loose hair and clothing is secure when in the lab.
- Handle glassware with care.
- Insure you have adequate clear space around your lab equipment before starting an experiment.
- Do not wear open toe shoes or short pants in the laboratory.
- Allow heated objects and liquids to return to room temperature before moving.
- Never run or joke around in the laboratory.
- Do not perform unauthorized experiments.

- Students should use a buddy system in case of trouble.

- Keep the work area neat and free from any unnecessary objects.

Water Related Safety Precautions and Procedures

- Keep water away from electrical outlets.

- Keep water away from all electronic equipment.

Chemical Related Safety Precautions and Procedures

- Consult the manufacturer's Material Safety Data Sheets (MSDS) for instructions on handling, storage, and disposing of chemicals. Your instructor should provide the MSDS sheets of the chemicals you are using. Keep these instructions available in case of accidents.

- Many chemicals are hazardous to the environment and should not be disposed of down the drain. Always follow your instructor’s instructions for disposing of chemicals.

- Sodium hydroxide, hydrochloric acid, sulfuric acid, and acetic acid are corrosive irritants. Avoid contact with your eyes and wash your hands after handling. In case of skin exposure, wash it off with plenty of water.

- Always add acids and bases to water, not the other way around, as the solutions may boil vigorously.

- Diluting acids and bases creates heat; be extra careful when handling freshly prepared solutions and glassware, as they may be very hot.

- Handle concentrated acids and bases in a fume hood; the fumes are caustic and toxic.

- Wear eye protection, lab apron, and protective gloves when handling acids. Splash-proof goggles are recommended. Either latex or nitrile gloves are suitable. Use nitrile gloves if you have latex allergy.

- Read labels on all chemicals and pay particular attention to hazard icons and safety warnings.

- When handling any bacterial species, follow aseptic techniques.

- Wash your hands before and after a laboratory session.

- If any solution comes in contact with skin or eyes, rinse immediately with a copious amount of running water for a minimum of 15 minutes.

- Follow the instructor’s instructions for disposing of chemicals.

- Check the label to verify it is the correct substance before using it.

- Never point the open end of a test tube containing a substance at yourself or others.

- Use a wafting motion when smelling chemicals.

- Do not return unused chemicals to their original container.

- Keep flammable chemicals from open flame.

Dangerous or Harmful Substance Related Lab Safety Precautions

- When handling any bacterial species, follow aseptic techniques.
- Always flame inoculating loops and spreaders before setting them down on the lab bench.
- Pipetting suspension cultures can create an aerosol. Keep your nose and mouth away from the tip of the pipet to avoid inhaling any aerosol
- Use caution when working with acids.
- Use appropriate caution with the matches, burning splint and foods, and other hot materials.
- Be careful using a knife or scalpel.

Other Safety Precautions

- If water is boiled for an experiment involving heat, make sure it is never left unattended. Remember, too, that the hot plate will stay hot well after it is unplugged or turned off.
- Any injury must be reported immediately to the instructor; an accident report has to be completed by the student or a witness.
- If you are suffering from any allergy, illness, or are taking any medication, you must inform the instructor. This information could be very important in an emergency.
- Try to avoid wearing contact lenses. If a solution spills in your eye, the presence of a contact lens makes first aid difficult and can result in permanent damage. Also, organic solvents tend to dissolve in soft contact lenses, causing eye irritation.

Additional Resources

- Flinn Scientific
- The Laboratory Safety Institute (LSI)
- National Science Education Leadership Association (NSELA)/Safe Science Series

Master Materials and Equipment List

Italicized entries indicate items not available from PASCO. The quantity indicated is per student or group. NOTE: These activities also require protective gear for each student (for example, safety goggles, gloves, apron, or lab coat).

Instructors can conduct some lab activities with sensors other than those listed here. For assistance with substituting compatible sensors for a lab experiment, contact PASCO Instructor Support (800-772-8700 inside the United States or http://www.pasco.com/support).

Lab	Title	Materials and Equipment	Qty
Chemical Composition and Stoichiometry			
1	**Determining the Empirical Formula of a Compound** Use a crucible and Bunsen burner to react a chemical with air in order to determine the stoichiometric composition of an ionic compound.	*Crucible with lid*	1
		Ring stand	1
		Bunsen burner	1
		Balance	1 per class
		Crucible tongs	1
		Wash bottle with deionized water	1
		Clay triangle	1
		Paper clip	1
		Magnesium powder	0.5 g
2	**Determine the Percentage of Water in a Hydrate** Use a crucible and Bunsen burner to determine the water content of a hydrated salt.	*Crucible with lid*	1
		Ring stand	1
		Bunsen burner	1
		Balance	1
		Crucible tongs	1
		Wash bottle with deionized water	1 per class
		Clay triangle	1
		Copper sulfate, $CuSO_4$, hydrated	4.5 g
3	**Mole Relationships in a Chemical Reaction** Use a conductivity sensor to determine the stoichiometric coefficients of the reactants of a chemical reaction.	Data Collection System	1
		PASPORT Conductivity Sensor	1
		Test tubes, 15-mL	9
		Beaker, 100-mL	1
		Graduated pipet, 10-mL	2
		Pipet bulb	1
		Test tube rack	1
		Unknown solution (use potassium chromate)	50 mL
		0.01 M Silver nitrate ($AgNO_3$)	50 mL
		Wash bottle with deionized water	1
		Parafilm®	1
		Marking pen	1

Lab	Title	Materials and Equipment	Qty
4	**Gravimetric Determination of a Precipitate** Use a stainless steel temperature sensor with gravimetric analysis to determine the amount of sulfate in a sample of an unknown alkali sulfate.	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		Ring stand with ring	1
		Clamp, utility	1
		Clamp, buret	1
		Crucible with lid	1
		Tongs	1
		Beaker, glass, 400-mL	1
		Beaker, glass, 250-mL	1
		Beaker, 25-mL	3
		Beaker or flask, 400-mL,	1
		Graduated cylinder, 100-mL	1
		Graduated cylinder, 10-mL	1
		Buret, 50 mL	1
		Funnel	1
		Dropper	1
		Hot plate	1
		Bunsen burner	1
		Clay triangle	1
		0.5 M Barium chloride ($BaCl_2$)	30 mL
		0.1 M Silver nitrate ($AgNO_3$)	5 mL
		6 M Hydrochloric acid (HCl)	5 mL
		Unknown alkali sulfate (use K_2SO_4 and Na_2SO_4)	0.35 g
		Filter paper, Whatman® Ashless, #42	1
		Rubber policeman and stirring rod	1
		Watch glass, 100-mm	1
		Distilled water	100 mL
		Wash bottle with distilled water	1
5	**Identifying an Unknown Metal** Use an absolute pressure sensor and stainless steel temperature sensor to identify an unknown metal by applying the Ideal Gas Law.	Data Collection System	1
		PASPORT Absolute Pressure Sensor	1
		PASPORT Stainless Steel Temperature Sensor	1
		PASPORT Sensor Extension Cable	1
		Quick-release connector**	1
		Tubing connector**	1
		Tubing, 1- to 2-cm**	1
		Graduated cylinder, 10-mL or 25-mL	1
		Graduated cylinder, 250-mL	1
		Erlenmeyer flask, 250-mL	1
		Beaker, 1500-mL	1
		Balance	1 per class
		Rubber stopper with one hole	1
		3 M Hydrogen chloride (HCl)	100 mL
		Unknown metal, 0.2 g (use magnesium ribbon)	3 pieces
		Electrical tape	1 roll

Lab	Title	Materials and Equipment	Qty
6	**Synthesis of a Coordination Compound** Use a series of reactions to synthesize a coordination compound, potassium aluminum sulfate dodecahydrate (alum), and calculate the theoretical and percent yields.	Balance	1 per class
		Hot plate	1
		Fume hood	1
		Beaker, 400-mL	1
		Beaker, 250-mL	2
		Beaker, 100-mL	1
		Graduated cylinder, 50-mL	1
		Büchner funnel	1
		Büchner filter flask	1
		Stirring rod, glass	1
		Watch glass	1
		Scissors	1
		Beaker tongs	1
		Filter paper	3
		Wire gauze	1
		3 M Sulfuric acid (H_2SO_4)	35 mL
		3 M Potassium hydroxide (KOH)	25 mL
		50% Ethanol	50 mL
		100% Ethanol	50 mL
		Acetone (C_3H_6O)	50 mL
		Aluminum foil	1.1 g
		Distilled water for rinsing equipment	1
		Ice	400 mL
7	**Analysis of a Coordination Compound** Use a stainless steel temperature sensor to help confirm the identity of a sample of alum synthesized in Lab 15a by conducting both qualitative and quantitative analyses.	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		Ring stand with ring	1
		Clay triangle	1
		Clamp, buret	1
		Clamp, utility	1
		Crucible with lid	1
		Tongs	1
		Test tubes, 10 mL	2
		Beaker, 250-mL	1
		Capillary tube	1
		Stirring rod	1
		Watch glass, 100-mm	2
		Balance	1 per class
		Centrifuge	1 per class
		Wire with a loop on the end, 4 in.	1
		Hot plate	1
		Bunsen burner	1
		Striker	1
		0.2 M Barium chloride ($BaCl_2$)	1 mL
		6 M Sodium hydroxide (NaOH)	5 mL
		6 M Hydrochloric acid (HCl)	5 mL
		Borax	0.5 g
		Alum from Synthesis of a Coordination Compound experiment	3 g
		Rubber band	1
		Water	200 mL
		Distilled water	10 mL

Lab	Title	Materials and Equipment	Qty
Thermochemistry and Thermodynamics			
8	**Enthalpy of a Chemical Reaction** Use a stainless steel temperature sensor to derive the enthalpy change of a reaction.	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		Polystyrene cup, 8 oz.	1
		Clamp, utility	1
		Beaker, 250-mL	1
		Graduated cylinder, 50-mL or 100-mL	1
		Ring stand	1
		2.00 M Sodium hydroxide (NaOH)	50 mL
		2.00 M Hydrochloric acid (HCl)	50 mL
		2.00 M Ammonium chloride (NH_4Cl)	50 mL
		2.00 M Ammonia (NH_3)	50 mL
Atomic and Nuclear Structure			
9	**Absorption Spectra** Use a spectrometer to learn about the composition of the electromagnetic radiation in the visible range, to develop an understanding of how the interaction of objects and solutions with light result in the perception of color, and to dispel misconceptions of objects "having color."	Data Collection System	1
		PASPORT Sensor Extension Cable	1
		Amadeus Spectrometer System	1
		Glass cuvette with cap**	1
		Test tubes, large	6
		Test tube rack	1
		Graduated cylinder, 10-mL	1
		0.1 M Iron(III) chloride ($FeCl_3$)	10 mL
		0.1 M Copper(II) chloride ($CuCl_2$)	10 mL
		0.1 M Cobalt chloride ($CoCl_2$)	10 mL
		0.1 M Nickel(II) chloride ($NiCl_2$)	10 mL
		0.1 M Sodium chloride (NaCl)	10 mL
		Color chart	1
		Wash bottle with distilled water	1
		Marking pen	1
10	**Determining the Half-Life of an Isotope** Use an alpha beta gamma radiation sensor to investigate the radioactive decay and half-life of an isotope.	Data Collection System	1
		PASPORT Alpha Beta Gamma Radiation Sensor	1
		Isotope Generator Kit (Barium-137m)	1 per class
		Barium-137m solution	1
		Aluminum plate	1

Lab	Title	Materials and Equipment	Qty
Gas Laws			
11	**Determine the Molar Mass of a Volatile Liquid** Use a stainless steel temperature sensor to determine the molar mass of an unknown volatile liquid at the boiling temperature of water and atmospheric pressure.	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		PASPORT Absolute Pressure Sensor	1
		Quick-release connector**	1
		Tubing connector**	1
		Tubing, 1- to 2-cm**	1
		Beaker, 400-mL	2
		Erlenmeyer flask, 125-mL	1
		Graduated cylinder, 100-mL	1
		Hot plate with magnetic stirrer and stir bar	1
		Balance	1 per class
		Ring stand	1
		Clamp	2
		Unknown volatile liquid (use acetone)	8 mL
		Aluminum foil, about 4-cm by 4-cm	1
		Paper towel, sheets	2 or 3
		Dropper	1
		Water	600 mL
12	**Molar Volume of a Gas** Use an absolute pressure sensor and stainless steel temperature sensor to determine the molar volume of a gas by relating pressure, volume, and temperature.	Data Collection System	1
		PASPORT Absolute Pressure Sensor	1
		PASPORT Stainless Steel Temperature Sensor	1
		PASPORT Sensor Extension Cable	1
		Quick-release connector**	1
		Tubing connector**	1
		Tubing, 1- to 2-cm**	1
		Beaker, 600-mL	1
		Erlenmeyer flask, 250-mL	1
		Graduated cylinder, 10-mL or 25-mL	1
		Graduated cylinder, 100-mL	1
		Balance	1 per class
		Rubber stopper with one hole	1
		3 M Hydrochloric acid (HCl)	20 mL
		Magnesium ribbon	about 0.20 g
		Water	300 mL
		Electrical tape (optional)	1 roll

Lab	Title	Materials and Equipment	Qty
13	**Exploring Gas Laws** Use an absolute pressure sensor and stainless steel temperature sensor to explore the relationship between pressure and volume, and pressure and temperature, for a gas.	Data Collection System	1
		PASPORT Absolute Pressure Sensor	1
		PASPORT Sensor Extension Cable	1
		PASPORT Stainless Steel Temperature Sensor	1
		Quick-release connector**	1
		Tubing connector**	1
		Tubing, 1- to 2-cm**	1
		Ring stand	1
		Clamp, utility	1
		Beaker, 1500-mL	1
		Erlenmeyer flask, 250-mL	1
		Syringe, 60-mL	1
		Hot plate with magnetic stirrer and stir bar	1
		Rubber stopper, 2-hole	1
		Glycerin	several drops
		Electrical tape	1 roll
		Water	1200 mL
Intermolecular Forces and States of Matter			
14	**Molecular Interaction in Ethanol and Acetone** Use an absolute pressure sensor and stainless steel temperature sensor to determine and relate the heat of vaporization of substances to the interactions between molecules.	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		PASPORT Absolute Pressure Sensor	1
		PASPORT Sensor Extension Cable	1
		Quick-release connector**	1
		Tubing connector**	1
		Tubing, 1- to 2-cm**	1
		Beaker, 1500-mL	1
		Beaker, 50-mL	1
		Erlenmeyer flask, 250-mL	1
		Graduated cylinder, 50-mL	1
		Hot plate with magnetic stirrer and stirring bar	1
		Clamp, utility	1
		Ring stand	1
		100% Ethanol (C_2H_5OH)	50 mL
		Acetone ($(CH_3)_2CO$)	50 mL
		Rubber stopper, 2-hole	1
		Glycerin	2 drops
		Water	1200 mL

Lab	Title	Materials and Equipment	Qty
Solutions and Solubility			
15	**Molecular Weight by Freezing Point Depression** Use a stainless steel temperature sensor to determine the molecular weight of a compound by measuring the freezing point depression of a solution.	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		Erlenmeyer flask, 250-mL	1
		Beaker, 400-mL	1
		Test tube, 20-mL	1
		Copper wire coil	1
		Ring stand	1
		Hot plate	1
		Stirring bar	1
		Clamp, utility	2
		Lauric acid, $CH_3(CH_2)_{10}COOH$	8 g
		Unknown solute (use benzoic acid)	0.5 g
		Water	300 mL
16	**Colorimetric Analysis** Use a colorimeter to learn how the factors of concentration and path length affect the absorbance of a colored solution.	Data Collection System	1
		PASPORT Colorimeter	1
		PASPORT Sensor Extension Cable**	1
		Glass cuvette with cap**	1
		Beakers, 100-mL	2
		Test tubes, large	6
		Test tube rack	1
		Graduated cylinder, 50-mL	1
		Pipet with pump or bulb 10-mL	1
		Pipet bulb	1
		Glass stirring rod	1
		0.40 M copper(II) sulfate ($CuSO_4$)	30 mL
		Distilled water	30 mL
		Marking pen	1
		Wash bottle with distilled water	1
17	**Separation by Liquid Chromatography** Use liquid chromatography to separate the ingredients of a mixture.	*C18 Sep-Pak® cartridge*	1
		Syringe, 1-mL	1
		Syringe, 10-mL, or dropper bottle or wash bottle	1
		Graduated cylinder, 10-mL	1
		18% Isopropanol	100 mL
		Unsweetened Kool-Aid® drink	10 mL
		Distilled water	10 mL

Lab	Title	Materials and Equipment	Qty
18	**Conductometric Titration** Use a conductivity sensor and drop counter to determine the concentration of a solution with titration.	Data Collection System	1
		PASPORT Conductivity Sensor	1
		PASPORT High Accuracy Drop Counter	1
		Micro stir bar**	1
		Magnetic stirrer	1
		Buret, 50-mL	1
		Beaker, 100-mL	2
		Beaker, 50-mL	1
		Buret or volumetric pipet, 50-mL	1
		Ring stand	1
		Clamp, right-angle	1
		Clamp, buret	1
		0.0200 M H_2SO_4 solution	50 mL
		Barium hydroxide ($Ba(OH)_2$), unknown concentration	50 mL
		Deionized water	50 mL
		Wash bottle with deionized water	1
		Cotton swab or tissue	1
19	**Separation and Analysis of Cations** Use chemical reactions and chemical properties to identify the cations present in a mixture by systematically reacting the unknown with various reagents.	*Test tube, 10-mL*	10
		Test tube rack	1
		Pipet, graduated, 10-mL	1
		Pipet bulb	1
		Pipet, plastic, 1-mL	7
		Centrifuge	1
		Beaker, 250-mL	1
		Evaporating dish	1
		Stirring rod	1
		Hot plate	1
		Litmus paper	10
		pH paper	1 roll
		6 M Sodium hydroxide (NaOH)	20 mL
		6 M Ammonia (NH_3)	20 mL
		0.1 M Potassium chromate (K_2CrO_4)	20 mL
		1% Aluminon dye	2 mL
		6 M Hydrochloric acid (HCl)	20 mL
		Dimethylglyoxime (DMG) reagent	5 drops
		0.2 M Potassium ferrocyanide ($K_4[Fe(CN)_6]$)	2 mL
		3 M Sulfuric acid (H_2SO_4)	3 mL
		3 % Hydrogen peroxide (H_2O_2)	2 mL
		Unknown cation solution (use $AlCl_3$, $NiCl_3$, $Pb(NO_3)_2$, $AgNO_3$, $MnSO_4$, $(NH_4)_2Fe(SO_4)_2$)	20 mL
		Deionized water	5 mL
		Marking pen	1

Lab	Title	Materials and Equipment	Qty
20	**Analysis of Anions** Use chemical reactions and chemical properties to analyze solutions of known anions, using the results to analyze a solution of unknown anions.	*Test tube, 10-mL*	13
		Test tube rack	1
		Pipets, 1 mL, disposable	13
		Stirring rods	5
		Litmus paper	15
		0.2 M Sodium sulfate (Na_2SO_4)	10 mL
		0.2 M Monopotassium phosphate (KH_2PO_4)	5 mL
		0.2 M Sodium nitrate ($NaNO_3$)	5 mL
		0.2 M Sodium chloride (NaCl)	5 mL
		Unknown anion solution (use Na_2SO_4, KH_2PO_4, $NaNO_3$, *NaCl)*	20 mL
		0.2 M Barium nitrate ($Ba(NO_3)_2$)	5 mL
		Saturated iron(II) sulfate ($FeSO_4$)	2 mL
		0.1 M Silver nitrate ($AgNO_3$)	5 mL
		6 M Nitric acid (HNO_3)	5 mL
		5 M Ammonia (NH_3)	5 mL
		3 M Sulfuric acid (H_2SO_4)	5 mL
		Concentrated H_2SO_4	2 mL
		Distilled water	10 mL
		Centrifuge	1
		Marking pen	1
Acid–Base Chemistry			
21	**Standardizing a Solution of Sodium Hydroxide** Use a pH sensor and drop counter to determine the concentration of a sodium hydroxide solution by titrating it with a standard solution of known concentration.	Data Collection System	1
		PASPORT pH Sensor	1
		PASPORT High Accuracy Drop Counter	1
		Micro stir bar**	1
		Magnetic stirrer	1
		Ring stand	1
		Beaker, 250-mL	1
		Beaker, 100-mL	1
		Beaker, 10-mL	2
		Volumetric flask, 250-mL	1
		Buret, 50-mL	1
		Clamp, buret	1
		Clamp, right-angle	1
		Funnel	1
		Potassium hydrogen phthalate (KHP)	0.6 g
		Sodium hydroxide (NaOH)	1.0 g
		Buffers, pH 4 and pH 10	10 mL
		Water, deionized	500 mL
		Wash bottle with deionized water	1
		Parafilm® or aluminum foil	1
		Cotton swab or tissue	1

Lab	Title	Materials and Equipment	Qty
22	**Acid–Base Titration** Use a pH sensor and drop counter to determine the molar concentration of a strong acid solution by titrating measured volumes with a strong base of known concentration.	Data Collection System	1
		PASPORT pH Sensor	1
		PASPORT High Accuracy Drop Counter	1
		Micro stir bar**	1
		Magnetic stirrer	1
		Buret, 50-mL	1
		Graduated pipet, 25-mL	1
		Pipet bulb	1
		Beaker, 100-mL	2
		Beaker, 25-mL	2
		Clamp, right-angle	1
		Clamp, buret	1
		Ring stand	1
		Parafilm® or aluminum foil	1
		Funnel	1
		Hydrochloric acid, unknown concentration	70 mL
		Sodium hydroxide (NaOH), standardized by students in Standardizing a Solution of Sodium Hydroxide experiment	100 mL 10 mL
		Buffers, pH 4 and pH 10	100 mL
		Deionized water	1
		Wash bottle with deionized water	1
		Cotton swab or tissue	1
23	**Using Different Indicators for pH Determination** Use a drop counter and pH sensor to determine the CO_2 content of a beverage by performing titrations with multiple acid-base indicators.	Data Collection System	1
		PASPORT High Accuracy Drop Counter	1
		PASPORT pH Sensor	1
		Micro stir bar**	1
		Clamp, right-angle	1
		Clamp, buret	1
		Buret, 50-mL	1
		Beaker, 25-mL	2
		Beaker, 250-mL	2
		Erlenmeyer flask, 250-mL	1
		Graduated cylinder, 100-mL	1
		Phenolphthalein	5 drops
		Methyl orange	5 drops
		Magnetic stirrer and stir bar	1
		Ring stand	1
		Commercial soda drink	1 can
		Kimwipes®	1
		4.00 M HCl solution	100 mL
		1 M NaOH solution	100 mL
		Wash bottle with deionized water	1
		Funnel	1
		Balloon (fits on Erlenmeyer flask; holds 100 mL)	1
		Buffers, pH 4 and pH 10	10 mL
		Cotton swab or tissue	1

Lab	Title	Materials and Equipment	Qty
24	**Properties of Buffer Solutions** Use a pH sensor to demonstrate the properties of buffer solutions and buffer capacity.	Data Collection System	1
		PASPORT pH Sensor	1
		Beaker, 400-mL	1
		Buret, 50-mL	1
		Pipet, 5-mL	1
		Pipet bulb	1
		Beaker, 100-mL	1
		Beaker, 25-mL	2
		Graduated cylinder, 250-mL	1
		Magnetic stirrer and stirring bar	1
		Ring stand	1
		Clamp, buret	1
		Clamp, utility	1
		Funnel	1
		2.000 M Sodium hydroxide (NaOH)	250 mL
		0.1 M Acetic acid (HOAc)	250 mL
		0.3 M Acetic acid (HOAc)	250 mL
		0.5 M Acetic acid (HOAc)	250 mL
		6.00 M Hydrochloric acid (HCl)	5 mL
		Buffers, pH 4 and pH 10	10 mL
		Wash bottle with deionized water	1
25	**Determining K_a by Half-Titration of a Weak Acid** Use a pH sensor and drop counter to determine the equilibrium constant for the ionization of a weak acid to ascertain the identity of the acid.	Data Collection System	1
		PASPORT pH Sensor	1
		PASPORT High Accuracy Drop Counter	1
		Ring stand	1
		Clamp, right-angle	1
		Clamp, buret	1
		Beaker, 100-mL	2
		Buret, 50-mL	1
		Graduated cylinder, 100-mL	1
		Funnel	1
		Magnetic stirrer and stir bar	1
		0.20 M Sodium hydroxide (NaOH)	75 mL
		Unknown weak acid solution (use acetic acid)	50 mL
		Buffer solutions, pH 4 and pH 10	10 mL

Lab	Title	Materials and Equipment	Qty
26	**Determination of the K_a Values of Two Isomeric Multi-Protic Acids** Use a pH sensor and drop counter to determine the acidity constants of two isomeric multi-protic acids and relate the acidity constants to their structural differences.	Data Collection System	1
		PASPORT pH Sensor	1
		PASPORT High Accuracy Drop Counter	1
		Micro stir bar**	1
		Ring stand	1
		Clamp, right-angle	1
		Clamp, buret	1
		Beaker, 250-mL	2
		Beaker, 25-mL	2
		Buret , 50-mL	1
		Graduated cylinder, 100-mL	1
		Magnetic stirrer	1
		Unidentified fumaric acid solution	50 mL
		Unidentified maleic acid solution	50 mL
		0.500 M Sodium hydroxide (NaOH)	150 mL
		Funnel	1
		Buffers, pH 4 and pH 10	10 mL
		Wash bottle with deionized water	1
		Cotton swab or tissue	1
	Kinetics and Equilibrium		
27	**Determine the Equilibrium Constant for a Chemical Reaction** Use a colorimeter to determine the equilibrium constant for a chemical reaction.	Data Collection System	1
		PASPORT Colorimeter and cuvette	1
		PASPORT Sensor Extension Cable**	1
		Beaker, 50-mL	2
		Test tube, 15-mL	5
		Test tube rack	1
		Graduated pipet, 10-mL	2
		Pipet bulb	1
		0.01 M Iron (Fe^{3+})	20 mL
		0.00300 M Potassium thiocyanate (KSCN)	20 mL
		Kimwipes®	1
		Deionized water	40 mL
		Marker	1
28	**Determination of the Rate of the Decomposition of Hydrogen Peroxide** Use an absolute pressure sensor and stainless steel temperature sensor to determine the rate constant of a chemical reaction.	Data Collection System	1
		PASPORT Absolute Pressure Sensor	1
		PASPORT Stainless Steel Temperature Sensor	1
		PASPORT Sensor Extension Cable	1
		Quick-release connector**	1
		Tubing connector**	1
		Tubing, 1- to 2-cm**	1
		Beaker, 100-mL	3
		Erlenmeyer flask, 250-mL	1
		Graduated pipet, 25-mL	3
		Pipet bulb	3
		Stopper, two holes, for the Erlenmeyer flask	1
		Beaker, 50-mL	1
		Glycerin	several drops
		0.1000 M Potassium iodide (KI)	60 mL
		3% Hydrogen peroxide (H_2O_2)	40 mL
		Deionized water	100 mL
		Electrical tape, 60 in. (optional)	1

Lab	Title	Materials and Equipment	Qty
29	**Determination of a Solubility Product** Use a pH sensor and drop counter to determine the solubility product of an ionic compound through titration and calculations.	Data Collection System	1
		PASPORT pH Sensor	1
		PASPORT High Accuracy Drop Counter	1
		Micro stir bar**	1
		Ring stand	1
		Clamp, buret	1
		Clamp, right-angle	1
		Beaker, 100-mL	1
		Beaker, 150-mL	2
		Beaker, 25-mL	2
		Pipet, graduated or volumetric, 50-mL	1
		Pipet bulb	1
		Buret, 50-mL	1
		Büchner filter flask	1
		Büchner funnel	1
		Pipet, transfer	1
		Filter paper	1
		Magnetic stirrer	1
		0.1000 M Hydrochloric acid (HCl)	200 mL
		Calcium hydroxide ($Ca(OH)_2$), saturated	200 mL
		Buffers, pH 4 and pH 10	10 mL
		Wash bottle with distilled water	1
		Parafilm® or aluminum foil	1
		Cotton swab or tissue	1
30	**Order of Reaction** Use a colorimeter to determine the rate constant and the order of reaction.	Data Collection System	1
		PASPORT Colorimeter	1
		PASPORT Sensor Extension Cable**	1
		Glass cuvette with cap**	1
		Beaker, 50-mL	3
		Syringe, 5-mL	3
		Watch glass, 4 in	1
		0.1 M Sodium hydroxide (NaOH)	20 mL
		1.2×10^{-5} M Crystal violet	20 mL
		Water, distilled	30 mL
		Marking pen	1
		Kimwipes®	1

Lab	Title	Materials and Equipment	Qty
		Electrochemistry	
31	**Oxidation–Reduction Titration** Use an oxidation reduction potential electrode and drop counter to determine the concentration of a commercial, nominally 3% hydrogen peroxide solution, measuring the change in potential during an oxidation-reduction reaction.	Data Collection System	1
		PASPORT Chemistry Sensor	1
		PASPORT Oxidation Reduction Potential Electrode	1
		PASPORT High Accuracy Drop counter	1
		Magnetic stirrer and stir bar	1
		Buret, 50-mL	1
		Beaker, 150-mL	2
		Volumetric pipet, 10-mL	1
		Pipet bulb	1
		Graduated cylinder, 50-mL	1
		Clamp, right-angle	1
		Clamp, buret	1
		Ring stand	1
		Hydrogen peroxide, ~ 3%, 1:20 dilution	40 mL
		1.000×10^{-2} M Potassium permanganate ($KMnO_4$)	100 mL
		4 M Sulfuric acid (H_2SO_4)	70 mL
		Water, deionized	250 mL
32	**Determination of Electrochemical Series** Use a voltage sensor to determine the half-reactions that relate to the anode and cathode of a galvanic cell and to calculate the electromotive force for a battery.	Data Collection System	1
		PASPORT Voltage Sensor	1
		Beaker, 50-mL	6
		Glass plate (5 × 5 in)	1
		Disposable droppers, 1 mL	6
		Iron strip, 1-cm × 1-cm	1
		Lead strip, 1-cm × 1-cm	1
		Copper strip, 1-cm × 1-cm	1
		Silver wire, 1-cm	1
		Zinc strip, 1-cm × 1-cm	1
		Circular filter paper, 11-cm diameter	1
		1.0 M Zinc sulfate ($ZnSO_4$)	10 mL
		1.0 M Iron sulfate ($FeSO_4$)	10 mL
		1.0 M Copper sulfate ($CuSO_4$)	10 mL
		1.0 M Silver nitrate ($AgNO_3$)	10 mL
		1.0 M Lead nitrate ($Pb(NO_3)_2$)	10 mL
		1.0 M Sodium nitrate ($NaNO_3$)	20 mL
		Steel wool	1
		Scissors	1

Lab	Title	Materials and Equipment	Qty
33	**Electroplating** Use a voltage-current sensor to construct an electrochemical cell that deposits copper onto another metal surface and to apply Faraday's law to relate the total electric charge to the mass of metal deposited.	Data Collection System	1
		PASPORT Voltage–Current sensor	1
		DC power supply	1
		Banana plug cords, red	2
		Banana plug cord, black	1
		Alligator clip, red	1
		Alligator clip, black	1
		Ring stand	1
		Clamps	2
		Beaker, 100-mL	1
		Magnetic stir plate	1
		Balance	1
		Metal object (key or spoon)	1
		Copper strip or heavy gauge copper wire (3 in)	1
		1.0 M Copper sulfate ($CuSO_4$)	50 mL
		Steel wool	1
		Electrical tape	1
		Paper towel	1 sheet
		Magnetic stirring bar	1
34	**The Breathalyzer™ Test for Alcohol** Use a colorimeter to determine the concentration of an ethanol solution using the Breathalyzer™ test: chemical oxidation of ethanol by acidic dichromate.	Data Collection System	1
		PASPORT Colorimeter	1
		PASPORT Sensor Extension Cable**	1
		Glass cuvette with cap**	1
		Erlenmeyer flask, 125-mL	7
		Volumetric flask, 100-mL	1
		Graduated pipet, 10-mL	1
		Graduated pipet, 5-mL	1
		Pipet, plastic, 1-mL	1
		Graduated cylinder, 100-mL	1
		Beaker, 25-mL	2
		Beaker, 100-mL	1
		Beaker, 400-mL	2
		Beaker, 250-mL	1
		Beaker, 1-L	1
		Ring stand	1
		Clamps, utility	2
		Hot plate	1
		15% Sulfuric acid (H_2SO_4)	800 mL
		Silver nitrate ($AgNO_3$)*, 15%*	10 mL
		5.10×10^{-2} *M Potassium dichromate* ($K_2Cr_2O_7$)	30 mL
		Ethanol solution, unknown concentration	5 mL
		Marking pen	1
		Wash bottle with distilled water	1

Lab	Title	Materials and Equipment	Qty
Organic Chemistry			
35	**Organic Synthesis I—Preparation** Use a stainless steel temperature sensor to synthesize an organic compound (aspirin).	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		Ring stand	1
		Clamp	2
		Erlenmeyer flask, 125-mL	1
		Graduated cylinder, 10-mL	1
		Beaker, 100-mL	1
		Beaker, 400-mL	1
		Hot plate	1
		Büchner filter flask	1
		Büchner funnel	1
		Filter paper	1
		Salicylic acid ($C_7H_6O_3$)	2 g
		Acetic anhydride ($C_4H_6O_3$)	4 mL
		Concentrated phosphoric acid (H_3PO_4)	1 mL
		Wash bottle with distilled water	1
		Eye dropper	1
		Rubber policeman	1
		Ice cold distilled water	50 mL
		Ice for ice bath	300 mL
		Forceps	1

Lab	Title	Materials and Equipment	Qty
36	**Organic Synthesis II—Analysis** Use a stainless steel temperature sensor, pH sensor, and drop counter to perform qualitative and quantitative analytical methods, including melting point determination and titration, to analyze the purity of the aspirin synthesized in Lab 22a.	Data Collection System	1
		PASPORT Stainless Steel Temperature Sensor	1
		PASPORT pH Sensor	1
		PASPORT High Accuracy Drop Counter	1
		Micro stir bar**	1
		Ring stand	1
		Clamp, utility	1
		Clamp, right-angle	1
		Clamp, buret	1
		Beaker, 150-mL	2
		Beaker, 100-mL	1
		Beaker, 25-mL	2
		Test tubes, 15-mL	3
		Melting point capillary tube	1
		Buret, 50-mL	1
		Graduated cylinder, 100-mL	1
		Magnetic stirrer and stir bar	1
		Hot plate with magnetic stirrer and stir bar	1
		Mortar and pestle	1
		Product from Organic Synthesis I experiment	1
		Aspirin tablet	1
		Ethanol	15 mL
		0.1 M Sodium hydroxide (NaOH)	75 mL
		1% Iron chloride ($FeCl_3$)	2 mL
		Mineral oil	150 mL
		Buffers, pH 4 and pH 10	10 mL
		Water, distilled	100 mL
		Rubber band, small	1
		Wash bottle with deionized water	1

*Either the PASPORT Fast Response Temperature Sensor or the PASPORT Stainless Steel Temperature Sensor can be used for this experiment.

** These items are included with the specific apparatus or sensor used in the experiment.

Calibration materials

If you want to calibrate various sensors, you will need the following:

pH Sensor

Item	Quantity	Where Used
Buffer solution, pH 4 Buffer solution, pH 10 Beaker, small Wash bottle with deionized or distilled water	25 mL 25 mL 3 1	21, 22, 23, 24, 25, 26, 29, 36

Colorimeter

Item	Quantity	Where Used
Cuvette (included with colorimeter) Distilled water	1 7 mL	16, 27, 30, 34

Experiment by PASCO Equipment

This list shows the sensors and other PASCO equipment used in the lab activities.

Items Available from PASCO	Qty	Experiment Where Used
Data Collection System	1	3, 4, 5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36
PASPORT Alpha Beta Gamma Radiation Sensor	1	10
PASPORT Absolute Pressure Sensor[1]	1	5, 11, 12, 13, 14, 28
PASPORT Colorimeter	1	16, 27, 30, 34
PASPORT Conductivity Sensor	1	3, 18
PASPORT High Accuracy Drop Counter	1	18, 21, 22, 25, 26, 29, 31, 36
PASPORT Oxidation-Reduction Potential Electrode	1	31
PASPORT pH Sensor[1]	1	21, 22, 23, 24, 25, 26, 29, 36
PASPORT Sensor Extension Cable	1	5, 9, 12, 13, 14, 16, 27, 28, 30, 34
PASPORT Stainless Steel Temperature Sensor[1]	1	4, 5, 7, 8, 11, 12, 13, 14, 15, 28, 35, 36
PASPORT Voltage Sensor[1]	1	32
PASPOST Voltage–Current Sensor	1	33
Amadeus Spectrometer System	1	9
Isotope Generator Kit (Barium-137m)	1	10

[1] This sensor is part of the PASPORT Chemistry Sensor, a MultiMeasure Sensor™

Chemical Composition and Stoichiometry

1. Determining the Empirical Formula of a Compound

Objectives

Students determine the stoichiometric composition of an ionic compound.

Procedural Overview

Students gain experience conducting the following procedures using a balance and a Bunsen burner to:

- Perform a reaction under controlled conditions—heating a metal to form the metal oxide
- Eliminate the byproduct of a reaction and convert it to a desired product
- Determine the change in mass to find the stoichiometric composition of the metal oxide

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	180 minutes

Materials and Equipment

For each student or group:

- Crucible with lid
- Ring stand
- Bunsen burner
- Balance (1 per class)
- Crucible tongs
- Wash bottle with deionized water
- Clay triangle
- Paper clip
- Magnesium powder, 0.5 g[1]

[1] Refer to the Lab Preparation section for alternate forms of magnesium.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- The meaning of a chemical formula
- Balancing chemical equations
- The composition of air

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Percent Water in a Hydrate
- Synthesis of a Coordination Compound

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Note: As this lab experiment does not use a data collection system, no Tech Tips (indicated by the symbol "�" and a superscripted number following a step) are needed.

Background

The empirical formula of a compound is the simplest whole number ratio of the elements in the compound. The stoichiometric ratio of the different types of atoms in a compound is given by that ratio of whole numbers. One mole of a substance has the number of moles of different types of atoms in the same ratio as the stoichiometric ratio.

For example, the formula H_2O reflects a 2:1 stoichiometric ratio between hydrogen and oxygen atoms. Also, one mole of H_2O molecules has a 2:1 molar ratio between the total number of hydrogen and oxygen atoms. That is, there are 2 moles of hydrogen and 1 mole of oxygen atoms in 1 mole of H_2O molecules.

The empirical formula of a compound can be determined if the amount of each element in the compound can be experimentally determined. This process requires three steps: determining the mass of each element in the compound; calculating the number of moles of each element in the sample; and expressing the molar ratio of each element as the smallest whole number.

Pre-Lab Experiment

Setting the stage for the experiment

Molecular oxygen is very reactive, whether in pure form or in a mixture such as air. The most abundant component of air, nitrogen, is relatively unreactive. An element reacting with oxygen forms an oxide. For example, magnesium and oxygen form magnesium oxide:

$$x\,\mathrm{Mg} + \frac{y}{2}\mathrm{O_2} \rightarrow \mathrm{Mg}_x\mathrm{O}_y$$

The reaction of nitrogen with an element forms a nitride. Oxygen has a greater reactivity than nitrogen, therefore the oxide is more likely to form.

In this experiment, you will burn magnesium (Mg) in air to form magnesium oxide and magnesium nitride. The magnesium nitride will be converted to magnesium hydroxide and ammonia by adding water. Upon heating, the magnesium hydroxide will be converted to magnesium oxide with the release of water vapor.

$$3\mathrm{Mg(s)} + \mathrm{N_2(g)} \rightarrow \mathrm{Mg_3N_2(s)} \qquad (1)$$

$$\mathrm{Mg_3N_2(s)} + 6\mathrm{H_2O(l)} \rightarrow 3\mathrm{Mg(OH)_2(aq)} + 2\mathrm{NH_3(g)}$$

$$\mathrm{Mg(OH)_2(aq)} + \text{heat} \rightarrow \mathrm{MgO(s)} + \mathrm{H_2O(g)}$$

Example calculation to try

Chemical analysis of a solid found it contains 1.76 g of aluminum and 1.57 g of oxygen. The simplest whole number ratio was found to be 2:3. Therefore the empirical formula is Al_2O_3 for aluminum oxide.

$$\frac{1.76\ \text{g Al}}{26.98\ \frac{\text{g}}{\text{mol}}\ \text{Al}} = 0.0652\ \text{mol Al}$$

$$\frac{1.57\ \text{g O}}{16.00\ \frac{\text{g}}{\text{mol}}\ \text{O}} = 0.0981\ \text{mol O}$$

The molar ratio between the Al and O is

$$\left(\frac{0.0652\ \text{mol Al}}{0.0652\ \text{mol Al}}\right):\left(\frac{0.0981\ \text{mol O}}{0.0652\ \text{mol Al}}\right) = 1.00\ \text{mol Al} : 1.50\ \text{mol O}$$

$$= 2.00\ \text{mol Al} : 3.00\ \text{mol O}$$

Therefore, the empirical formula is Al_2O_3.

1. Based on the information in the Background section, propose a chemical equation for the reaction between Mg and O_2. (Hint: Refer to Equation 1 between Mg and N_2).

$2\mathrm{Mg} + \mathrm{O_2} \rightarrow 2\mathrm{MgO}$

2. What stoichiometric ratio do you expect between the Mg and O? Why?

Mg : O = 1 : 1

Equation 1 suggests that nitrogen has a –3 charge and magnesium has a +2 charge in its compounds. Also, knowing that oxygen has a –2 charge in oxides would suggest a 1:1 ratio between Mg and O.

3. The N_2 molecule is extremely stable, yet it appears to react with Mg in this experiment. Propose an explanation for the reaction between Mg and N_2. (Hint: Think about the amount of energy required to break the bonds in a stable molecule.)

The Mg burns at an extremely high temperature, releasing sufficient energy to break up the N_2 molecule.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. Magnesium powder is best because it oxidizes most readily. Magnesium chips will also work. Magnesium ribbon is acceptable but is difficult to oxidize. If ribbon is used, loosely wind the ribbon around itself into a spiral to improve oxidation. With magnesium ribbon, you may need sandpaper or steel wool to clean it.
2. Explain to students how the Bunsen burner works and how the air flow can be controlled.

Safety

Add these important safety precautions to your normal laboratory procedures:

- Be very careful when using the Bunsen burner.
- Never place a hot crucible or other hot objects on a balance pan.
- Do not move the hot crucible from the clay triangle until it has cooled.
- Make sure there is nothing flammable around the setup.

Procedure with Inquiry

Note: This experiment does not use a data collection system, so there are no Tech Tips (indicated by the symbol "�" and a superscripted number following a step).

1. Obtain a crucible and lid, and inspect the crucible for cracks, nicks, and other defects.

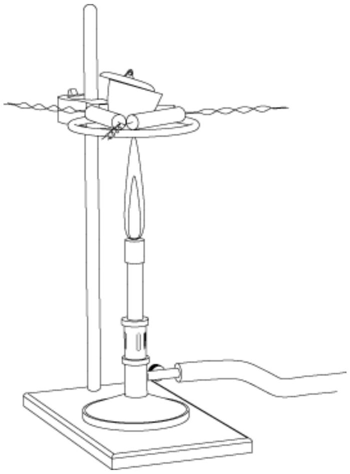
Note: Replace a defective crucible.

2. Measure and record the mass of the crucible and lid in Table 1.

3. You will be heating the crucible before the experiment is performed. Why is it necessary to heat the crucible before performing the experiment?

Heating eliminates error from such things as contamination or moisture that may be present in the crucible. These could change the mass of the crucible.

4. Prepare the crucible as follows:



- **a.** Place the crucible and lid on the clay triangle over the Bunsen burner. Make sure the lid is slightly ajar.
- **b.** Heat the crucible with a gentle flame for 5 minutes by moving the burner around the bottom of the crucible.
- **c.** After the bottom of the crucible has become red-hot, increase the flame by allowing more air into the burner.
- **d.** Continue moving the burner around the bottom of the crucible.
- **e.** Heat the crucible for 10 to 12 minutes.
- **f.** Allow the crucible to cool to room temperature.

Note: For the rest of the experiment handle the crucible and lid using only crucible tongs. Also, do not set the crucible on the lab bench or it may crack or become contaminated.

5. Why do you have to use tongs to hold the lid?

Touching the lid with bare hands contaminates the lid and changes its mass, introducing error in the mass measurement. Also, the crucible may still be hot and cause injury.

6. After the crucible has cooled, measure and record the mass of the "fired" crucible together with its lid in Table 1.

Table 1: Mass of the empty crucible measured to the nearest milligram

Measurement	Trial 1	Trial 2
Crucible and lid before heating (g)	28.233	30.213
Crucible and lid after the first heating (g)	28.230	30.211
Crucible and lid after the second heating (g)	28.231	30.210
Crucible and lid after the third heating (g)		
Crucible and lid after the fourth heating (g)		

7. Repeat the steps above for heating, cooling, and measuring the mass of the crucible and lid until you have two readings for the mass that are within 10 mg of each other.

8. Copy the last measurement in Table 1 into Table 3.

Collect Data

9. Obtain between 0.17 and 0.23 g of magnesium powder or chips. (Magnesium ribbon is acceptable, although it does not burn as easily.)

10. Add the magnesium sample to the crucible.

Note: If magnesium ribbon is used, you may need to clean it first with sandpaper or steel wool until it is bright and shiny. Also, wind the magnesium ribbon into a loose spiral so that it will fit into the crucible and oxidize.

11. Measure the mass of the crucible, lid, and magnesium to the nearest milligram and record it in Table 3.

12. Return the crucible, with the sample and lid, to the clay triangle over the Bunsen burner.

13. To react all of the metal:

a. Gently heat the sample for 2 to 3 minutes by moving the burner around the bottom of the crucible.

b. Increase the heat and continue heating until the sample starts to glow.

Note: Remember that the top third of the flame is the hottest.

c. Continue moving the burner around the bottom of the crucible.

d. Manage the burning so the magnesium glows for about 3 minutes:

Do not remove the lid. Using the crucible tongs, slightly lift the lid for a few seconds to admit air into the crucible.

Note: Quickly cover the crucible with the lid if the metal bursts into flame. When done correctly, the content of the crucible will begin to glow.

e. Continue heating for about 3 more minutes, carefully lifting the lid to observe the contents of the crucible.

f. When the bright glow of the contents of the crucible turns to a pale glow, stop the heating.

g. Allow the crucible to cool to room temperature with the lid in place.

h. Using the tongs to lift the lid, break the crust over the contents of the crucible with a straightened paper clip.

i. Hold the lid with the tongs and mix the contents carefully so that any unreacted metal comes to the surface.

Note: Make sure no residue remains on the paper clip.

14. Why do you need to bring the unreacted metal to the surface?

Bringing the unreacted metal to the surface allows it to be exposed to the air, and therefore to oxygen, for the next time the sample is heated.

15. Repeat all parts of the step, "To react all of the metal," until no unreacted metal is visible.

16. When the sample has cooled and no metal is present, use the squeeze bottle to add three drops of deionized water.

17. By wafting the air towards your nose over the crucible, try to identify and describe the smell.

Ammonia has a distinct pungent odor that irritates the sense of smell.

18. Heat the crucible and sample again. It takes a considerable amount of time and heat to decompose $Mg(OH)_2$ to MgO and H_2O.

a. With the lid slightly open to allow water vapor to escape, begin heating the crucible and sample over a gentle flame for about 3 minutes.

b. Gradually increase the heat, being careful not to let the crucible heat up too fast such that water spatters out.

c. Continue at high heat for about 15 to 20 minutes, carefully lifting the lid to observe the contents of the crucible.

d. When the sample has a pale glow, stop the heating.

e. Allow the crucible to cool to room temperature with the lid in place.

19. After the crucible and sample have cooled, measure and record the mass of the crucible, lid, and metal oxide, to the nearest milligram, in Table 2.

Table 2: Mass of the crucible and magnesium oxide, measured to the nearest milligram

Measurement	Trial 1	Trial 2
Crucible, lid, and MgO after the first heating (g)	28.527	30.520
Crucible, lid, and MgO after the second heating (g)	28.526	30.521
Crucible, lid, and MgO after the third heating (g)		
Crucible, lid, and MgO after the fourth heating (g)		

20. Reheat the crucible and sample at high heat for 5 minutes. Allow the crucible and sample to cool, then measure and record the mass in Table 2. Repeat this step until you obtain two consecutive readings within 10 mg of each other.

21. Copy the last measurement in Table 2 into Table 3.

22. Dispose of the metal oxide in the appropriate container.

23. Beginning with preparing the crucible, repeat the entire procedure with a new sample of magnesium (between 0.17 and 0.23 g). Record the results for Trial 2 in the specified tables and column.

24. Wash the crucible with soap, and then rinse three times with tap water to clean the crucible of magnesium oxide residue.

25. After rinsing three times with tap water, rinse again with deionized water.

26. Clean up according to your instructor's instructions.

Data Analysis

1. Calculate the mass of magnesium and mass of magnesium oxide. Record those values in Table 3.

Table 3: Measurements and calculations of the crucible, magnesium, and magnesium oxide mass

Parameter	Trial 1	Trial 2
Mass of the crucible and lid (g)	28.231	30.210
Mass of the crucible, lid, and magnesium (g)	28.413	30.405
Mass of magnesium (g)	0.182	0.195
Mass of crucible, lid, and magnesium oxide (g)	28.526	30.521
Mass of magnesium oxide (g)	0.295	0.311
Amount of magnesium in the compound (mol)	7.49×10^{-3}	8.02×10^{-3}
Mass of oxygen in the compound (g)	0.113	0.116
Amount of oxygen in the compound (mol)	7.06×10^{-3}	7.25×10^{-3}
Simplest whole number ratio of oxygen to magnesium	1:1	1:1
Experimental empirical formula of the compound using significant figures	$Mg_{1.00}O_{0.94}$	$Mg_{1.00}O_{0.90}$
Suggested empirical formula of the compound using whole numbers	MgO	MgO

2. What is the mass of magnesium in the magnesium oxide compound? How many moles of magnesium is this? Record your answers in Table 3.

The mass of magnesium in magnesium oxide is the mass that was originally measured, 0.182 g, for Trial 1. Magnesium has an atomic weight of 24.305 g/mol.

$$\frac{0.182\ \text{g Mg}}{24.305\ \frac{\text{g}}{\text{mol}}\ \text{Mg}} = 0.00749\ \text{mol Mg}$$

3. Calculate the mass and number of moles of oxygen in the magnesium oxide. Record your answers in Table 3.

Subtracting the mass of magnesium from the mass of magnesium oxide for Trial 1:

0.295 g – 0.182 g = 0.113 g of oxygen

$$\frac{0.113\ \text{g O}}{16.00\ \frac{\text{g}}{\text{mol}}\ \text{O}} = 0.00706\ \text{mol O}$$

4. What is the molar ratio between magnesium and oxygen? Use this to write the experimental empirical formula of the compound using significant figures in Table 3.

$$\left(\frac{0.00749\text{ mol Mg}}{0.00749\text{ mol Mg}}\right):\left(\frac{0.00706\text{ mol O}}{0.00749\text{ mol Mg}}\right) = 1.00\text{ mol Mg}:0.940\text{ mol O}$$

5. What is the empirical formula of the magnesium oxide compound, using whole numbers? Record your answer in Table 3.

MgO

Analysis Questions

1. Using available reference sources, what is the accepted empirical formula of magnesium oxide?

The empirical formula appears to be MgO.

2. Compare your results to the accepted empirical formula for magnesium oxide. What are some sources of experimental error and what could be done to prevent such error?

Imperfect burning could be one reason. More thorough mixing with the paper clip between heating cycles could help the exposure of unreacted magnesium to air. Also, if an insufficient amount of water is added, not all the Mg_3N_2 will decompose. Any sample stuck on the paper clip would introduce error as well. All of these sources of error would result in a lower final mass than expected, therefore lower oxygen to magnesium ratio.

Synthesis Questions

Use available resources to help you answer the following questions.

1. If some unreacted magnesium metal remains in the crucible, explain how this will affect the empirical formula.

The final mass of the sample would be less if the magnesium had not reacted completely. Therefore, the difference between the final mass and the mass of magnesium would result in less oxygen and a higher magnesium to oxygen ratio.

2. If there is insufficient oxygen from the air, some magnesium nitride (Mg_3N_2) will form. If this is not converted to magnesium oxide, will the ratio of oxygen to magnesium appear to be high or low? Explain your answer.

Since the same amount of magnesium would yield less Mg_3N_2 than MgO, the amount of considered oxygen would be less, yielding higher magnesium to oxygen ratio.

3. Recalling the smell that you sensed, where you have smelled ammonia in the past?

One can smell ammonia on the human body after running or in urine as it is the byproduct of the metabolic process. Also it is an ingredient of household cleaners such as window cleaner.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. What information, other than the number of moles of magnesium, was necessary to calculate the stoichiometric ratio between the magnesium and oxygen in the magnesium oxide?

- **A.** The number of moles of oxygen, calculated from the final loss of mass of the sample.
- **B. The number of moles of oxygen from the increased mass of the sample.**
- **C.** The number of moles of oxygen from the increased mass of the nitrogen and oxygen in the sample.
- **D.** The number of moles of nitrogen from the increased mass of the nitrogen in the sample.

2. Why did you have to add water and reheat the sample?

- **A.** Without water, Mg would not react with O_2.
- **B.** Water is necessary to convert $Mg(OH)_2$ to MgO, which is a byproduct of the reaction.
- **C. Water is necessary to convert to MgO from Mg_3N_2, which is a byproduct of the reaction.**
- **D.** Water is a catalyst of the reaction.
- **E.** All of the above.

3. Consider an experiment where we obtain $Mg_{1.5}O_1$ as the empirical formula. Which of the following can be the reason for this kind of error?

- **A.** There was unreacted metal left at the end of the experiment.
- **B.** There was unreacted Mg_3N_2 left at the end of the experiment.
- **C.** Some of the sample stuck on the paper clip used for mixing.
- **D. All of the above can be responsible for this kind of error.**
- **E.** None of the above can be responsible for this kind of error.

4. Why may unreacted magnesium remain after the heating process?

- **A.** Magnesium is extremely hard to burn.
- **B.** The most important reason is contamination of the elemental magnesium.
- **C.** The presence of nitrogen is the reason, to the extent that a byproduct Mg_3N_2 forms.
- **D. Insufficient amounts of oxygen gas result in leftover magnesium metal.**

Extended Inquiry Suggestions

Discuss with your students the reaction between aluminum and iron oxide. Aluminum burns less readily than magnesium. However, once it starts burning, it burns at an equally high temperature to form Al_2O_3. Therefore if aluminum is mixed with Fe_2O_3 (which mix is called "thermite") aluminum removes the oxygen from Fe_2O_3 to form iron. Because of the high temperature the iron melts which is why it is used to weld rails together in railroad constructions. The chemical reaction for this is:

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$$

This reaction is also known as "thermite" reaction.

Another reaction to look at is the one between magnesium and sand (silicon dioxide):

$$2Mg + SiO_2 \rightarrow 2MgO + Si$$

A mixture of magnesium powder and sand, when lit by a magnesium strip, burns at such a high temperature that magnesium takes the oxygen from the SiO_2 to form MgO and amorphous silicon. This can be done as a demonstration experiment. Perform the experiment in a fired clay flower pot since most materials would burn through, due to the extremely high temperature.

2. Determine the Percentage of Water in a Hydrate

Objectives

Students determine the water content of a hydrated salt.

Procedural Overview

Students gain experience conducting the following procedures, using a balance and a Bunsen burner:

- Carefully heat the hydrated sample in a crucible
- Take accurate measurements of the sample before and after it is thoroughly heated
- Calculate the percentage of water in the hydrate based on the measurements

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	150 minutes

Materials and Equipment

For each student or group:

- Crucible with lid
- Crucible tongs
- Bunsen burner
- Ring stand
- Clay triangle
- Balance (1 per class)
- Wash bottle with deionized water
- Copper sulfate, $CuSO_4$, hydrated, 4.5 g

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- What a chemical formula means
- Balancing chemical equations

Related Labs in This Guide

Labs conceptually related to this one include:

- ♦ Determine the Empirical Formula of a Compound
- ♦ Synthesis of a Coordination Compound

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Note: As this lab experiment does not use a data collection system, no Tech Tips (indicated by the symbol "�" and a superscripted number following the step) are needed.

Background

Many naturally occurring or manmade salts contain water molecules bound within the crystal structure of the solid. These are called hydrated salts. The water molecules are known as “water of crystallization” or “water of hydration.”

The number of moles of water will often remain in a fixed ratio to the number of moles of salt present. The formula for a hydrated salt is written as the formula of the anhydrous (without water) salt followed by a raised dot followed by the number of water molecules. For example, the formula for cobalt chloride hexahydrate is $CoCl_2 \cdot 6H_2O$.

In some cases the water is loosely bound to the salt, allowing the water to be removed by applying heat:

$$CoCl_2 \cdot 6H_2O(s) + \text{heat} \rightarrow CoCl_2(s) + 6H_2O(g)$$

Some salts have their water bound so tightly that producing an anhydrous salt is nearly impossible. In the case of iron trichloride hexahydrate, the salt will decompose before all the water can be removed.

The percentage of water, by mass, in a hydrate can be determined by heating a known quantity until complete dehydration is achieved.

$$\text{hydrated salt} + \text{heat} \rightarrow \text{anhydrous salt} + H_2O$$

Dehydration results in decreased mass. The difference of the mass before and after heating makes it possible to determine the amount of water that was present in the hydrate.

$$\text{Total mass of hydrated salt} = \text{mass of anhydrous salt} + \text{mass of water of hydration}$$

The percent mass of water in the hydrated salt may be easily calculated:

$$\%\text{water} = \frac{m_{\text{water}}}{m_{\text{hydrated salt}}} \times 100$$

Where:

m_{water} = mass of water of hydration

$m_{\text{hydrated salt}}$ = total mass of hydrated salt

Pre-Lab Experiment

Setting the stage for the experiment

The hydrated salt copper(II) sulfate is stable at room temperature and has a different color than the dehydrated version. The hydrated crystals are blue, while the dehydrated crystals are white. This makes it easy to see when the crystals are completely dehydrated.

You perform the same type of experiment as in "Determining the Empirical Formula of a Compound." You will heat a known amount of substance and test how much the mass changes due to the heating process. From the loss of mass, you can calculate the number of water molecules that are bound to each molecule of $CuSO_4$. Until you determine the number of water molecules, use the formula "$CuSO_4 \cdot xH_2O(s)$."

Example calculation to try

Analyze the following example: A 5.40 g sample of hydrated sodium sulfate, $Na_2SO_4 \cdot xH_2O$, was found to contain 2.34 g of anhydrous Na_2SO_4. This means that the sample had 3.06 g of water (5.40 g – 2.34 g). The water content of the sample is

$$\left(\frac{3.06\text{ g H}_2\text{O}}{5.40\text{ g Na}_2\text{SO}_4\cdot x\text{H}_2\text{O}}\right)\times 100 \;=\; 56.7\%\text{ H}_2\text{O}$$

The number of water molecules bound with one molecule of Na_2SO_4 can also be calculated by determining the number of moles of each and then determining the ratio of one to the other:

$$\left(\frac{2.34\text{ g Na}_2\text{SO}_4}{142\ \frac{\text{g}}{\text{mol}}\ \text{Na}_2\text{SO}_4}\right) \;=\; 0.0165\text{ mol Na}_2\text{SO}_4$$

$$\left(\frac{3.06\text{ g H}_2\text{O}}{18.02\ \frac{\text{g}}{\text{mol}}\ \text{H}_2\text{O}}\right) \;=\; 0.170\text{ mol H}_2\text{O}$$

The molar ratio between the Na_2SO_4 and H_2O:

$$\left(\frac{0.0165\text{ mol Na}_2\text{SO}_4}{0.0165\text{ mol Na}_2\text{SO}_4}\right):\left(\frac{0.170\text{ mol H}_2\text{O}}{0.0165\text{ mol Na}_2\text{SO}_4}\right) \;=\; 1.00\text{ mol Na}_2\text{SO}_4 : 10.3\text{ mol H}_2\text{O}$$

The stoichiometric ratio should be the nearest whole number ratio therefore, the empirical formula is $Na_2SO_4 \cdot 10H_2O$.

1. Using the generic formula of $CuSO_4{\cdot}xH_2O$, provide an equation for the water loss of your unknown sample.

$CuSO_4{\cdot}xH_2O(s) + \text{heat} \rightarrow CuSO_4(s) + xH_2O(g)$

2. How do you know when the dehydration is complete? (Hint: Research the color of the hydrated compound and the color of the anhydrous compound.)

The hydrated salt is blue while the anhydrous salt is white. The dehydration is complete when the substance is white.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. The hydrated $CuSO_4$ is hygroscopic. (It attracts moisture from the air.) Try to use a freshly opened container, or make sure that the crystals are not clumped together.
2. Remind students how the Bunsen burner works and how the air flow can be controlled.

Safety

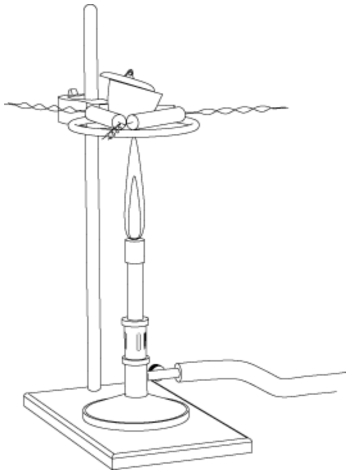
Add these important safety precautions to your normal laboratory procedures:

- Be very careful when using the Bunsen burner.
- Never place a hot crucible or other hot objects on a balance pan.
- Do not move the hot crucible from the clay triangle until it has cooled.
- Make sure there is nothing flammable around the setup.

Procedure with Inquiry

Note: This experiment does not use a data collection system, so there are no Tech Tips (indicated by the symbol "�" and a superscripted number following a step).

Set Up



1. Obtain a crucible and lid, and inspect the crucible for cracks, nicks, and other defects.

   Note: Replace a defective crucible.

2. Measure and record the mass of the crucible and lid in Table 1.

3. Assuming there are contaminations in the crucible that

remain even after heating, would such contaminations falsify the data? If so, why would they?

Since the contamination does not lose mass when heated, it would behave the same as the crucible itself. Therefore it can be considered part of the crucible and would not falsify the data.

4. Place the crucible and lid on the clay triangle over the Bunsen burner. Make sure the lid is slightly ajar.

Note: For the rest of the experiment handle the crucible and lid using only crucible tongs. Also, do not set the crucible on the lab bench or it may crack or become contaminated.

5. Name two reasons why you have to use tongs to hold the lid?

Touching the lid with bare hands would leave a residue of grease on the lid. The grease would add to the mass of the crucible. Because it would burn off, it would result in a higher mass for the evaporated water. Also, the crucible may be hot and cause injury.

Collect Data

Obtain data for the empty crucible

6. The steps for heating, cooling, and measuring the mass of the crucible are as follows:

- **a.** Heat the crucible with a gentle flame for 5 minutes by moving the burner around the bottom of the crucible.
- **b.** After the bottom of the crucible has become red-hot, increase the flame by allowing more air into the burner.
- **c.** Continue moving the burner around the bottom of the crucible.
- **d.** Heat the crucible for 10 to 12 minutes.
- **e.** Allow the crucible to cool to room temperature.
- **f.** After the crucible has cooled, measure and record the mass of the “fired” crucible and lid in Table 1.

Table 1: Mass of the empty crucible measured to the nearest milligram

Measurement	Trial 1	Trial 2
Crucible and lid before heating (g)	27.494	29.142
Crucible and lid after the first heating (g)	27.426	29.039
Crucible and lid after the second heating (g)	27.423	29.038
Crucible and lid after the third heating (g)		
Crucible and lid after the fourth heating (g)		

7. Repeat the steps above for heating, cooling, and measuring the mass of the crucible and lid until you have two readings for the mass that are within 10 mg of each other.

8. Copy the last measurement into both Table 1 and Table 3.

Obtain data for the crucible and sample

9. Place between 1.75 g and 2.25 g of hydrated copper sulfate in the crucible.

10. Measure the mass of the crucible, lid, and hydrated copper sulfate to the nearest milligram and record it in Table 3.

11. Return the crucible with the sample and lid to the clay triangle over the Bunsen burner.

12. Gently heat the sample for 2 to 3 minutes by moving the burner around the bottom of the crucible.

13. Increase the heat and continue heating for 3 minutes.

Note: Remember that the top third of the flame is the hottest.

14. Carefully lifting the lid with the tongs, check the sample. If the sample hasn't turned white, replace the lid and continue heating for a few more minutes

15. With the lid in place, remove the heat source and allow the crucible to return to room temperature.

16. Measure the mass of the crucible, lid, and sample, and record it to the nearest milligram in Table 2.

Table 2: Mass of the crucible and copper sulfate salt after heating, measured to the nearest milligram

Measurement	Trial 1	Trial 2
Crucible, lid, and salt after the first heating (g)	27.426	29.039
Crucible, lid, and salt after the second heating (g)	27.423	29.038
Crucible, lid, and salt after the third heating (g)		
Crucible, lid, and salt after the fourth heating (g)		

17. Why should the lid remain on the crucible?

If the anhydrous salt is exposed to open air, it will absorb moisture from the air.

18. Reheat the crucible and sample at high heat for 5 minutes. Allow the crucible and sample to cool, then measure and record the mass in Table 2 as before.

19. Continue to reheat the crucible and sample until you obtain two consecutive readings that are within 10 mg of each other.

20. Copy the last measurement into both Table 2 and Table 3.

21. What would you observe if you added a few drops of deionized water to the anhydrous sample?

The sample would become hydrated again and would turn blue.

22. Squeeze a few drops of deionized water into the anhydrous sample to check your prediction.

23. Dispose of the sample in the appropriate container.

24. Repeat the procedure from "Obtain data for the empty crucible" with a new sample of hydrated copper sulfate (between 1.75 g and 2.25 g). Record the results for Trial 2 in the specified tables and column.

25. Wash the crucible with soap. Then rinse 3 times with tap water to clean the crucible of copper sulfate residue.

26. After rinsing three times with tap water, rinse again with deionized water.

27. Clean up according to your instructor's instructions.

Data Analysis

1. Calculate a) the mass of the hydrated salt, b) the mass of the anhydrous salt, c) the mass of the water lost, d) the percentage of water in the hydrated salt, and e) the average percentage of water in the hydrated salt. Record your answers in Table 3.

Shown for Trial 1:

a) Mass of the hydrated salt: 29.327 g – 27.423 g = 1.904 g

b) Mass of the anhydrous salt: 28.637 g – 27.423 g = 1.214 g

c) Mass of the water lost: 1.904 g – 1.214 g = 0.690 g

d) Percent water in the hydrated salt: $\left(\frac{0.690\text{ g } H_2O}{1.904\text{ g } Cu_2SO_4 \cdot xH_2O}\right) \times 100 = 36.2\%\ H_2O$

e) Average percent water from trials 1 and 2: (36.2% + 32.4%)/2 = 34.3%

Table 3: Determine the percent water in the sample

Parameter	Trial 1	Trial 2
Mass of crucible, lid, and hydrated salt (g)	29.327	31.106
Mass of crucible, lid, and anhydrous salt (g)	28.637	30.436
Mass of crucible and lid (g)	27.423	29.038
Mass of hydrated salt (g)	1.904	2.068
Mass of anhydrous salt (g)	1.214	1.398
Mass of water lost (g)	0.690	0.670
Percent of water in the hydrated salt (%)	36.2	32.4
Average percent water in the hydrated salt (%)	34.3	
Number of moles of anhydrous salt (mol)	7.61×10^{-3}	8.76×10^{-3}
Number of moles of water lost (mol)	3.83×10^{-2}	3.72×10^{-2}
Ratio between salt and water	1:5.040	1:4.30
Formula of hydrated salt	$CuSO_4 \cdot 5H_2O$	

2. Record the formula weight (or molar mass) of anhydrous copper(II) sulfate and the formula weight of water below:

$FW_{\text{anhydrous copper(II) sulfate}}$ (g/mol): 159.61

FW_{water} (g/mol): 18.02

3. Calculate the number of moles of anhydrous salt used for each trial and record the values in Table 3.

Shown for Trial 1:

$$\left(\frac{1.214\text{ g }CuSO_4}{159.62\ \frac{\text{g}}{\text{mol}}\ CuSO_4}\right) = 7.609 \times 10^{-3}\text{ mol }CuSO_4$$

4. Calculate the number of moles of water lost after heating for each trial and record the values in Table 3.

Shown for Trial 1:

$$\left(\frac{0.6900\text{ g }H_2O}{18.02\ \frac{\text{g}}{\text{mol}}\ H_2O}\right) = 3.833 \times 10^{-2}\text{ mol }H_2O$$

5. How many water molecules are bound with one molecule of $CuSO_4$, that is, what is the molar ratio between $CuSO_4$ and H_2O for each trial? Show your work and record the values in Table 3.

Shown for Trial 1:

$$\left(\frac{0.00761\text{ mol CuSO}_4}{0.00761\text{ mol CuSO}_4}\right):\left(\frac{0.0383\text{ mol H}_2\text{O}}{0.00761\text{ mol CuSO}_4}\right) = 1.00\text{ mol CuSO}_4 : 5.03\text{ mol H}_2\text{O}$$

The stoichiometric ratio should be the nearest whole number ratio, therefore the formula is $CuSO_4 \cdot 5H_2O$.

Analysis Questions

1. If your results do not yield a molar ratio of whole numbers for the $CuSO_4$ and H_2O, is it justified to round the numbers to the nearest whole numbers? Explain.

The molar ratio between $CuSO_4$ and H_2O must be a ratio between whole numbers. Deviation from that is a result of experimental error, so rounding is justified.

2. Why would leaving the dehydrated sample exposed to air introduce a significant error?

Dehydrated $CuSO_4$ is very hygroscopic. That is, it absorbs moisture from air. This increases the mass of the sample.

3. Why must the crucible cool to room temperature before taking any mass measurement?

The balance could be damaged if anything significantly higher than room temperature is place on the balance. It also increases the chance of someone getting burned by trying to measure the mass of items that are hot. Additionally, convection currents will cause an unstable reading (the reading fluctuates).

4. If the crucible was heated too rapidly and some sample material spattered out, how would this affect the final percent water calculations? Explain.

Slower heating assures that water separates from the hydrate without losing any of the salt. If some of the salt is lost, the mass of the lost salt will be included in the mass of the water lost through heating. This will result in a larger proportion of water in the hydrated salt, leading to an erroneously high ratio of water.

5. What would you observe if you removed the lid from the crucible while the sample was being heated and held a cold watch glass over the crucible?

Water being eliminated from the sample would condense on the cold surface of the watch glass.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Using available reference sources, what is the empirical formula of hydrated $CuSO_4$?

The empirical formula is $CuSO_4 \cdot 5H_2O$.

2. When heated, why do $Na_2SO_4 \cdot 10H_2O$ crystals "melt" at a much lower temperature than the ionic compound Na_2SO_4 normally does (it occurs below the boiling point of water)? (Hint: There is Na_2SO_4 and water present in the crystals)

The crystals contain sufficient water to dissolve the substance, Na_2SO_4. The heating actually produces a solution and does not melt the crystals.

3. Are the hydrated and dehydrated forms of a substance two different chemical substances? (Hint: What happened when you added water drops to the dehydrated crystals?)

No, they are the same chemical substance. Adding water reverses the process of losing water. Since the process is reversible it is a physical change, not a chemical change.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. What is the molar ratio between $CuSO_4$ and its water content in the hydrated form?

- **A.** It cannot be calculated. Only the percent water content can.
- **B.** **It can be calculated from the number of moles of $CuSO_4$ remaining after heating and from the loss of mass, which can be converted to the number of moles of water.**
- **C.** It depends on how high the temperature is during the heating process.
- **D.** It is not a fixed ratio and varies between samples.

2. In an analysis of a hydrated $CuSO_4$ sample, what could the source of error be for a lower than actual water to $CuSO_4$ ratio?

- **A.** Heating too quickly resulted in spattering and loss of some of the sample.
- **B.** There was partial decomposition of the already anhydrous $CuSO_4$.
- **C.** **The sample did not completely lose its water content.**
- **D.** None of the above.
- **E.** All of the above.

3. How are anhydrous and hydrated $CuSO_4$ related chemically?

- **A.** They are different compounds with different chemical and physical properties.
- **B.** **They are the same compound with somewhat different physical properties.**
- **C.** They are different but similar to other hydrated and anhydrous compounds.

4. For what reason might you *not* obtain a ratio of whole numbers for the molar ratio between the $CuSO_4$ and H_2O?

- **A.** The composition of the hydrated compound is not constant and it varies between samples.
- **B.** The ratio between the $CuSO_4$ and H_2O does not have to be a ratio between whole numbers.
- **C.** **The most likely reason is experimental error.**
- **D.** None of the above options can account for the deviation.

Extended Inquiry Suggestions

Discuss with students how $CoCl_2$ is used as an "indicator" in desiccators:

> Desiccators are closed glass containers with drying agents. When a wet sample is placed in a desiccator, the drying agent absorbs moisture and the wet sample dries. In the indicator, traces of $CoCl_2$ start to absorb moisture when the drying agent can no longer absorb moisture. Since $CoCl_2$ is blue in its anhydrous state and pink in its hydrated form, pink indicates that the drying agent needs to be replaced. As long as the $CoCl_2$ remains blue, the drying agent is still capable of absorbing moisture.

3. Mole Relationships in a Chemical Reaction

Objectives

Students determine the stoichiometric coefficients of the reactants of a chemical reaction using conductivity.

Procedural Overview

Students gain experience conducting the following procedures:

- Using conductivity to monitor a reaction
- Determining the stoichiometric ratio of the reactants

Time Requirement

Preparation time	15 minutes
Pre-lab discussion and experiment	15 minutes
Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Conductivity sensor
- Test tubes (9), 15-mL
- Beaker, 100-mL
- Graduated pipet (2), 10-mL
- Rubber bulb
- Test tube rack
- Unknown solution, 50 mL[1]
- 0.01 M Silver nitrate ($AgNO_3$), 50 mL[2]
- Wash bottle with deionized water
- Parafilm®
- Marking pen

[1-2] To prepare the solutions, refer to the Lab Preparation section. The unknown solution is 0.01 M potassium chromate (K_2CrO_4).

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Balancing chemical equations
- Dissociation
- Molarity
- Precipitate-forming reactions
- Stoichiometric calculations

Related Labs in This Guide

Labs conceptually related to this one include:

- Determining the Empirical Formula of a Compound
- Determine the Percentage of Water in a Hydrate
- Analysis of a Coordination Compound
- Gravimetric Determination of a Precipitate

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to your data collection system �(2.1)
- Monitoring live data without recording �(6.1)
- Displaying digits in a digits display �(7.3.1)

Background

Ionic compounds dissociate in an aqueous medium to form ions. Ions are responsible for the ability of solutions to conduct electricity. The electrical conductivity of a solution increases with greater ion concentration or with solutions of ions that have a greater charge.

When a chemical reaction between two solutions removes the ions from the combined solution in the form of a gas or precipitate, the conductivity of the solution is reduced. For example, when an $AgNO_3$ solution and a NaCl solution are combined, the Ag^+ and Cl^- ions are removed in the form of AgCl, since AgCl is not soluble in water:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

When the two solutions are combined in a ratio other than the stoichiometric ratio, the ions of one of the reactants will be in excess, resulting in greater conductivity. When the two solutions are combined in a ratio that has an equal amount of the reactants, the maximum number of ions is removed. In that case, the conductivity will be least.

Pre-Lab Experiment

Setting the stage for the experiment

You will study the reaction between Ag^+ and an unknown ion, B^{n-}:

$$nAg^+(aq) + B^{n-}(aq) \rightarrow Ag_nB(s)$$

where

n = the number of silver ions in Ag_nB; also, the number of negative charges on the unknown anion, B

B = the formula of the unknown anion

You will combine various volume combinations of the solution containing the unknown anion and the solution of Ag^+ ions, until the conductivity is minimized. If the concentrations of the two solutions are the same, the ratio of the two solutions will allow you to determine the ratio between the stoichiometric coefficients of the two reactants.

The two solutions will be mixed in test tubes and the conductivity of the resulting solution will be measured with the conductivity sensor.

Example calculation to try

In an experiment, various ratios of volumes of Ag^+ solution and the solution of an unknown anion, Q^{n-}, with equal concentrations, were combined. Since the concentrations were the same, the ratio of the volumes combined is the same as the ratio of number of moles combined. The conductivity of the resulting solutions was measured, in microsiemens (μS), and the following data was obtained:

Table 1: Determination of the stoichiometric ratio using conductivity

Volume of Ag^+ (mL)	Volume Q^{n-} (mL)	Volume Ratio $Ag^+:Q^{n-}$	Likely Stoichiometric Ratio	Conductivity (µS)
2.00	8.00	1 : 4	1 : 4	2545
2.50	7.50	1 : 3	1 : 3	2134
3.00	7.00	1 : 2.33	1 : 2	1876
4.00	6.00	1 : 1.5	2 : 3	1544
5.00	5.00	1 : 1	1 : 1	1265
6.00	4.00	1.5 : 1	3 : 2	987
7.00	3.00	2.33 : 1	2 : 1	544
7.50	2.50	3 : 1	3 : 1	125
8.00	2.00	4 : 1	4 : 1	899

Since the minimum conductivity, 125 µS, was achieved at the 3:1 ratio, it is most likely that the Ag^+ ions react with the Q^{n-} ions in the 3:1 ratio:

$$3Ag^+(aq) + Q^{3-}(aq) \rightarrow Ag_3Q(s)$$

If the minimum conductivity was achieved with a ratio of solutions other than a ratio between integers, the numbers would have to be multiplied with an integer to obtain a ratio between the lowest possible integers. For example, if the ratio was 1.5:1, after multiplying by 2 we will get 3:2, which is a plausible result.

Keep in mind that the whole-number ratio has to make sense for the particular chemical reaction. Since we know that silver always has the charge of +1, combinations like 2:1 or 3:1 are possible. However, combinations like 3:2 are not feasible, since that would assume that a +3 charge is compensated by two anions, which is impossible.

1. Why isn't the conductivity zero when the solutions are combined with the stoichiometric amounts?

The conductivity is not zero because not all of the ions are removed by the precipitation reaction. For example, the combination of NaCl and $AgNO_3$ solution removes the Ag^+ and Cl^- ions in the form of AgCl, but the Na^+ and NO_3^- ions remain in solution.

2. Why is it that we can use volumes of solutions with the same concentration instead of the number of moles to determine the stoichiometric ratio?

The number of moles of a solute is proportional to the volume of the solution. Therefore, the ratio of the number of moles combined is the same as the ratio of the combined volumes of solutions having the same concentration.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.01 M K_2CrO_4:*** Dissolve 3.884 g of K_2CrO_4 in some water and dilute it to the mark in a 2-L volumetric flask.

2. ***0.01 M $AgNO_3$:*** Dissolve 3.398 g of $AgNO_3$ in some water and dilute it to the mark in a 2-L volumetric flask.

CAUTION: Be aware of the potential toxicity from breathing or touching chemicals used in this lab. Prepare the room and oversee the experiment accordingly.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect the conductivity sensor to the data collection system. �(2.1)

   Note: The conductivity sensor does not need to be calibrated because the absolute value of the conductivity is not relevant. Only the relative conductivity values among the solution are important.

3. Display Conductivity in a digit display. �(7.3.1)

4. Label the nine test tubes with numbers, from “1” to “9”.

Collect Data

5. Pipet the amount of $AgNO_3$ solution prescribed in Table 2 into each test tube.

6. Use the second pipet to pipet the amount of unknown solution prescribed in Table 2 into each test tube.

7. All of the solutions have the same final volume. Why is it important to compare solutions with the same volume?

The same volume is used to avoid variability in concentration of ions arising from the dilution of the reactants. That way, the volume of each reactant is proportional to the established ion concentration in the final solution. Furthermore, considering that $c = n/V$, since the volume is the same, concentrations can be used in place of the number of moles in stoichiometric calculations.

8. Place a small piece of Parafilm on the top of the first test tube. Holding it firmly with your thumb, shake the test tube to mix the contents thoroughly.

9. Shake the other test tubes to mix the contents thoroughly.

10. Why must you mix the contents of the test tubes thoroughly?

The test tubes must be mixed thoroughly to assure that the solution will be homogeneous.

11. Allow the mixtures to settle for a minute.

12. Rinse the conductivity sensor with deionized water into a waste beaker (100-mL beaker).

13. Set the conductivity sensor to monitor live data without recording. �(6.1)

14. Place the conductivity sensor into the first test tube.

15. Wait until the conductivity reading stabilizes (up to 30 seconds).

16. Measure the conductivity of the first solution and record it in Table 2 in the Data Analysis section.

17. Rinse the conductivity sensor with deionized water into a waste beaker.

18. Measure the conductivity of the remaining solutions. Rinse the sensor thoroughly with deionized water between measurements. Record each conductivity reading in Table 2 in the Data Analysis section.

19. Why is it important to rinse the sensor thoroughly between measurements?

It is important to rinse the sensor in order to avoid contamination of the solutions.

20. Clean up according to your instructor's instructions.

Data Analysis

Record the measurements from the procedure.

Table 2: Determination of the stoichiometric ratio using conductivity

Test Tube	Volume of Ag^+ (mL)	Volume B^{n-} (mL)	Volume Ratio Ag^+:B^{n-}	Likely Stoichiometric Ratio	Conductivity (µS)
1	2.00	8.00	1:4	1:4	2173
2	2.50	7.50	1:3	1:3	1943
3	3.00	7.00	1:2.3	1:2	1802
4	4.00	6.00	1:1.5	2:3	1548
5	5.00	5.00	1:1	1:1	1357
6	6.00	4.00	1.5:1	3:2	1074
7	7.00	3.00	2.33:1	2:1	972
8	7.50	2.50	3:1	3:1	981
9	8.00	2.00	4:1	4:1	987

Analysis Questions

1. Which ratio of solutions provided the lowest conductivity?

2:1

2. What is the balanced equation between Ag^+ and B^{n-}? What is the value of n? Explain.

$2Ag^+(aq) + B^{2-}(aq) \rightarrow Ag_2B(s)$

The value of *n* is 2. Since two Ag^+ ions react with one B^{n-} ion to form a neutral precipitate, B has to have two negative charges.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Can the stoichiometry of a gas-forming reaction be determined with the method applied in this experiment? Explain, considering the example of a reaction between solutions of hydrochloric acid and sodium carbonate. (Write the balanced equation as part of your answer.)

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O + CO_2(g)$$

Yes, as long as the gas can be quantitatively removed from the solution. It is not relevant if the ions are removed as a precipitate or as a gas. The important thing is that ions are removed.

2. Assume you are given three unlabeled solutions with the same concentration: 0.001 M. The solutions are Na_3PO_4, Na_2HPO_4, and NaH_2PO_4. (In an aqueous medium the sodium ions dissociate in these compounds, and they are replaced with Ag^+ to form a precipitate.) Using a 0.001M $AgNO_3$ solution, propose a strategy to identify the solutions. Provide the corresponding equations.

Each of the compounds would bind as many Ag^+ ions as it does Na^+ ions. Therefore, each solution would have to be combined with 0.001 M $AgNO_3$ in 3:1, 2:1, and 1:1 ratios. Among the solutions that were made with the 3:1 ratio, the one with the lowest conductivity is Na_3PO_4. Among the solutions that were made with the 2:1 ratio, the one with lowest conductivity is Na_2HPO_4. Among the solutions that were made with the 1:1 ratio, the one with lowest conductivity is NaH_2PO_4.

The corresponding ionic equations are

$$3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)$$

$$2Ag^+(aq) + HPO_4^{2-}(aq) \rightarrow Ag_2HPO_4(s)$$

$$Ag^+(aq) + H_2PO_4^{-}(aq) \rightarrow AgH_2PO_4(s)$$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. What would you conclude regarding the stoichiometric coefficients if the lowest conductivity obtained was with the 2.33:1 ratio?

- **A.** Since volumes are proportional to the number of moles, the Ag^+ would react with the unknown anion in the 2.33:1 ratio.
- **B. Stoichiometric coefficients have to be integers. The closest ratio of integers is most likely the proper stoichiometric ratio, 2:1.**
- **C.** In order to obtain a ratio of integers, we would have to multiply the numbers by 3, and the proper ratio therefore is 7:3 between Ag^+ and the unknown B^{n-} anion.
- **D.** The experiment would have to be repeated.

2. Why is it necessary to use deionized water in this experiment?

- **A.** We always use deionized water in experiments just to be on the safe side.
- **B.** Tap water would have been equally acceptable as it dissolves the compounds that we worked with.
- **C. Tap water has ions at a high concentration and that would have falsified our data.**
- **D.** The solubility of Ag^+ ions is better in deionized water.

3. Presume in the conductivity measurements that one data point is much higher than expected, and upon measuring that solution again, it is much lower than expected. What is the *most likely* reason for this discrepancy?

- **A. The solutions were not mixed sufficiently**.
- **B.** The sensor was not rinsed thoroughly and it was contaminated.
- **C.** The test tube was contaminated.
- **D.** The pipet is not accurate enough to measure the desired volume.

Extended Inquiry Suggestions

Conductivity is the lowest when the solutions of two compounds that form a precipitate are combined in a stoichiometric ratio. This fact can be utilized in quantitative analysis as well. A sample of one of the components with unknown concentration can be titrated with the solution of the other compound with known concentration. This method is called gravimetric titration. To challenge your students already familiar with titration, ask them how the method used in this experiment can also be used to detect the end point of a titration.

4. Gravimetric Determination of a Precipitate

Objectives

In this experiment, students use gravimetric analysis to determine the amount of sulfate in a sample of an unknown alkali sulfate.

Procedural Overview

Students gain experience conducting the following procedures:

- Isolating sulfate from an unknown sample by precipitation with barium chloride
- Collecting, drying, and obtaining the mass of the precipitate
- Calculating the amount of sulfate in the unknown from collected data

Time Requirement

◆ Preparation time	30 minutes
◆ Pre-lab discussion and experiment	15 minutes
◆ Lab experiment	120 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- Ring stand with ring
- Clamp, utility
- Clamp, buret
- Crucible with lid
- Tongs
- Beaker, glass, 400-mL
- Beaker, glass, 250-mL
- Beaker (3), 25-mL
- Beaker or flask, 400-mL,
- Graduated cylinder, 100-mL
- Graduated cylinder, 10-mL
- Buret, 50 mL
- Funnel
- Dropper
- Hot plate
- Bunsen burner
- Clay triangle
- 0.5 M Barium chloride ($BaCl_2$), 30-mL[1]
- 0.1 M Silver nitrate ($AgNO_3$), 5-mL[2]
- 6 M Hydrochloric acid (HCl), 5-mL[3]
- Unknown alkali sulfate, 0.35 g[4]
- Filter paper, Whatman® Ashless, #42
- Rubber policeman and stirring rod
- Watch glass, 100-mm
- Distilled water, 100 mL
- Wash bottle with distilled water

[1–4] To prepare the solutions and the unknown samples of K_2SO_4 and Na_2SO_4, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Stoichiometry of chemical reactions
- Reactions of anions and cations
- Using the analytical balance

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Empirical Formula of a Compound
- Determine the Percentage of Water in a Hydrate
- Separation and Analysis of Cations
- Analysis of Anions
- Analysis of a Coordination Compound
- Determination of a Solubility Product

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them are in the appendix that corresponds to your PASCO data collection system (identified by the number following the symbol: "�"). Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �$^{(1.2)}$
- Connecting a sensor to your data acquisition system �$^{(2.1)}$
- Monitor live data without recording �$^{(6.1)}$

Background

Gravimetric analysis is one of the oldest and most accurate quantitative methods for determining the amount of an analyte in a sample. Strategies usually involve transforming the analyte into a water insoluble form which precipitates out of solution and can be isolated by filtration and drying. The final stage of the analysis is obtaining the mass. From the measured mass and stoichiometric considerations, the mass, number of moles, and percentage of the sulfate content in the precipitate can be determined.

In this experiment, the mass of a sample containing a sulfate of an alkali metal is measured and then dissolved in dilute hydrochloric acid. The sulfate is isolated by precipitation with barium chloride. The precipitate is digested in a heated solution to form coarser, easily filtered particles, and to purify the precipitate. The precipitate is then collected by filtration, washed, dried, and its mass measured. The amount of sulfate in the original sample can be calculated from the mass of the precipitate and its chemical composition.

Pre-Lab Experiment

Setting the stage for the experiment

In this experiment, you will analyze an unknown alkali sulfate sample to obtain the mass of the SO_4^{2-} content. You will remove the SO_4^{2-} ions with Ba^{2+} ions in the form of barium sulfate ($BaSO_4$). By obtaining the mass of the dried precipitate, you can calculate the SO_4^{2-} content of the sample.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Example calculation to try

0.3550 g of an alkali sulfate sample was dissolved in 50 mL of water in a 400-mL beaker. Five milliliters of 6 M HCl was added, followed by an additional 200 mL of water. The solution was heated to 90 °C and then 25 mL of 0.5 M barium chloride ($BaCl_2$) solution was added. The solution was maintained at 90 °C for an hour.

The precipitate was filtered on an ashless filter paper and washed until the filtrate showed no reaction with $AgNO_3$. Any chloride contamination would yield white AgCl precipitate:

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

An empty crucible (35.446 g) was heated to a constant mass and was found to be 35.409 g. The wet precipitate was transferred into the crucible along with the filter paper and heated slowly until the paper was burned and the precipitate appeared to be dry. The mass of the cooled crucible with the precipitate was 36.055 g. After a second and third heating, the mass remained 36.020 g. The mass of the precipitate was

$$36.020\text{ g} - 35.409\text{ g} = 0.611\text{ g}$$

which is

$$0.611\text{ g BaSO}_4\left(\frac{1\text{ mol BaSO}_4}{233.39\text{ g BaSO}_4}\right) = 2.62 \times 10^{-3}\text{ mol BaSO}_4$$

Therefore, there was 2.62×10^{-3} mol of SO_4^{2-}, which is

$$2.62 \times 10^{-3}\text{ mol SO}_4^{2-}\left(\frac{96.1\text{ g SO}_4^{2-}}{1\text{ mol SO}_4^{2-}}\right) = 0.252\text{ g SO}_4^{2-}$$

The percent sulfate content was

$$\left(\frac{0.252\text{ g}}{0.355\text{ g}}\right) \times 100 = 71.0\%$$

Table 1: Determination of the amount of sulfate in the unknown

Parameter	Value
Mass of unknown sample (g)	0.355
Mass of precipitate (g)	0.611
Number of moles of precipitate (mol)	2.62×10^{-3}
Number of moles of SO_4^{2-} in precipitate (mol)	2.62×10^{-3}
Mass of SO_4^{2-} in precipitate (g)	0.252
Percent SO_4^{2-} (%)	71.0

1. What are the molecular, ionic, and net ionic equations of the reaction of the sample with $BaCl_2$? Use "M^+"to symbolize the metal ion.

Molecular: $M_2SO_4(aq) + BaCl_2(aq) \rightarrow 2MCl(aq) + BaSO_4(s)$

Ionic: $2M^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2Cl^-(aq) \rightarrow 2M^+(aq) + 2Cl^-(aq) + BaSO_4(s)$

Net ionic: $SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(aq)$

2. Why do you think it is necessary to check the filtrate with $AgNO_3$?

We need to make sure that all Cl^- is washed out to prevent Cl^- contamination of the precipitate.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.5000 M $BaCl_2$***: Dissolve 61.080 g of $BaCl_2 \cdot 2H_2O$ in some water in a 500-mL volumetric flask and fill it to the mark.
2. ***0.1000 M $AgNO_3$:*** Dissolve 1.700 g of $AgNO_3$ in some water in a 100-mL volumetric flask and fill it to the mark.
3. ***6 M HCl:*** Add 250 mL of 36% HCl solution slowly into about 200 mL of water in a 500-mL volumetric flask and fill it to the mark.
4. ***Unknown samples:*** Provide approximately 0.36 g of K_2SO_4 or Na_2SO_4 (or 0.80 g of $Na_2SO_4 \cdot 10H_2O$) per group in a weighing dish. Identify the unknowns by assigning each a number or use a preferred strategy.

Safety

Add these important safety precautions to your normal laboratory procedures:

- If the HCl comes in contact with skin or eyes, rinse the contacted surface thoroughly with running water.
- Barium is a strong poison if ingested. Avoid contact with barium solution. In case of contact with skin, wash the barium off with plenty of water. If ingested, seek medical attention immediately.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

Prepare the unknown in solution

1. Make sure the 400-mL beaker, the stirring rod, rubber policeman, and the 100-mm watch glass are clean.

2. Obtain a weighing dish containing a sample of unknown substance from your instructor. Record the number below.

Sample number: ____________

3. Carefully measure the mass by difference of approximately 0.350 g or 0.800 g of unknown, as instructed by your instructor, into the 400-mL beaker.

Note: You can achieve this by obtaining the mass of the unknown substance with the tared weighing dish and sample and then removing some of the sample directly into the beaker until the desired amount of the sample is transferred (that is, the remaining mass on the balance is less by the desired amount). Record the mass of the unknown substance to the nearest tenth of a milligram in Table 4.

Mass of unknown transferred to the beaker (g): 0.3580

4. Why do you measure the mass of the sample by difference rather than putting it straight into the beaker?

It is more accurate to measure from the original sample directly into the beaker (measuring by difference) than to measure the sample in the beaker (the beaker has rather large mass compared to the small sample) or to measure some of the sample into a weighing dish and transfer the sample into the beaker because, in that case, some of the sample is lost in the transfer.

5. Add 50 mL of distilled water to the beaker and dissolve the sample with gentle swirling.

CAUTION: Be careful not to spill any of the solution.

6. Slowly add 5 mL of 6 M HCl to the solution in the beaker.

7. Add additional distilled water until there is about 250 mL of the solution in the beaker (use the scale on beaker).

8. Cover the beaker with the 100-mm watch glass and, if necessary, store it in a safe place until you are ready to proceed with the determination.

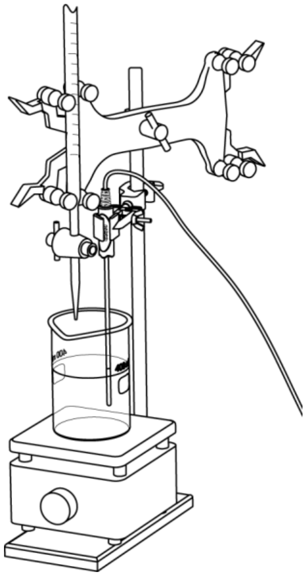
Form the precipitate

9. Start a new experiment on the data collection system. �(1.2)

10. Use the buret clamp to attach the buret to the ring stand.

11. Connect the stainless steel temperature sensor to the data collection system. �(2.1)

12. Set the data collection system to monitor live data without recording. �(6.1)



13. Place the beaker with the solution on the hot plate and begin heating it to about 90 °C. Do not allow the solution to boil because some of the solution might be lost through spattering.

Note: Keeping the solution hot will promote the formation of large, filterable crystals and minimize the inclusion of impurities in the precipitate.

14. Immerse the temperature sensor in the solution so that it is not touching the beaker.

Note: When you remove the temperature sensor from the solution, be sure to rinse the solution adhering to the sensor back into the beaker with a small quantity of distilled water.

15. Why do you need to rinse any residue on the temperature sensor back into the beaker?

Rinsing is necessary to minimize the loss of the sample.

16. When the solution has reached 90 °C, begin adding, drop by drop, the 0.5 M $BaCl_2$ solution from the buret into the beaker while you gently swirl the solution with the rubber policeman. Make sure you do not spill any of the solution.

17. When 25 to 35 mL of $BaCl_2$ solution has been added, stop the addition and let the precipitate settle.

18. When the precipitate has settled, test for completeness of precipitation by adding 1 to 2 drops of $BaCl_2$. If you see any sign of precipitation, add 5 more milliliters of $BaCl_2$.

19. Why is it necessary to test for completeness?

Testing for completeness assures that all sulfate ions are removed quantitatively from the solution.

20. After adding a sufficient amount of $BaCl_2$ to the beaker, rinse the rubber policeman over the beaker with the solution with a few drops of deionized water. Cover the beaker with a watch glass and continue heating at 90 °C for one hour. After this “digestion,” the precipitate should be coarse and the supernatant should be clear.

Collect the precipitate

21. Fold a piece of Whatman® Ashless #42 filter paper by following the steps below.

- **a.** Fold the filter paper in half and fold that in half again.
- **b.** Hold three of the four parts of the filter paper on one side.
- **c.** Pull out the fourth part of the filter paper and form a cone.
- **d.** Place the cone-shaped paper into the funnel.

- **e.** Wet the paper with a few drops of distilled water so the paper sticks to the wall of the funnel.

22. Support the funnel in the ring mounted on a ring stand over a beaker or flask of sufficient size (400-mL) to hold all of the supernatant.

Collect Data

23. In the 250-mL beaker, heat 100 mL of distilled water to about 80 °C for rinsing the precipitate.

24. Pour the mixture with the precipitate through the funnel with the filter paper.

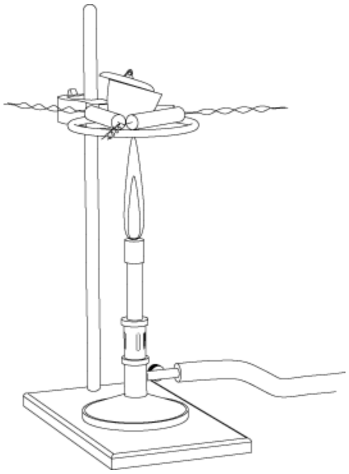
25. Use a rubber policeman and small washes of hot distilled water to remove any remaining precipitate from the beaker.

26. Wash the material in the funnel with three 5-mL portions of the hot, distilled water. Collect the washes separately in the small, 25-mL beakers.

27. Add two drops of the $AgNO_3$ solution to the last wash. If any cloudy white precipitate is observed, the precipitate still contains chloride ions and must be washed with hot distilled water a fourth time in a rinsed beaker.

Dry the precipitate

28. Clean and dry a porcelain crucible and lid. Then prepare the crucible as follows:



- **a.** Place the crucible and lid on the clay triangle over the Bunsen burner. Make sure the lid is slightly ajar.
- **b.** Heat the crucible with a gentle flame for 5 minutes by moving the burner around the bottom of the crucible.
- **c.** After the bottom of the crucible has become red-hot, increase the flame by allowing more air into the burner.
- **d.** Continue moving the burner around the bottom of the crucible.
- **e.** Heat the crucible for 10 to 12 minutes.
- **f.** Turn off the burner and allow the crucible to cool to room temperature.

Note: For the rest of the experiment, handle the crucible and lid using only crucible tongs. Also, do not set the crucible on the lab bench or it may crack or become contaminated.

29. Why do you have to use tongs to hold the lid?

Touching the lid with bare hands contaminates the lid and changes its mass, introducing error in the mass measurement. Also, the crucible may still be hot and cause injury.

30. After the crucible has cooled, measure and record the mass of the "fired" crucible, together with its lid, in Table 2.

Table 2: Mass of the empty crucible measured to the nearest tenth of a milligram

Measurement	Mass
Crucible and lid before heating (g)	31.3714
Crucible and lid after the first heating (g)	31.3576
Crucible and lid after the second heating (g)	31.3501
Crucible and lid after the third heating (g)	
Crucible and lid after the fourth heating (g)	

31. Repeat the steps above for heating, cooling, and measuring the mass of the crucible and lid until you have two readings for the mass that are within 10 mg of each other.

32. Copy the last measurement in Table 2 into Table 4.

33. Remove the filter paper containing the precipitate from the funnel. *Carefully* fold the filter paper so that the precipitate is trapped inside and the final shape is small enough to be placed into the crucible.

Note: To prevent the loss of precipitate, avoid tearing or breaking the folded filter paper.

34. Place the crucible on a wire triangle on a ring stand over a Bunsen burner.

35. Heat the crucible with a small flame so the filter paper does not burst into flame.

Note: Keep the tongs and crucible lid ready to quickly cover the crucible and extinguish any flame from the paper before material is expelled from the crucible.

36. Move the burner around and gradually increase the size of the flame so that all parts of the crucible are heated.

37. When all of the carbon residue from the filter paper has been removed, the temperature should be maximized by bringing the tip of the blue cone of the flame to a point just below the crucible. Continue heating the crucible for ten minutes.

38. Allow the crucible to cool for a few minutes and then place it into a desiccator, if available, using crucible tongs. Allow it to cool to room temperature. Measure and record the mass of the crucible, lid, and precipitate in Table 3.

Table 3: Mass of the crucible and sample, measured to the nearest tenth of a milligram

Measurement	Mass
Crucible, lid, and precipitate before heating (g)	32.8005
Crucible, lid, and precipitate after the first heating (g)	31.7656
Crucible, lid, and precipitate after the second heating (g)	31.7605
Crucible, lid, and precipitate after the third heating (g)	
Crucible, lid, and precipitate after the fourth heating (g)	

39. Repeat the heating, cooling, and measuring procedure until two successive mass measurements are within 10 mg of each other.

40. Record all measurements in Table 3. Copy the final measurement into Table 4.

41. You do not need to save your experiment in this experiment.

42. Clean up according to your instructor's instructions.

Data Analysis

1. Calculate the mass of the dried precipitate from the mass of the empty crucible and the mass of the crucible with the dried precipitate. Record the value in Table 4.

31.7605 g – 31.3501 g = 0.4104 g

2. Calculate the number of moles of precipitate from its mass and formula weight. Record the value in Table 4.

$$(0.4104 \text{ g BaSO}_4)\left(\frac{1 \text{ mol BaSO}_4}{233.43 \text{ g BaSO}_4}\right) = 1.758 \times 10^{-3} \text{ mol BaSO}_4$$

3. Calculate the number of moles of sulfate ions in the precipitate from the number of moles of precipitate. Record the value in Table 4.

The number of moles of sulfate ions is the same as the number of moles of precipitate since there is 1 mol of sulfate in 1 mol of precipitate. Therefore, there is 1.758×10^{-3} mol of sulfate ions in the precipitate.

4. Calculate the mass of the sulfate ions from the number of moles of sulfate ions. Record the value in Table 4.

$$(1.758 \times 10^{-3} \text{ mol SO}_4^{2-})\left(\frac{96.10 \text{ g SO}_4^{2-}}{1 \text{ mol SO}_4^{2-}}\right) = 0.1688 \text{ g SO}_4^{2-}$$

5. Calculate the theoretical percentage of sulfate content in the unknown sulfate sample based on the mass of the sulfate ions and the total mass of the sample. Record the value in Table 4.

$$\left(\frac{0.1688\text{ g}}{0.3580\text{ g}}\right) \times 100 = 47.15\%$$

Table 4: Determination of the amount of sulfate in the unknown

Parameter	**Value**
Mass of unknown sample (g)	0.3580
Mass of the crucible and lid (g)	31.3501
Mass of the crucible, lid, and precipitate (g)	31.7605
Mass of precipitate (g)	0.4104
Number of moles of precipitate (mol)	1.758×10^{-3}
Number of moles of SO_4^{2-} in precipitate (mol)	1.758×10^{-3}
Mass of SO_4^{2-} in precipitate (g)	0.1688
Percent SO_4^{2-} (%)	47.15

6. Complete the table below and use it to identify the unknown. Consider that the unknown is the sulfate of either an alkali or alkaline earth metal. Consider also that alkaline earth sulfates are not very soluble in water with the exception of $MgSO_4$. Select the one that is closest to your experimental result.

Table 5: Possible unknowns

Formula	**Formula Weight (g/mol)**	**SO_4^{2-} Content (%)**	**Solubility in Water**
Li_2SO_4	109.9	87.37	Soluble
Na_2SO_4	142.0	67.62	Soluble
$Na_2SO_4 \cdot H_2O$	322.0	29.81	Soluble
K_2SO_4	174.2	55.11	Soluble
$CaSO_4$	120.3	79.80	Slightly soluble
$MgSO_4$	136.1	70.54	Soluble
$SrSO_4$	183.6	52.29	Slightly soluble

Based on the data in Table 5, possible unknowns are K_2SO_4 and $SrSO_4$. Considering the fact that the unknown is extremely soluble in water, $SrSO_4$ can be ruled out since it is an alkaline earth metal sulfate. Therefore, most likely the unknown was K_2SO_4.

7. Calculate the percent error based on the experimental value of the percent sulfate content of the sample and the percent sulfate content of the proposed unknown.

$$\text{Percent Error} = \frac{|\text{Theoretical Value} - \text{Experimental Value}|}{\text{Theoretical Value}} \times 100$$

$$\text{Percent Error} = \frac{|55.11 - 47.17|}{55.11} \times 100 = 14.41\%$$

Analysis Questions

1. If ordinary filter paper had been used instead of ashless paper, how would your results be affected? Explain.

The ash residue would have contributed to the mass, resulting in error.

2. Why are the washes of the precipitate tested with $AgNO_3$?

$AgNO_3$ forms white AgCl precipitate with Cl^- ions:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

To make sure all Cl^- ions are removed the filtrate needed to be tested. Cl^- ions would have introduced an error.

3. What are the most likely sources of error in your procedure? Would they cause your result to be high or low?

Loss of precipitate during transfer would have yielded less precipitate and a lower percentage of sulfate content. If, however, the precipitate was not dried completely, that would have yielded higher mass and higher percent sulfate content.

4. Why do we have to make sure that the crystals are big?

Small crystals clog the filter paper, making the filtration process much longer.

5. Explain how you would determine the percent sulfate content in a $CaSO_4$ sample, since it is not very water soluble?

The sample would have to be converted to a water soluble form with, for example, HCl. This would produce $CaCl_2$, which is water soluble. Then the sulfate ions can be removed with $BaCl_2$ solution in the form of $BaSO_4$ as in this experiment.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Which other cation, if any, could have been used instead of Ba^{2+} to form a precipitate with the SO_4^{2-} ions?

Pb^{2+} ions would have worked, except $Pb(NO_3)_2$ solution would have been necessary because $PbCl_2$ is not soluble in water at room temperature.

2. What method might you use to analyze a sample that has both SO_4^{2-} and PO_4^{3-} ions? (Hint: Can you recall what is soluble in $Ba_3(PO_4)_2$ that is not soluble in $BaSO_4$?)

The analysis would need to be performed one time as described above. This would provide the total amount of SO_4^{2-} and PO_4^{3-} content. For the second analysis, after the precipitate was made, excess HCl solution can be added to dissolve the PO_4^{3-} ions. Only $BaSO_4$ remains as precipitate, therefore the SO_4^{2-} content can be obtained. The difference between the sulfate content and the total amount of SO_4^{2} and PO_4^{3-} content provides the PO_4^{3-} content.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Adding an excess amount of $BaCl_2$ solution:

- **A.** Results in an error because the excess amount will show up in the precipitate.
- **B. Makes no difference if the precipitate is thoroughly washed with water.**
- **C.** Is necessary for completion of the precipitation.
- **D.** Ruins the experiment.

2. Incomplete precipitation results in:

- **A.** Higher sulfate content than expected.
- **B. Lower sulfate content than expected.**
- **C.** Accurate sulfate content.
- **D.** Unpredictable results.

3. Incomplete transfer of precipitate from the beaker to the funnel results in:

- **A.** Higher sulfate content than expected.
- **B. Lower sulfate content than expected.**
- **C.** Accurate sulfate content.
- **D.** Unpredictable results.

4. Incomplete washing of the precipitate and incomplete drying of the precipitate:

- **A.** Have no effect on the results.
- **B.** Increases the sulfate content.
- **C.** Lowers the sulfate content.
- **D. Have opposite effects, as the incomplete drying increases the mass while the incomplete washing decreases the expected sulfate content.**

Extended Inquiry Suggestions

The analysis of a mixture of two different alkali sulfates can be performed and the challenge is to determine the percentage of the components of the mixture:

$$n_1 + n_2 = n$$

$$\left(2\mathrm{AW}_{\mathrm{M}_1} + 96\right)n_1 + \left(2\mathrm{AW}_{\mathrm{M}_2} + 96\right)n_2 = m$$

where

n_1 = number of moles of one of the alkali sulfate in the sample that was measured (mol)

n_2 = number of moles of the other alkali sulfate in the sample that was measured (mol)

$\mathrm{AW}_{\mathrm{M1}}$ = atomic weight of the first alkali metal (g/mol)

$2\mathrm{AW}_{\mathrm{M1}} + 96$ = formula weight of first alkali sulfate (g/mol)

$\mathrm{AW}_{\mathrm{M2}}$ = atomic weight of the second alkali metal (g/mol)

$2\mathrm{AW}_{\mathrm{M2}} + 96$ = formula weight of second alkali sulfate (g/mol)

m = mass of the sample that was measured (g)

n = total number of moles of $BaSO_4$ which is the same as the total number of moles of SO_4^{2-} in the sample (mol)

There are two equations with two unknowns to solve.

5. Identifying an Unknown Metal

Objectives

Students identify an unknown metal by applying and relating the Ideal Gas Law, the three possible oxidation numbers of metals, and the periodic table of elements.

Procedural Overview

Students gain experience conducting the following procedures:

- Employing a data collection system to monitor temperature and pressure in order to calculate the number of moles of hydrogen produced by a chemical reaction
- Using an electronic balance
- Applying the calculated number of moles of hydrogen gas produced to determine three possible atomic weights of the starting material
- Using the calculated atomic weights and the periodic table to identify the unknown metal

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Absolute pressure sensor with quick-release connectors and plastic tubing
- Stainless steel temperature sensor
- Graduated cylinder, 10-mL or 25-mL
- Graduated cylinder, 250-mL
- Erlenmeyer flask, 250-mL
- Beaker, 1500-mL
- Balance (1 per class)
- Rubber stopper with one hole
- 3 M Hydrogen chloride (HCl), 100 mL[1]
- Unknown metal (3 pieces), 0.2 g[2]
- Electrical tape, roll

---

[1] To prepare 3.0 M HCl, refer to the Lab Preparation section.

[2] Use magnesium ribbon as the unknown metal for this experiment.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Definition of an ideal gas
- Ideal Gas Law
- Standard temperature and pressure (STP) conditions
- Avogadro's Law
- Dalton's Law
- Chemical formula
- Balancing chemical equations
- Stoichiometric calculations

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Molar Mass of a Volatile Liquid
- Molar Volume of a Gas
- Exploring Gas Laws

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a temperature sensor and a pressure sensor to your data collection system �(2.2)
- Starting and stopping data recording �(6.2)

Background

Metals that have a more negative reduction potential than H^+ ions can reduce H^+ ions to H_2:

$$2\text{Me} + 2\text{H}^+ \rightarrow 2\text{Me}^+ + \text{H}_2 \tag{1}$$

$$\text{Me} + 2\text{H}^+ \rightarrow \text{Me}^{2+} + \text{H}_2 \tag{2}$$

$$2\text{Me} + 6\text{H}^+ \rightarrow 2\text{Me}^{3+} + 3\text{H}_2 \tag{3}$$

where "Me" refers to a metal.

A sample of the unknown metal can be reacted with an acid and the hydrogen formed can be collected. The amount of hydrogen collected can be calculated from its pressure, volume, and temperature. From the amount of hydrogen and the mass of the unknown metal sample, an approximation of the atomic weight of the metal can be calculated based on all three stoichiometric possibilities.

Pre-Lab Experiment

Setting the stage for the experiment

To identify an unknown metal reacted with an acid, the released H_2 gas is first captured in a closed container with known volume and known temperature. The Ideal Gas Law can be used to calculate the number of moles of hydrogen:

$$n = \frac{PV}{RT}$$

where

n = number of moles of hydrogen released in the reaction (mol)

P = partial pressure of hydrogen in the container (kPa)

T = temperature of the hydrogen gas (K)

R = universal gas constant (L kPa mol^{-1} K^{-1})

From the number of moles of hydrogen released and applying each of the possible three stoichiometric ratios, three atomic weights can be calculated. Based on the three calculations and the physical properties of the unknown, a match can be found in the periodic table.

Knowing the amount of hydrogen gas produced, the number of moles of the metal can be calculated for the three stoichiometric possibilities:

$$n \text{ mol H}_2 \left(\frac{x \text{ mol Me}}{y \text{ mol H}_2} \right) = \left(n \frac{x}{y} \right) \text{mol Me}$$

where n = number of moles of hydrogen collected and the three possibilities for x and y are shown in Table 1.

Table 1: Stoichiometric ratios, from Equations 1, 2, and 3, of metal ions to hydrogen gas

Possibility	x	y
1	2	1
2	1	1
3	2	3

The atomic weight of the unknown metal is then

$$\mathrm{AW_{Me}} = \frac{m}{n\,\frac{x}{y}} \tag{4}$$

where

m = mass of the unknown metal sample (g)

$\mathrm{AW_{Me}}$ = atomic weight of the unknown metal (g/mol)

n = number of moles of hydrogen collected

x = assumed stoichiometric coefficient for the unknown metal

y = assumed stoichiometric coefficient for hydrogen gas

Along with the three calculations, the apparent physical and chemical properties, such as color and reactivity with air, can also help to identify the metal.

Example calculation to try

Pennies used to be made of copper; currently however, pennies are made from a grey metal with a shiny, very thin, copper coating. We filed 0.340 g of a penny into a measuring dish and transferred it into a 250-mL Erlenmeyer flask. For the purpose of this experiment, we ignore the very thin copper coating.

Twenty milliliters of 3 M HCl solution was transferred into the Erlenmeyer flask. The flask was closed quickly with a two-holed rubber stopper containing a temperature sensor and a hose connected to a pressure sensor. The final pressure in the flask was 154.4 kPa. The atmospheric pressure in the lab was 101.0 kPa and the temperature of the gas was 298 K.

The volume of the Erlenmeyer flask was determined by filling the empty flask with water up to the rubber stopper and was found to be 261 mL. The number of moles of H_2 was:

$$n = \frac{PV}{RT}$$

$$n = \frac{(154.4\ \mathrm{kPa} - 101.0\ \mathrm{kPa})\left[\left(2.61 \times 10^{-1}\ \mathrm{L}\right) - \left(2.00 \times 10^{-2}\ \mathrm{L}\right)\right]}{\left(8.314\ \frac{\mathrm{L\,kPa}}{\mathrm{mol\,K}}\right)(298\,\mathrm{K})} = 5.20 \times 10^{-3}\ \mathrm{mol\,H_2}$$

Using Equation 4 and applying the stoichiometric ratio of Possibility 2 (substituting $x = 1$ and $y = 1$) the atomic weight will be

$$AW_{Me} = \frac{0.340\ \text{g}}{(5.20 \times 10^{-3}\ \text{mol H}_2) \times \left(\frac{1\ \text{mol Me}}{1\ \text{mol H}_2}\right)} = 65.4\ \text{g/mol}$$

Repeating the above calculation for the other two possibilities for x and y results in Table 2.

Table 2: Calculated atomic weight for each possible stoichiometric ratio

Possibility	***x***	***y***	**AW(g/mol)**	**Possible Oxidation Number of Me**
1	2	1	32.8	+1
2	1	1	65.5	+2
3	2	3	98.1	+3

The atomic weight of sulfur is 32 g/mol and the next element in the periodic table, chlorine, is 35.5 g/mol; neither of these are metals, so the results using Possibility 1 can be omitted. The element corresponding to the atomic weight resulting from applying the stoichiometric considerations of Possibility 2 would be zinc, a feasible option since zinc combines as Zn^{2+} in compounds.

For Possibility 3, the closest elements are molybdenum, 96.0 g/mol, technetium, 97.9 g/mol, and ruthenium, 101.07 g/mol. All three are rather uncommon, and not appropriate for coins. None is electronegative enough to reduce H^+ ions. Technetium is also radioactive.

Therefore, we concluded that the penny is made from zinc. The fact that zinc is cheap and commonly available also suggests the likelihood of its use in coins.

1. Why do you have to subtract the atmospheric pressure from the final pressure to obtain the pressure of the formed hydrogen gas?

We do this because the final pressure includes the atmospheric pressure and we need the partial pressure of hydrogen for the calculations.

2. Would it matter if the volume of the Erlenmeyer flask used in the experiment had been 250 mL?

No, because the number of moles of hydrogen depends only on the number of moles of unknown metal.

3. Why did we subtract the volume of the HCl solution from the volume of the flask?

The gas cannot occupy the portion of the flask where the HCl solution is; the available volume for the gas molecules is that much less.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***3 M HCl:*** Dilute concentrated hydrochloric acid solution in a 1:4 ratio with distilled water. The exact concentration is not critical in this experiment.

Safety

Add these important safety precautions to your normal laboratory procedures:

- If you get hydrochloric acid on your skin, wash it off with large amounts of water.
- Use goggles and rubber gloves for this experiment.
- Handle the Erlenmeyer flask very carefully when it is pressurized. A knock on the glass can cause it to crack. Because of the pressure, a slight explosion can occur.

Procedure with Inquiry

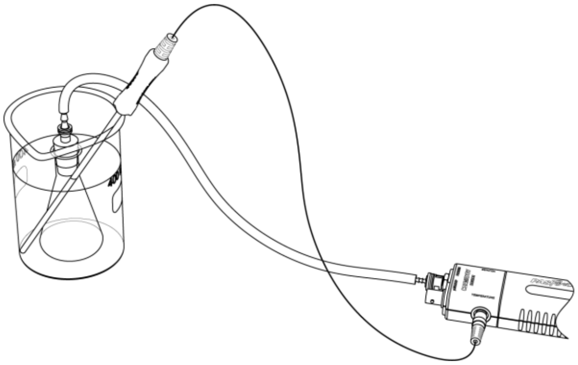
Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect a stainless steel temperature sensor and a pressure sensor to the data collection system. �(2.2)

3. Place the barbed connector tightly into the rubber stopper. Connect the barbed connector to the pressure port of the sensor with a piece of tubing.



4. Wrap the Erlenmeyer flask with 10 to 15 rounds of electric tape. This is a preventive measure in case the flask cracks. The tape keeps the glass pieces together.

5. Mount the 250-mL Erlenmeyer flask in a water bath in a 1500-mL beaker. The water should cover as much of the flask as possible.

6. Place the temperature sensor in the water bath.

7. Why is it necessary to immerse the flask as much as possible in the water bath?

It is necessary because we need to know the temperature of the gas in the flask. If the flask is not completely immersed, the temperature of the gas will not be the same as the temperature of the water bath and we will not know what the temperature of the gas is.

Collect Data

8. Perform the following steps. Repeat this part of the procedure three times.

a. Measure between 0.150 g and 0.180 g of the unknown metal to the nearest milligram. Record the mass of the sample in Table 3.

b. Using a graduated cylinder, measure 20.0 mL of 3.0 M HCl solution and transfer it into the 250-mL Erlenmeyer flask.

c. Display pressure and temperature data in a digits display. �(7.3.2)

d. Start data recording. �(6.2)

e. Record the initial pressure in Table 3.

f. What does the pressure reading on the sensor represent at this point?

The pressure sensor shows the atmospheric pressure of air.

g. Drop the measured piece of unknown metal into the flask and immediately insert the rubber stopper airtight.

Important: Make sure that the stopper is sitting firmly as pressure will build in the flask and a loose stopper may pop out. If that happens, you will need to repeat the experiment.

h. Continue to monitor the pressure. Once the hissing in the flask is over and the pressure has leveled off, record the final pressure and temperature readings in Table 3.

i. Stop data recording. �(6.2) You do not need to save your data.

j. What does the final pressure reading represent? (Hint: What components contribute to the final pressure?)

The final pressure reading represents the atmospheric pressure plus the pressure from the hydrogen gas produced.

k. Remove the stopper carefully and dispose of the spent acid solution properly.

l. Repeat the experiment for a total of three times.

9. Fill the Erlenmeyer flask to the top with water and, over a sink or waste container, insert the stopper (without tubing). Using the 250-mL graduated cylinder, measure the volume of the water to obtain the volume of the flask and record the value in Table 3.

Data Analysis

1. Calculate the number of moles of H_2 for each trial. Record your answers in Table 3.

For Trial 1:

$$n = \frac{PV}{RT}$$

$$n = \frac{(44.0\ \text{kPa})(2.42 \times 10^{-1}\ \text{L})}{\left(8.314\ \frac{\text{L kPa}}{\text{mol K}}\right)(302\ \text{K})} = 4.24 \times 10^{-3}\ \text{mol H}_2$$

Table 3: Number of moles *n* of H_2 calculated from the measured values

Parameters	Trial 1	Trial 2	Trial 3
Mass of unknown metal (g)	0.106	0.104	0.106
Pressure			
Initial pressure (kPa)	102	102	102
Final pressure (kPa)	146	147	149
Pressure of H_2 (kPa)	44.0	45.0	47.0
Temperature			
Mean temperature of water bath (K)	302	302	302.9
Volume			
Volume of flask (mL)	262		
Volume of flask (L)	2.62×10^{-1}		
Volume H_2 can occupy (mL)	242		
Volume H_2 can occupy (L)	2.42×10^{-1}		
Calculated Number of Moles of H_2			
Calculated number of moles of H_2 (mol)	4.24×10^{-3}	4.34×10^{-3}	4.52×10^{-3}

2. Using the mass of the unknown metal in Table 3, calculate the atomic weight for each run for each stoichiometric possibility and record calculations into Table 4.

$$2\text{Me} + 2\text{H}^{+} \rightarrow 2\text{Me}^{+} + \text{H}_2 \qquad (1)$$

$$\text{Me} + 2\text{H}^{+} \rightarrow \text{Me}^{2+} + \text{H}_2 \qquad (2)$$

$$2\text{Me} + 6\text{H}^{+} \rightarrow 2\text{Me}^{3+} + 3\text{H}_2 \qquad (3)$$

$$\text{AW}_{\text{Me}} = \frac{m}{n\frac{x}{y}}$$

For Trial 1, Equation 1 (Table 4: Possibility 1):

$$\text{AW}_{\text{Me}} = \frac{0.106\ \text{g}}{(4.24 \times 10^{-3}\ \text{mol H}_2) \times \left(\frac{2\ \text{mol Me}}{1\ \text{mol H}_2}\right)} = 12.5\ \text{g/mol}$$

For Equation 2 (Table 4: Possibility 2):

$$\text{AW}_{\text{Me}} = \frac{0.106\ \text{g}}{(4.24 \times 10^{-3}\ \text{mol H}_2) \times \left(\frac{2\ \text{mol Me}}{1\ \text{mol H}_2}\right)} = 25.0\ \text{g/mol}$$

For Equation 3 (Table 4: Possibility 3):

$$\text{AW}_{\text{Me}} = \frac{0.106\ \text{g}}{(4.24 \times 10^{-3}\ \text{mol H}_2) \times \left(\frac{2\ \text{mol Me}}{3\ \text{mol H}_2}\right)} = 37.5\ \text{g/mol}$$

Table 4: Calculation of atomic weight

Possibility	x	y	AW (g/mol)				Oxidation Number of Me
			Trial 1	Trial 2	Trial 3	Average	
1	2	1	12.5	12.0	11.7	12.1	+1
2	1	1	25.0	24.0	23.5	24.1	+2
3	2	3	37.5	35.9	35.2	36.2	+3

Analysis Questions

1. What elements can be assigned to Possibility 1 based on the obtained atomic weight? Argue if it is or is not a feasible option.

The atomic weight of 12.1 g/mol falls into the non-metal section between boron and carbon, which makes this an unlikely option.

2. What elements can be assigned to Possibility 2 based on the obtained atomic weight? Argue if it is or is not a feasible option.

The atomic weight of 24.1 g/mol suggests magnesium, which is indeed feasible since it forms compounds with a +2 oxidation state.

3. What elements can be assigned to Possibility 3 based on the obtained atomic weight? Argue if it is or is not a feasible option.

The atomic weight of 35.2 g/mol suggests chlorine, a non-metal. Even if we allow for some experimental error, chlorine falls on the wrong side of the periodic table. Therefore, Possibility 3 can also be ruled out.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Identify a common metal that usually has a +3 oxidation state and explain why you didn't consider it in Possibility 3?

Aluminum has a +3 oxidation state. However, it has the atomic weight of 27.0 g/mol—too much less than the atomic weight determined for Possibility 3, 35.2 g/mol to be considered.

2. If your unknown metal was zinc, would you have generated more or less hydrogen gas than the unknown metal you had (assuming you measured the same amount of the sample)?

Zinc has a substantially higher atomic weigh than magnesium does, so the same mass of zinc would have been fewer moles. Fewer moles of zinc would have generated less hydrogen gas.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. There were three options for identifying the unknown metal because:

- **A.** The unknown can be any metal.
- **B. There are three possible combinations of stoichiometry by which the unknown metal can react with the H^+ ions.**
- **C.** The experiment could have been performed three different ways.
- **D.** Metals can have three different oxidation states: +1, +2, and +3.

2. The reaction between the unknown metal and HCl was highly exothermic, resulting in a warm reaction mixture. Did this temperature change introduce an experimental error?

- **A.** Yes, but not too significant and we neglected it.
- **B.** Yes, since higher temperature would cause a higher pressure reading.
- **C. No, as long as equilibrium was established between the gas and the water bath.**
- **D.** No, temperature doesn't affect pressure

3. Would we have introduced an error if we used 50 mL of the HCl solution instead of 20 mL?

- **A.** Yes, a greater volume of HCl would have resulted in higher pressure.
- **B. No, it would not have introduced an error since the number of moles of hydrogen generated would have been the same.**
- **C.** Possibly we would have introduced an error as there may not have been enough HCl solution.

Extended Inquiry Suggestions

Have students carry out the experiment presented as the example in the Pre-Lab Experiment section. This experiment reinforces the metal experiment series, as H^+ can oxidize zinc but not copper. Old pennies are made from copper only; therefore, those pennies will not dissolve in HCl. This provides an excellent topic for discussion.

6. Synthesis of a Coordination Compound

Objectives

Students synthesize a coordination compound, potassium aluminum sulfate dodecahydrate (alum), and calculate the theoretical and percent yields.

Procedural Overview

Students gain experience conducting the following procedures:

- Carrying out a series of reactions that result in the synthesis of alum
- Practicing laboratory techniques
- Performing basic laboratory separation processes such as filtration, decanting, and recrystallization

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Balance (one per class)
- Hot plate
- Fume hood
- Beaker, 400-mL
- Beaker (2), 250-mL
- Beaker, 100-mL
- Graduated cylinder, 50-mL
- Büchner funnel
- Filter flask (also called a Büchner filter)
- Stirring rod, glass
- Watch glass
- Scissors
- Beaker tongs
- Filter paper (3)
- Wire gauze
- 3 M Sulfuric acid (H_2SO_4), 35 mL[1]
- 3 M Potassium hydroxide (KOH), 25 mL[2]
- 50% Ethanol, 50 mL[3]
- 100% Ethanol, 50 mL
- Acetone, 50 mL
- Aluminum foil, 1.1 g
- Distilled water for rinsing equipment
- Ice, 400 mL

[1-3] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Acid-base reactions
- Amphoteric behavior
- Balancing chemical equations
- Reduction-oxidation reactions
- Stoichiometry of chemical reactions

Related Labs in This Guide

Labs conceptually related to this one include:

- Analysis of a Coordination Compound
- Organic Synthesis I—Preparation

Using Your Data Collection System

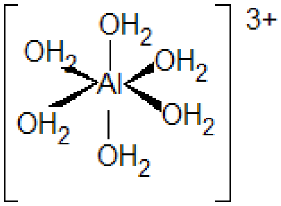
Note: As this lab experiment does not use a data collection system, no Tech Tips (indicated by the symbol "�" and a superscripted number following the step) are needed.

Background

Synthesis is an especially important procedure for manufacturing chemicals we use in everyday life. Along with naturally available chemicals, synthetic chemicals help make our lives more comfortable. This lab experiment is an excellent example of the synthesis process.

Alum is the name for a group of crystallized hydrated double sulfates. The following represents a general formula for alum, where M^+ refers to an alkali metal or ammonium ion, and M^{3+} refers to one of the trivalent metal ions:

$$M^+M^{3+}(SO_4)_2{\cdot}12H_2O$$



Hydrated aluminum ion

These salts are used in dyeing, water purification, and food preservation. They are also used as fire retardants and in various industrial processes. Potassium aluminum sulfate dodecahydrate, or potassium alum as it is known, is the commonly used form of alum. Although the aluminum ion exists in the $Al(H_2O)_6^+$ form in aqueous solution, we just usually omit writing the water molecules, since they play no role in the chemistry of the aluminum ion. The crystal of potassium alum forms with twelve water molecules.

Potassium alum, $KAl(SO_4)_2{\cdot}12H_2O$, can be synthesized through the following reactions: Potassium hydroxide (KOH) oxidizes aluminum to form soluble aluminum ions. The amphoteric aluminum ions form $Al(OH)_4^-$, which forms insoluble aluminum hydroxide, $Al(OH_3)$, when treated with sulfuric acid. Applying excess sulfuric acid, however, dissolves the aluminum hydroxide into Al^{3+} ions. As the nearly saturated solution cools, octahedral crystals of alum form.

Pre-Lab Experiment

Setting the stage for the experiment

Synthesizing alum starts with dissolving a piece of aluminum foil in a KOH solution. This forms $Al(OH)_4^-$ which reacts to create Al^{3+} ions (as one of the products) with H_2SO_4. After evaporating most of the water, crystals of $KAl(SO_4)_2 \cdot 12H_2O$ form.

To facilitate the precipitation process, the reaction mixture needs to cool and is then transferred into a filtration funnel. Filtration is a common technique to separate solid components from a mixture.

A chilled mixture of ethanol and water washes out the contaminating ions but minimizes the loss of the crystal product.

Example calculation to try

A sample of 1.012 g of aluminum foil was dissolved in 25 mL of 3 M KOH. The solution was filtered and 3 M H_2SO_4 was added to the supernatant (the clear, filtered solution). A sufficient amount of sulfuric acid was added so that the $Al(OH)_3$ that precipitated when sulfuric acid was first added, dissolved again.

Next, the reaction mixture was heated until the volume was reduced to about half of the original volume. After the reaction mixture was cooled, precipitated alum crystals were filtered and washed with 50% chilled ethanol. The crystals were dried and their mass measured. The mass of the crystals was 10.50 g.

The theoretical yield is:

$$(1.012\text{ g Al})\left(\frac{474.1\text{ g KAl(SO}_4)_2\cdot 12\text{H}_2\text{O}}{26.98\text{ g Al}}\right) = 17.77\text{ g KAl(SO}_4)_2\cdot 12\text{H}_2\text{O}$$

The actual yield was

$$\left(\frac{10.50\text{ g}}{17.77\text{ g}}\right) \times 100 = 59.09\%$$

1. What are the molecular, ionic, and net ionic equations of the dissolution of aluminum in KOH?

Molecular: $2Al(s) + 2KOH(aq) + 6H_2O \rightarrow 2KAl(OH)_4(aq) + 3H_2(g)$

Ionic: $2Al(s) + 2K^+(aq) + 2OH^-(aq) + 6H_2O \rightarrow 2K^+(aq) + 2Al(OH)_4^-(aq) + 3H_2(g)$

Net ionic: $2Al(s) + 2OH^-(aq) + 6H_2O \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$

2. What are the molecular, ionic, and net ionic equations converting the $KAl(OH)_4$ solution to $Al_2(SO_4)_3$ solution?

Molecular: $2KAl(OH)_4(aq) + 4H_2SO_4(aq) \rightarrow K_2SO_4(aq) + Al_2(SO_4)_3(aq) + 8H_2O$

Ionic: $2K^+(aq) + 2Al(OH)_4^-(aq) + 8H^+(aq) + 4SO_4^{2-}(aq) \rightarrow 2K^+(aq) + 4SO_4^{2-}(aq) + 2Al^{3+}(aq) + 4H_2O$

Net ionic: $Al(OH)_4^-(aq) + 4H^+(aq) \rightarrow Al^{3+}(aq) + 4H_2O$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***3 M H_2SO_4:*** Very slowly add 330 mL of 98% H_2SO_4 to at least 500 mL water in a 2-L volumetric flask. Once the solution has cooled, fill the flask to the mark.
2. ***3 M KOH:*** Dissolve 336 g KOH in water in a 2-L volumetric flask and fill it to the mark.
3. ***50% Ethanol:*** Combine 500 mL ethanol and some water in a 1-L volumetric flask and fill it to the mark.

Safety

Add these important safety precautions to your normal laboratory procedures:

♦ Both KOH and H_2SO_4 can cause serious burns. Handle them carefully. Wash off KOH or H_2SO_4 with plenty of water in case of skin contact.

Procedure with Inquiry

The procedure section of this set of labs typically comes with Tech Tips (indicated by the symbol "❖" and a superscripted number following a step). No Tech Tips apply to this particular lab.

Set Up

1. Measure the mass of a piece of aluminum foil. Trim the piece or add small pieces until the mass of the aluminum is about 1 g.

2. Record the mass of the aluminum, to two decimal places, in Table 1 in the Data Analysis section.

3. Cut the aluminum foil into small pieces and place them into a 250-mL beaker.

4. Set up the Büchner funnel and flask and insert a piece of filter paper into the funnel.

Collect Data

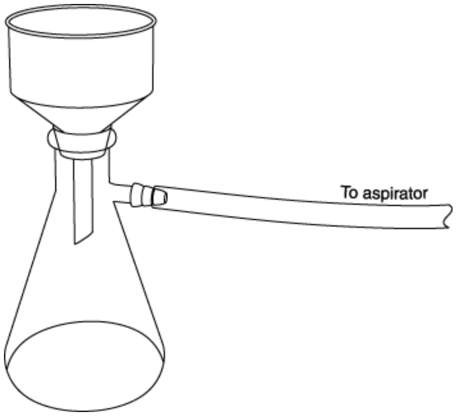
5. Under a fume hood, use the 50-mL graduated cylinder to slowly add 25 mL of 3 M KOH solution to the 250-mL beaker with the aluminum foil.

6. When all the aluminum has dissolved and the solution has cooled, carefully filter the solution through the Büchner funnel into the filter flask with the vacuum on.

7. Rinse the 250-mL beaker with distilled water while the vacuum is still on, and pour the filtered solution back into the beaker.

8. Why do you need to rinse the beaker?

The beaker needs to be rinsed to ensure all of the product is transferred into the funnel.



9. Clean the Büchner funnel and filter flask, and place a piece of filter paper into the funnel.

10. Allow the solution to cool to room temperature.

11. Rinse the graduated cylinder with distilled water.

12. Pour 5 mL of the 3 M H_2SO_4 into the graduated cylinder.

13. Stirring constantly with the glass rod, slowly add the 5 mL portion of the 3 M H_2SO_4 from the graduated cylinder to the beaker of reaction mixture with constant stirring. A precipitate should form as the OH^- ions are neutralized.

CAUTION: This reaction is exothermic—it generates heat.

14. Continue to add 5 mL portions of sulfuric acid until the precipitate dissolves.

15. What happens after enough H_2SO_4 is added to neutralize the KOH? What happens if excess H_2SO_4 is added?

When all the KOH is neutralized, $Al(OH)_3$ precipitates and then dissolves when additional H_2SO_4 is added and the solution becomes acidic, forming Al^{3+} ions.

16. Place the beaker on the hot plate and gently boil the solution until about 40 to 45 mL of solution remain and all the precipitate is dissolved.

17. Why is it necessary to evaporate a little more than half of the solvent?

Evaporating some of the solvent increases the concentration of the product, which promotes the precipitation.

18. Using beaker tongs, remove the beaker from the hot plate and place it on a piece of wire gauze. Allow the solution to cool to room temperature.

19. Prepare an ice bath, using the 400-mL beaker, for the 250-mL beaker and carefully place the beaker inside it. Do not disturb the ice bath or the beaker.

Note: Ice should be packed around the beaker above the level of the solution.

20. Why is it necessary to cool the mixture?

The solubility decreases as the temperature decreases. At lower temperature more product precipitates.

21. While the alum solution is in the ice bath, prepare a second ice bath in a 250-mL beaker.

22. Put 50 mL of 50% ethanol in a 100-mL beaker and place it carefully in the second ice bath.

Note: Ice should be packed around the beaker above the level of the solution.

23. After about 15 minutes, check the contents of the first beaker for the presence of alum crystals.

Note: If no crystals are visible, scratch the bottom of the beaker with a glass stirring rod to promote crystal formation.

24. Turn on the filtration system.

25. Pour the mixture through the funnel.

26. Wash the product remaining on the filter paper with the 50 mL of cold 50% ethanol solution.

27. Rinse the product with 50 mL of pure ethanol while continuing the filtration.

28. Rinse the product with 50 mL of acetone in order to dry the product.

29. After the acetone has drained from the Büchner funnel, continue the suction for another five minutes to ensure that the product is dry and then turn off the vacuum.

30. Carefully remove the filter paper and crystals and place them on a watch glass.

31. Allow the crystals to dry at room temperature.

32. Measure and record the mass of alum in Table 1 in the Data Analysis section.

33. Clean up according to your instructor’s directions.

Data Analysis

Record the necessary measurements and complete the calculations.

1. ☐ Calculate the amount of aluminum that was dissolved.

$$\frac{1.009\text{ g Al}}{26.98\ \frac{\text{g}}{\text{mol}}\text{ Al}} = 0.03740\text{ mol Al}$$

2. ☐ Calculate the theoretical number of moles of alum considering the stoichiometric ratio between aluminum and alum.

$$0.03740\text{ mol Al} = 0.03740\text{ mol alum}$$

3. ☐ Calculate the theoretical mass of alum that can be synthesized from the aluminum foil used for this procedure.

$$(0.03740\text{ mol KAl(SO}_4)_2{\cdot}12\text{H}_2\text{O})\left(\frac{474.3\text{ g KAl(SO}_4)_2{\cdot}12\text{H}_2\text{O}}{1\text{ mol KAl(SO}_4)_2{\cdot}12\text{H}_2\text{O}}\right) = 17.73\text{ g KAl(SO}_4)_2{\cdot}12\text{H}_2\text{O}$$

4. ☐ Calculate the yield from the theoretical amount and experimental amount of alum.

$$\left(\frac{15.33\text{ g}}{17.73\text{ g}}\right) \times 100 = 86.46\%$$

Table1: Determination of the yield of synthesized alum

Parameter	**Value**
Mass of aluminum foil (g)	1.009
Amount of aluminum (mol)	0.03740
Theoretical amount of alum (mol)	0.03740
Theoretical mass of alum (g)	17.73
Actual mass of alum (g)	15.33
Yield (%)	86.46

Analysis Questions

1. How could you increase the yield?

Reducing the volume of the reaction mixture by boiling as well as lowering the temperature of the ice bath could promote more precipitation.

2. How would contamination, such as dust, affect the formation of the crystals?

Contamination such as dust particles would serve as centers to initiate precipitation. Because of this, more but smaller crystals would form.

3. During crystallization, byproducts can also crystallize. What are two possible byproducts that can crystallize along with alum?

K_2SO_4 and $Al_2(SO_4)_3$ can crystallize along with alum.

4. How could you purify the crystals further? What is the drawback of purifying the crystals?

Recrystallization from water would purify the crystals. However, it would lower the yield.

Synthesis Questions

Use available resources to help you answer the following questions.

1. The term "alum" is a collective term for a group of salts. Briefly, how can you make alum with NH_4^+ instead of K^+?

The combination of solutions with stoichometric quantities of $(NH_4)_2SO_4$ and $Al_2(SO_4)_3$ would yield the $(NH_4)Al(SO_4)_2$ product. The rest of the process would be the same as the one performed in this experiment.

2. What is another metal ion that has a +3 oxidation state and would form an alum?

Cr^{3+} would be a good candidate to form $KCr(SO_4)_2$.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. What property of aluminum explains that it dissolves in KOH?

- **A.** It is a metal.
- **B. Since it is amphoteric, it can react with acids and bases.**
- **C.** Anything would dissolve in a strong base like KOH.
- **D.** None of the above.

2. What can be a potential problem if the volume of the solution is too large after boiling?

- **A.** No alum is produced.
- **B. Too much of the product remains in the solution, decreasing the yield.**
- **C.** A significant amount of the contaminants precipitates and necessitates recrystallization.
- **D.** Undesired byproducts form.

3. What happens if the alum solution isn't cooled sufficiently?

- **A.** No alum is produced.
- **B. Too much of the product remains in the solution, decreasing the yield.**
- **C.** A significant amount of the contaminants precipitates and necessitates recrystallization.
- **D.** Undesired byproducts form.

Extended Inquiry Suggestions

Suggest that students prepare more than one kind of alum. Combining saturated K_2SO_4 and $Cr_2(SO_4)_3$ solutions yields $KCr(SO_4)_2 \cdot 12H_2O$. This forms amazing-looking purple crystals.

CAUTION: Be sure to use excess K_2SO_4 to avoid contamination by $Cr_2(SO_4)_3$.

7. Analysis of a Coordination Compound

Objectives

Students confirm the identity of a sample of alum by conducting both qualitative and quantitative analyses.

Procedural Overview

Students gain experience conducting the following procedures:

- Conducting substance identification tests such as a melting point analysis and a flame test
- Performing a stoichiometric analysis, using a crucible and Bunsen burner, to determine the amount of water in a hydrated compound
- Conducting qualitative analyses for sulfate and aluminum

Time Requirement

Preparation time	30 minutes
Pre-lab discussion and experiment	30 minutes
Lab experiment	80 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- Ring stand with ring
- Clay triangle
- Clamp, buret
- Clamp, utility
- Crucible with lid
- Tongs
- Test tubes (2), 10 mL
- Beaker, 250-mL
- Capillary tube
- Stirring rod
- Watch glass (2), 100-mm
- Balance (1 per class)
- Centrifuge (1 per class)
- Wire with a loop on the end, 4 in.
- Hot plate
- Bunsen burner
- Striker
- 0.2 M Barium chloride ($BaCl_2$), 1 mL[1]
- 6 M Sodium hydroxide (NaOH), 5 mL[2]
- 6 M Hydrochloric acid (HCl), 5 mL[3]
- Borax, 0.5 g
- Alum from previous experiment, 3 g[4]
- Rubber band
- Water, 200 mL
- Distilled water, 10 mL

[1-3] To prepare the solutions refer to the Lab Preparation section.

[4] Use the alum prepared by the students in the "Synthesis of a Coordination Compound" experiment.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Stoichiometry of chemical reactions
- Reactions of anions

Related Labs in This Guide

Labs conceptually related to this one include:

- Mole Relationships in a Chemical Reaction
- Separation and Analysis of Cations
- Analysis of Anions
- Synthesis of a Coordination Compound
- Organic Synthesis II—Analysis

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system �(2.1)
- Starting and stopping data recording �(6.2)

Background

Once the synthesis of a compound has been completed, the identity of the compound produced should be confirmed. A number of tests can be used to confirm the identity of potassium alum, $KAl(SO_4)_2 \cdot 12H_2O$.

To verify that the substance is potassium alum, you will perform a melting point test and a flame test; you will measure the water of hydration, and you will verify the presence of aluminum and sulfate in the compound.

Pre-Lab Experiment

Setting the stage for the experiment

In this experiment, you will analyze the alum you synthesized in the previous experiment. The analysis includes quantitatively measuring the melting point and the amount of water of crystallization and qualitatively identifying potassium with a flame test, detecting sulfate ions in a reaction with Ba^{2+}, and detecting aluminum by dissolving the compound in both an acid and base.

Example calculation to try

Test 1

An alum sample prepared by a student was analyzed. First, a capillary tube was filled with some of the sample and mounted on a temperature sensor. The sensor was placed into a water bath and the water bath was heated slowly. The temperature was monitored. The crystals started to melt at 90 °C and melted completely at 91 °C.

Test 2

To determine the amount of water in the synthesized alum, an empty crucible, with an initial mass of 35.443 g, was heated to a constant mass (35.222 g). After a sample of the alum was placed in the crucible, the mass was found to be 35.791 g, so the mass of the alum was

$$35.791\text{ g} - 35.222\text{ g} = 0.569\text{ g}$$

The crucible was gently heated until no more vapor was released. After reheating until the mass of the crucible and remaining product was constant, the mass was 35.542 g. The amount of water lost was

$$35.791\text{ g} - 35.542\text{ g} = 0.249\text{ g}$$

0.249 g of water is

$$0.249\text{ g H}_2\text{O}\left(\frac{1\text{ mol H}_2\text{O}}{18.01\text{ g H}_2\text{O}}\right) = 1.38 \times 10^{-2}\text{ mol H}_2\text{O}$$

The mass and corresponding amount of the anhydrous alum was

$$0.569\text{ g} - 0.249\text{ g} = 0.320\text{ g}$$

$$0.320\text{ g alum}\left(\frac{1\text{ mol alum}}{258.1\text{ g alum}}\right) = 1.24 \times 10^{-3}\text{ mol alum}$$

The molar ratio between the water of crystallization and the anhydrous alum is

$$1.38 \times 10^{-2}{:}1.24 \times 10^{-3} = 11.1{:}1$$

The theoretical value is 12, therefore the percent error is

$$\text{Percent Error} = \frac{|\text{Theoretical Value} - \text{Experimental Value}|}{\text{Theoretical Value}} \times 100$$

$$\text{Percent Error} = \frac{12 - 11.1}{12} \times 100 = 7.50\%$$

Table 1: Synthesized alum analysis results

Measured Quantity	Values
Melting point (°C)	91.0
Mass of crucible and lid (g)	35.222
Mass of crucible, lid, and alum sample (g)	35.791
Mass of alum sample (g)	0.569
Mass of crucible, lid, and alum after final heating (g)	35.542
Water of hydration (g)	0.249
Water of hydration (mol)	1.38×10^{-2}
Mass of anhydrous alum (g)	0.320
Amount of anhydrous alum (FW: 258.1 g/mol) (mol)	1.24×10^{-3}
Experimental stoichiometric ratio between $KAl(SO_4)_2$ and water	11.1:1
% Error	7.50

Test 3

Another sample of the alum was dissolved in distilled water and reacted with $BaCl_2$ solution. A white precipitate was observed, indicating the presence of SO_4^{2-} ions.

Test 4

A piece of iron wire with a small loop on the end was heated in a Bunsen burner flame until it was red hot, then dipped into borax crystals on a watch glass and reheated until the borax formed a small bead on the tip of the wire. Then the borax bead on the tip was dipped into the alum sample and placed back into the Bunsen burner flame. Purple flames were observed, indicating the presence of K^+ ions.

Test 5

Another sample of the alum was dissolved in distilled water. Then NaOH solution was added, which formed a white precipitate. The precipitate was separated from the supernatant and split into two portions.

To one portion of the precipitate, HCl solution was added until the precipitate dissolved. To the other portion of the precipitate, NaOH solution was added until the precipitate dissolved. The result of these tests (the precipitate dissolved when both NaOH and HCl were added) substantiates the presence of Al^{3+}. (Aluminum hydroxide is amphoteric—it dissolves in both acid and base.)

1. What are the molecular, ionic, and net ionic equations of the reaction of alum with $BaCl_2$?

$KAl(SO_4)_2(aq) + 2BaCl_2(aq) \rightarrow KCl(aq) + AlCl_3(aq) + 2BaSO_4(s)$

$K^+(aq) + Al^{3+}(aq) + 2SO_4^{2-}(aq) + 2Ba^{2+}(aq) + 4Cl^-(aq) \rightarrow K^+(aq) + Al^{3+}(aq) + 4Cl^-(aq) + 2BaSO_4(s)$

$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

2. What are the molecular, ionic, and net ionic equations of the reactions of the precipitate obtained from reacting alum with NaOH and then with HCl?

$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O$

$Al(OH)_3(s) + 3H_3O^+(aq) + 3Cl^-(aq) \rightarrow Al^{3+}(aq) + 3Cl^-(aq) + 6H_2O$

$Al(OH)_3(s) + 3H_3O^+(aq) \rightarrow Al^{3+}(aq) + 6H_2O$

3. What are the molecular, ionic, and net ionic equations of the reactions between NaOH and the precipitate obtained from the alum solution with NaOH ?

$Al(OH)_3(s) + NaOH(aq) \rightarrow NaAl(OH)_4(aq)$

$Al(OH)_3(s) + Na^+(aq) + OH^-(aq) \rightarrow Na^+ + Al(OH)_4^-(aq)$

$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.2 M $BaCl_2$:*** Dissolve 4.88 g of $BaCl_2 \cdot 2H_2O$ in some water in a 100-mL volumetric flask and fill it to the mark.
2. ***6 M NaOH:*** Dissolve 24 g of NaOH in some water in a 100-mL volumetric flask and fill it to the mark.
3. ***6 M HCl:*** Under a hood, slowly add 128.5 mL of 36% HCl solution to about 100 mL of water in a 250-mL volumetric flask and fill it to the mark.

Safety

Add these important safety precautions to your normal laboratory procedures:

♦ If the NaOH or HCl solutions come in contact with your skin or eyes, rinse immediately with a large amount of running water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Part 1 – Melting point determination

Set Up

1. Set up the ring stand and hot plate as shown in the illustration.

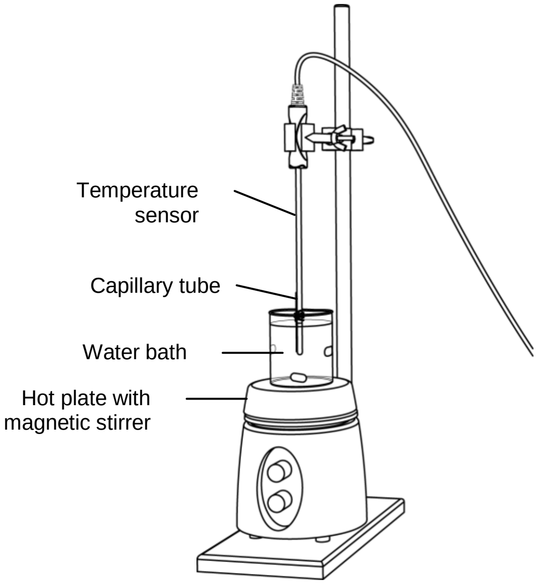
2. Fill a 250-mL beaker three-quarters full with water to use as a water bath. Place the beaker on the hot plate.

Note: Do not turn on the hot plate yet.

3. Start a new experiment on the data collection system. �(1.2)

4. Connect a stainless steel temperature sensor to the data collection system. �(2.1)

5. Create a graph display of Temperature (°C) versus Time (s). �(7.1.1)



6. Crush about 0.5 g of alum crystals to a fine powder in a watch glass using a glass stirring rod. Scrape the powdered alum into a pile in the center of the watch glass.

7. Push the open end of a capillary into the alum, then invert the capillary tube and tap the closed end on the bench top to pack the alum into the end. Repeat this procedure until the capillary tube contains about 1 cm of firmly packed alum.

8. Attach the capillary tube to the end of the temperature sensor with a small rubber band so that the bottom of the capillary tube is even with the end of the temperature sensor.

9. Why is it important to have the capillary attached to the end of the temperature sensor?

The tip of the sensor measures the temperature. Therefore, to measure the temperature accurately around the capillary the tip of the sensor should be close to the capillary.

10. Clamp the temperature sensor to the support stand using a utility clamp. Position the clamp so the tip of the temperature sensor and the portion of the capillary tube containing the alum are immersed in the water bath.

Note: Be sure that the open end of the capillary tube is above the water level so no water is able to get into the capillary.

Collect Data

11. Turn on the hot plate to heat the water bath at a gradual rate. Stir the water continuously while it heats.

12. Start data recording. �(6.2)

13. Observe the alum in the capillary tube until it has completely melted. Record the temperature in Table 4.

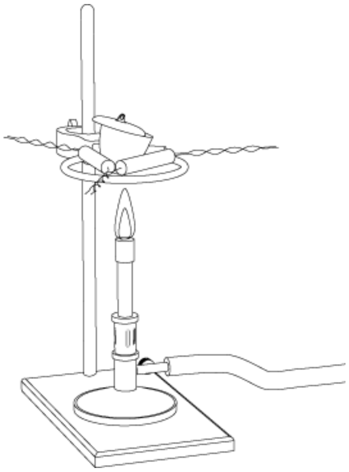
14. Stop data recording. �(6.2)

Part 2 – Water of hydration determination

Set Up

15. Clean and dry a porcelain crucible and lid.

16. Measure the mass of the crucible and lid. Record the measurement in Table 2.



17. To obtain a constant mass, prepare the crucible as follows:

- **a.** Place the crucible and lid on the clay triangle over the Bunsen burner. Make sure the lid is slightly ajar.
- **b.** Heat the crucible with a gentle flame for 5 minutes by moving the burner around the bottom of the crucible.
- **c.** After the bottom of the crucible has become red-hot, increase the flame by allowing more air into the burner.
- **d.** Continue moving the burner around the bottom of the crucible.
- **e.** Heat the crucible for 10 to 12 minutes.
- **f.** Turn off the burner and allow the crucible to cool to room temperature.

Note: For the rest of the experiment, handle the crucible and lid using only crucible tongs. Also, do not set the crucible on the lab bench or it may crack or become contaminated.

18. Why do you have to use tongs to hold the lid?

Touching the lid with bare hands contaminates the lid and changes its mass, introducing error in the mass measurement. Also, the crucible may still be hot and cause injury.

19. After the crucible has cooled, measure and record the mass of the "fired" crucible, together with its lid, in Table 2.

Table 2: Mass of the empty crucible measured to the nearest milligram

Measurement	Mass
Crucible and lid before heating (g)	29.851
Crucible and lid after the first heating (g)	29.835
Crucible and lid after the second heating (g)	29.833
Crucible and lid after the third heating (g)	
Crucible and lid after the fourth heating (g)	

20. Repeat the steps above for heating, cooling, and measuring the mass of the crucible and lid until you have two readings for the mass that are within 3 mg of each other.

21. Copy the last measurement in Table 2 into Table 4.

22. Why is it important to heat the crucible before using it?

It is important to remove contamination and moisture that would change the mass of the crucible when heating the sample.

23. Put about 2 g of alum into the crucible and measure the mass of the crucible, alum, and lid. Record the mass to the nearest 0.001 g in Table 3.

24. Place the crucible on the ring stand using the tongs and place the lid slightly ajar so that water vapor can escape.

Collect Data

25. Begin heating the crucible slowly with the Bunsen burner.

26. Why do you think it is important to heat the crucible slowly?

It is important to apply heat slowly because if the crucible is heated too quickly, the alum may splatter, resulting in error due to the loss of mass.

27. When vapor can no longer be seen escaping from the crucible, continue to move the burner around for 2 minutes, and gradually increase the size of the flame so that all parts of the crucible are heated.

28. Allow the crucible to cool for a few minutes and then place it into a desiccator, if available, using crucible tongs. Allow it to cool to room temperature. Measure and record the mass of the crucible, lid, and alum to the nearest milligram (0.001 g) in Table 3.

Table 3: Mass of the crucible and sample, measured to the nearest milligram

Measurement	**Mass**
Crucible, lid, and alum before heating (g)	31.813
Crucible, lid, and alum after the first heating (g)	30.972
Crucible, lid, and alum after the second heating (g)	30.972
Crucible, lid, and alum after the third heating (g)	
Crucible, lid, and alum after the fourth heating (g)	

29. Repeat the heating, cooling, and measuring procedure until two successive mass measurements are within 3 mg of each other.

30. Record all measurements in Table 3. Copy the final measurement into Table 4.

Part 3 – $BaCl_2$ test

Set Up

31. Dissolve a few alum crystals in 5 mL of distilled water

Collect Data

32. Add a few drops of $BaCl_2$ solution to the alum solution. Record your observations in Table 4.

33. Add 3 to 5 drops of the HCl solution to the precipitate. Record your observations in Table 4.

Part 4 – Flame test

Set Up

34. Place a few crystals of borax on a watch glass. On a separate watch glass place a few crystals of alum.

Collect Data

35. Place the tip of a wire with a little loop on the end in the Bunsen burner flame until the loop turns red hot.

36. Place the glowing loop into the borax crystals. The crystals will melt on the hot tip. Place the tip again into the flame until the borax forms a melted "pearl" on the tip.

37. Dip the hot tip into the alum crystals and back into the flame. Record your observations in Table 4.

Part 5 – Test for aluminum

Set Up

38. In one of the 10-mL test tubes, dissolve a few alum crystals in 5 mL of deionized water.

Collect Data

39. Add, by drops, 6 M NaOH while a white precipitate forms. Separate the supernatant from the precipitate. (If the solution does not separate, use a centrifuge.) Divide the precipitate into two 10-mL test tubes.

40. Slowly add 20 drops of 6 M NaOH solution to one test tube. Record your observations in Table 4.

41. Slowly add 20 drops of 6 M HCl solution to the other test tube. Record your observations in Table 4.

42. Clean up according to your instructor's directions.

Data Analysis

1. Calculate the error in the melting point between the literature value and from your experimental value. Record your results in Table 4.

$$\left(\frac{93.5\ ^{\circ}\text{C} - 92.5\ ^{\circ}\text{C}}{92.5\ ^{\circ}\text{C}}\right) \times 100 = 1.1\%$$

2. Determine the mass of the alum from the mass of the empty crucible and the mass of the crucible with the alum sample (before heating). Record your results in Table 4.

$$31.813\text{ g} - 29.833\text{ g} = 1.980\text{ g}$$

3. Determine the mass of the evaporated water from the mass of the crucible with the alum sample before heating and after heating. Record your results in Table 4.

$$31.8127\text{ g} - 30.9722\text{ g} = 0.840\text{ g}$$

4. Calculate the amount of water that evaporated. Record your results in Table 4.

$$\left(\frac{0.840\text{ g H}_2\text{O}}{18.02\ \frac{\text{g}}{\text{mol}}\ \text{H}_2\text{O}}\right) = 4.66 \times 10^{-2}\text{ mol H}_2\text{O}$$

5. Calculate the mass of the anhydrous alum from the mass of the crucible with the alum after heating and the mass of the empty crucible. Record your results in Table 4.

$$30.972\text{ g} - 29.833\text{ g} = 1.139\text{ g}$$

6. Calculate amount of the anhydrous alum from its mass and formula weight. Record your results in Table 4.

$$\left(\frac{1.139\text{ g alum}}{258.1\ \frac{\text{g}}{\text{mol}}\ \text{alum}}\right) = 4.413 \times 10^{-3}\text{ mol alum}$$

7. Calculate molar ratio between the water and the alum. Record your results in Table 4.

$$\left(\frac{4.664 \times 10^{-2}\text{ mol H}_2\text{O}}{4.413 \times 10^{-3}\text{ mol alum}}\right) = 10.57$$

8. Calculate the error in the ratio between the water and alum due to the difference between the literature value and the experimental value. Record your results in Table 4.

$$\left(\frac{12 - 10.57}{12}\right) \times 100 = 11.92\%$$

Table 4: Synthesized alum analysis results

Part 1 – Melting Point	
Theoretical melting point (°C)	92.5
Experimental melting point (°C)	93.5
Percent error (%)	1.08
Part 2 – Water of Hydration	
Mass of crucible and lid after heating (g)	29.833
Mass of alum (g)	1.980
Mass of crucible, cover, and alum before heating (g)	31.813
Mass of crucible, lid, and alum after heating (g)	30.972
Water of hydration (g)	0.840
Water of hydration (mol)	4.66×10^{-2}
Amount of anhydrous alum (g)	1.139
Amount of anhydrous alum (FW: 258.1 g/mol) (mol)	4.413×10^{-3}
Experimental stoichiometric ratio between $KAl(SO_4)_2$ and water	1:10.57
Percent error (%)	11.92
Part 3 – $BaCl_2$ Test	
$BaCl_2$	White precipitate forms
HCl	No change
Part 4 – Flame Test	
Flame turns purple	
Part 5 – NaOH Test	
Excess NaOH	Turns solution clear
HCl	Turns solution clear

Analysis Questions

1. How did the theoretical melting point compare to your experimental value? What is the reason for the deviation from the theoretical value (if there was any)?

The melting points were close—there was a difference of 1.08%. The deviation is probably due to contaminations such as K_2SO_4 and $Al_2(SO_4)_3$.

2. How did the theoretical water of hydration compare to your experimental value? What is the reason for the deviation from the theoretical value (if there was any)?

The difference was 10.50%. The deviation is probably due to contaminations such as K_2SO_4 and $Al_2(SO_4)_3$.

3. Why did we add HCl solution to the precipitate obtained with $BaCl_2$ from the alum solution? (Hint: Check the reactions of other possible anions.)

HCl was added to rule out the presence of PO_4^{3-} ions since $Ba_3(PO_4)_2$ dissolves in HCl.

4. Potassium ions color the Bunsen burner flame purple. Did you observe that color? Was there any other color you observed?

Sodium contamination may cause the flame to be yellow.

5. How does the reaction with NaOH, followed by the reactions with excess NaOH and HCl, prove the presence of aluminum? Write equations!

There is an $Al(OH)_3$ precipitate formed with NaOH. That precipitate is soluble in both NaOH and HCl:

$$Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O$$

$$Al(OH)_3(s) + NaOH(aq) \rightarrow NaAl(OH)_4(aq)$$

Synthesis Questions

Use available resources to help you answer the following questions.

1. Ionic compounds usually melt at very high temperatures. How do you explain that the alum melts below the boiling point of water? (Hint: What else, other than $KAl(SO_4)_2$, is present in the crystals?)

The alum does not actually melt; it dissolves in the water that is captured in the crystals.

2. What experiment would support your answer to the previous question? (Hint: Think back to the experiments you did in this experiment.)

You could continue heating the alum sample after the water evaporated in the melting point experiment. The anhydrous alum will not melt even when the crucible is glowing red hot.

3. What characteristics of aluminum does the reaction of $Al(OH)_3$ with NaOH and HCl underline? (Hint: To what category of substances do NaOH and HCl belong?)

The fact that $Al(OH)_3$ dissolves in both acids and bases demonstrates the amphoteric characteristic of aluminum.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. The melting point of alum is low because:

- **A.** Alum is a molecular compound.
- **B. Alum actually dissolves in its water of hydration and does not melt.**
- **C.** There are always contaminations present to lower the melting point.
- **D.** None of the above.

2. The experimental result for water of hydration does not show a ratio of integer numbers between $KAl(SO_4)_2$ and H_2O. What can you do?

- **A.** There is nothing to do other than report the experimental value.
- **B.** One has to multiply the numbers with integer numbers until the ratio becomes a ratio between two integer numbers.
- **C.** Repeat the experiment until you do get a ratio of integer numbers.
- **D. Round off the numbers to the nearest integer recognizing the experimental error of the process.**

3. A solution of the alum that you synthesized was combined with an $AgNO_3$ solution. There was no reaction observed. Does that contradict your claim that you synthesized alum?

- **A.** Yes, a yellow precipitate should have been observed.
- **B.** Yes, a white precipitate should have been observed.
- **C. No, no reaction was expected to occur.**
- **D.** It depends on the temperature at which the experiment was performed.

4. A solution of the alum you synthesized was combined with a $BaCl_2$ solution. There was no reaction observed. Does that contradict your claim that you synthesized alum?

- **A.** Yes, a yellow precipitate should have been observed.
- **B. Yes, a white precipitate should have been observed.**
- **C.** No, there no was reaction expected to occur.
- **D.** It depends on the temperature at which the experiment was performed.

Extended Inquiry Suggestions

If other types of alums were prepared previously (e.g. $KCr(SO_4)_2 \cdot 12H_2O$) they could be analyzed using the same methods found in this experiment.

Thermochemistry and Thermodynamics

8. Enthalpy of a Chemical Reaction

Objectives

Students use Hess's Law to calculate the enthalpy change of a reaction between ammonia and hydrochloric acid in aqueous solution.

Procedural Overview

Students gain experience conducting the following procedures:

- Carrying out and monitoring the temperature change of 3 reactions
- Comparing the results of the enthalpy calculated from the heat of reaction to that calculated using Hess's Law

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- Polystyrene cup, 8 oz.
- Clamp, utility
- Beaker, 250-mL
- Graduated cylinder, 50-mL or 100-mL
- Ring stand
- 2.00 M Sodium hydroxide (NaOH), 50 mL[1]
- 2.00 M Hydrochloric acid (HCl), 50 mL[2]
- 2.00 M Ammonium chloride (NH_4Cl), 50 mL[3]
- 2.00 M Ammonia (NH_3), 50 mL[4]

[1–4] To prepare the solutions using NaOH, 36% HCl, NH_4Cl, and 30% ammonia solution, refer to the Lab Preparation section

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Stoichiometric calculations
- Hess's Law
- First Law of Thermodynamics
- Balancing chemical equations

Related Labs in This Guide

Labs conceptually related to this one include:

- Determination of the Rate of the Decomposition of Hydrogen Peroxide

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �$^{(1.2)}$
- Connecting sensors to the data acquisition device �$^{(2.1)}$
- Starting and stopping data recording �$^{(6.2)}$
- Saving your experiment �$^{(11.1)}$

Background

Hess's Law

Hess's Law states that if a chemical reaction is the combination of other chemical reactions, then the heat of reaction is the sum of the heat of reactions of the combined reactions. There are two important components of Hess's Law. First, the heat of reaction is independent of the path of the reaction. This means the heat of reaction is the same if the reaction is performed in one step or through multiple reactions.

Second, if we know the heat of reaction for each step except one and we know the heat of reaction for the complete reaction, we can calculate the heat of reaction for the unknown step. This is an important tool for obtaining the heat of reaction for reactions that are difficult to perform.

To use Hess's Law, we often use the theoretical form of the equation even though it might not accurately represent how the reaction takes place. For example, Equation 1 is the theoretical representation for the production of water.

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H = 286 \text{ kJ/mol} \tag{1}$$

In the actual process, each O_2 molecule reacts with two H_2 molecules.

Often we must use the reverse of an equation when we combine multiple equations in order to get a final equation. The reverse of Equation 1 is

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \qquad \Delta H = -286 \text{ kJ/mol}$$

While this reaction does not occur naturally, the energy change of this theoretical process is accurate. (It is the same as the forward reaction but it has the opposite sign.)

The First Law of Thermodynamics

Thermochemistry studies are based on measuring the heat that is released or absorbed in a chemical process. The First Law of Thermodynamics states that energy is conserved in a process; therefore, any energy released or absorbed as heat can be measured by its direct effect on the environment. For example, if a reaction is performed in an aqueous solution, released heat will increase the temperature of the solution and we can determine the amount of heat involved in the reaction from the temperature change. The heat q lost or gained by the system can be calculated as follows:

$$q = mc\Delta T$$

where

q = heat lost or gained (J)

m = mass of the solution (g)

c = specific heat of the solution [J/(g °C)]

ΔT = change of temperature due to the reaction.

(The product of m and c is the "heat capacity" C (J/ °C) of the solution.)

Pre-Lab Experiment

Setting the stage for the experiment

In order to calculate the enthalpy change in a reaction, you will perform the following reactions:

$$NaOH + HCl \rightarrow NaCl + H_2O \qquad \Delta H_1$$

$$NaOH + NH_4Cl \rightarrow NH_3 + NaCl + H_2O \qquad \Delta H_2$$

Based on the heat of reaction of these reactions, you will predict how to calculate the heat of reaction for the following reaction:

$$NH_3 + HCl \rightarrow NH_4Cl \qquad \Delta H_3$$

You will perform the third reaction to confirm your prediction.

You will perform the reactions in a polystyrene cup placed inside a beaker. The polystyrene cup is a good heat insulator and insulation is enhanced by the beaker around it. Therefore, the escape of heat is reduced. The temperature change of the solution in the cup will be monitored with a temperature sensor.

Example calculation to try

The heat of reaction between magnesium (Mg) and oxygen (O_2) is to be measured. While this reaction occurs directly (quite spectacularly, actually), it would be very difficult to measure the heat of reaction directly. Instead, use Hess's Law to determine the heat of reaction indirectly.

The following reactions will be used:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \qquad \Delta H_1$$

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O \qquad \Delta H_2$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H_3 = -286 \text{ kJ/mol}$$

We measured the heat of reactions for the first two reactions and used the published value for the third.

To obtain the desired equation, the second equation has to be reversed, so that the sign of ΔH_2 is changed:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2 \qquad \Delta H_1 \quad \text{(to be measured)}$$

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl \qquad -\Delta H_2 \quad \text{(to be measured)}$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H_3 = -286 \text{ kJ/mol}$$

$$Mg + \tfrac{1}{2}O_2 \rightarrow MgO \qquad \Delta H_4 \quad \text{(to be measured)}$$

The heat of reaction will be: $\Delta H_4 = \Delta H_1 + (-\Delta H_2) + \Delta H_3$

The reactions were carried out in a calorimeter made from a polystyrene cup with 50.0 mL of a 2 M HCl solution, set in a beaker. The heat capacity of the calorimeter was:

$$C = (50.0 \text{ g})\left(4.18 \frac{\text{J}}{\text{g °C}}\right) + \left(15.0 \frac{\text{J}}{\text{°C}}\right) = 224 \frac{\text{J}}{\text{°C}}$$

where 4.18 J/(g °C) is the specific heat of water and 15.0 J/°C is the heat capacity of the cup. The heat capacity of the calorimeter, including the material of the calorimeter and the solution, is the amount of the heat that increases the temperature of the entire calorimeter by 1 °C.

In the calorimeter, the magnesium sample was added to the 50 mL of 2 M HCl and the change in temperature obtained. In the second experiment in the calorimeter, the sample of MgO was added to another 50 mL of 2 M HCl solution and the change in temperature also obtained. The experimental data was recorded in Table 1.

Table 1: Experimental and calculated data to determine the heat of reaction

Parameters	**Reaction 1 (Mg + HCl)**	**Reaction 2 (MgO + HCl)**
C (J/°C)	224	224
m (g)	0.4654	1.055
T_i (°C)	23.5	22.5
T_f (°C)	66.9	38.0
ΔT (°C)	43.4	15.5
q (J)	9.72×10^3	3.47×10^3
ΔH (kJ/mol)	508	133

The heat gain of Reaction 1 was

$$q = C\Delta T = \left(224\ \frac{\text{J}}{°\text{C}}\right)(43.4\ °\text{C}) = 9.72 \times 10^3\,\text{J}$$

This heat was produced by 0.4654 g of Mg, which is

$$\frac{(0.4654\ \text{g})}{\left(24.3\ \frac{\text{g}}{\text{mol}}\right)} = 1.92 \times 10^{-2}\ \text{mol Mg}$$

Therefore, the molar heat of reaction is

$$\Delta H_1 = \frac{(-9721.6\ \text{J})}{(1.92 \times 10^{-2}\,\text{mol})} = -508\ \frac{\text{kJ}}{\text{mol}}$$

The negative sign indicates the reaction was exothermic.

The value of ΔH_2 can be calculated the same way. Note that the sign of q is reversed because ΔH_4 is calculated with the second reaction reversed,.

The heat of reaction for the desired reaction is:

$$\Delta H_4 = \Delta H_1 - \Delta H_2 + \Delta H_3 = \left(-508\ \tfrac{\text{kJ}}{\text{mol}}\right) - \left(-133\ \tfrac{\text{kJ}}{\text{mol}}\right) + \left(-286\ \tfrac{\text{kJ}}{\text{mol}}\right) = -640\ \tfrac{\text{kJ}}{\text{mol}}$$

1. **Refer to the equations you will be studying during this experiment. Combine the first two reactions in such a way that the resulting combination will result in the third reaction. (Hint: If you reverse a reaction, the heat of reaction has the same value, but the opposite sign.)**

The second reaction would have to be reversed:

$$\begin{array}{rcll} \mathrm{NaOH + HCl} & \rightarrow & \mathrm{NaCl + H_2O} & \Delta H_1 \\ \mathrm{NH_3 + NaCl + H_2O} & \rightarrow & \mathrm{NaOH + NH_4Cl} & -\Delta H_2 \\ \hline \mathrm{NH_3 + HCl} & \rightarrow & \mathrm{NH_4Cl} & \Delta H_3 \end{array}$$

2. **How do you calculate the heat of reaction for the third reaction in terms of the heat of reactions for the first two reactions?**

$\Delta H_3 = \Delta H_1 + (-\Delta H_2)$ or $\Delta H_3 = \Delta H_1 - \Delta H_2$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***2.00 M NaOH:*** Dissolve 160 g of NaOH in some water in a 2-L volumetric flask. After the solution cools, fill the flask to the mark. (Do not store NaOH in a volumetric flask. Over time the NaOH reacts with the glass and will cause you to be unable to open the flask.)
2. ***2.00 M HCl:*** Under a hood, slowly add 330 mL of 36% HCl solution to about 500 mL of water in a 2-L volumetric flask. Fill the flask to the mark.
3. ***2.00 M NH_4Cl:*** Dissolve 214 g NH_4Cl in some water in a 2-L volumetric flask and fill it to the mark.
4. ***2.00 M NH_3 :*** Under a hood add 260 mL of 30% ammonia solution to some water in a 2-L volumetric flask. Fill the flask to the mark. If a hood is not available, obtain pre-made 2 M ammonia solution.

Safety

Add these important safety precautions to your normal laboratory procedures:

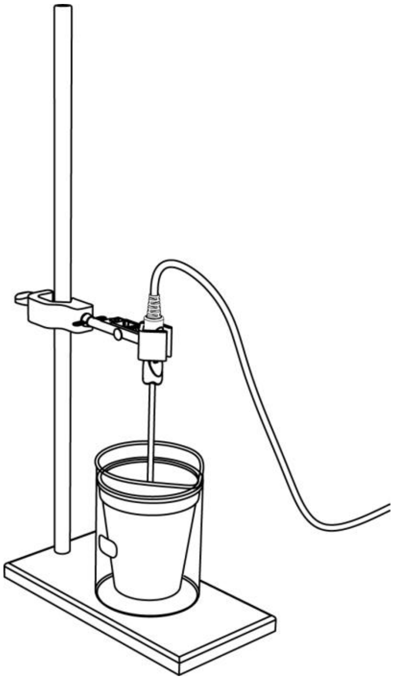
- Avoid contact with the ammonia solution. Ammonia can irritate your nose or eyes. If irritation occurs, breathe fresh air.

- If the NaOH or HCl solutions come in contact with your skin or eyes, rinse immediately with a large amount of running water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up



1. Start a new experiment on the data collection system. �(1.2)

2. Connect a temperature sensor to the data collection system.�(2.1)

3. Create a graph display of Temperature (°C) versus Time (s). �(7.1.1)

4. Place the polystyrene cup in the 250-mL beaker.

5. Mount the temperature sensor on the ring stand and set it into the cup about half an inch from the bottom.

6. Why do you place the cup in a beaker?

The air trapped between the wall of the cup and the beaker serves as further heat insulation to lower the heat loss.

Collect Data

7. Perform the three reactions in the calorimeter using the reactants shown in Table 2 following the steps below.

Table 2: Reactant volumes

Reaction	**Solution 1**	**Solution 2**
1	50.0 mL 2.00 M HCl	50.0 mL 2.00 M NaOH
2	50.0 mL 2.00 M NaOH	50.0 mL 2.00 M NH_4Cl
3	50.0 mL 2.00 M HCl	50.0 mL 2.00 M NH_3

For each reaction,

a. Measure Solution 1 and transfer it into the cup.

b. Rinse the graduated cylinder with deionized water.

c. Measure 50 mL of Solution 2.

d. Start recording data. �(6.2)

e. When the temperature readings stabilize, quickly add Solution 2 to the cup. Continue monitoring the temperature until the temperature starts to drop, then stop recording data. �(6.2)

f. Dispose of the solutions properly, wash the cup and graduated cylinder, and rinse them with deionized water.

Note: Please handle the ammonia solution with extra care. Allow the solution as little as possible exposure to air and make sure you do not breathe near the ammonia solution. If ammonia irritates your nose or eyes, go where there is fresh air.

8. Determine the initial and maximum temperature for each data run and record the values in Table 3 in the Data Analysis section. �(9.1)

9. Save your experiment and clean up according to your instructor's instructions �(11.1)

Data Analysis

Use the following value for the heat capacity of the calorimeter:

$$C = (100.0\text{ g})\left(4.18\ \frac{\text{J}}{\text{g °C}}\right) + \left(15.0\ \frac{\text{J}}{\text{°C}}\right) = 433\ \frac{\text{J}}{\text{°C}}$$

1. Write the equations for the three reactions you conducted.

$NaOH + HCl \rightarrow NaCl + H_2O$

$NH_3 + NaCl + H_2O \rightarrow NaOH + NH_4Cl$

$NH_3 + HCl \rightarrow NH_4Cl$

2. Calculate the change of temperature due to each reaction. Record your results in Table 3.

Calculating the change of temperature for Reaction 1:

$$31.8\ °\text{C} - 21.9\ °\text{C} = 9.9\ °\text{C}$$

3. Calculate the change of heat based on the change of temperature and the heat capacity of the reactor for each reaction. Record your results in Table 3.

Calculating the change of heat for Reaction 1

$$q = C\,\Delta T = \left(433\ \frac{\text{J}}{°\text{C}}\right)(9.9\ °\text{C}) = 4.3 \times 10^3\ \text{J}$$

4. Calculate the amount of each reactant present in each reaction. Record your results in Table 3.

Since the volume and the concentration of the two solutions were the same and the stoichiometric ratio between them is 1:1, the amount of the two reactants is the same. They are present in stoichiometric ratio.

For Reaction 1:

$$\left(2.00\ \frac{\text{mol}}{\text{L}}\right)(0.0500\ \text{L}) = 0.100\ \text{mol NaOH and HCl}$$

5. Calculate the molar change of heat for each reaction. Record your results in Table 3.

For Reaction 1:

$$\left(\frac{4.3 \times 10^3\ \text{J}}{0.100\ \text{mol}}\right) = 4.3 \times 10^4\ \frac{\text{J}}{\text{mol}} = 43\ \frac{\text{kJ}}{\text{mol}}$$

Table 3: Experimental and calculated data to determine the heat of reaction

Parameters	Reaction 1	Reaction 2	Reaction 3
Initial temperature (°C)	21.9	21.8	21.8
Maximum temperature (°C)	31.8	22.8	31.4
Change of temperature (°C)	9.9	1.0	9.0
q (J)	4.3×10^3	4.3×10^2	3.9×10^3
Amount of reactant (mol)	0.100	0.100	0.100
Molar heat of reaction (kJ/mol)	43	4.3	39

6. Verify that the heat of Reaction 3 can be calculated from Reactions 1 and 2 the way you proposed earlier.

Answers will depend on student's results. In the sample data set:

$\Delta H_3 = \Delta H_1 - \Delta H_2 = (43\text{ kJ}) - (4.3\text{ kJ}) = 39\text{ kJ}$

The experimental value was 39 kJ.

Analysis Questions

1. Identify potential sources of experimental error and propose solutions.

Imperfect heat insulation results in heat loss and, as a result, experimental error. To minimize heat loss, use a lid on the cup or use two cups (one placed inside the other) to double the wall thickness.

2. All solutions used the heat capacity of water ($4.18\text{ J g}^{-1}\,°\text{C}^{-1}$) to calculate the heat capacity of the colorimeter. Did this introduce an error? Explain!

The error introduced is negligible because the heat capacity of diluted solutions is very close to the heat capacity of pure water.

3. Suppose all of the temperature readings were off by 0.5 °C. How would that change your results?

A consistent deviation in temperature readings would not have any effect on the results because the difference between temperature readings is used to calculate the heat of reaction. That difference would be the same.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Use Hess's Law to obtain ΔH_4 for the following reactions.

$C_3H_6 + H_2 \rightarrow C_3H_8$ ΔH_1

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ ΔH_2

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ ΔH_3

$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O$ ΔH_4

Reversing the third reaction yields the right combination:

$\Delta H_4 = \Delta H_1 + \Delta H_2 - \Delta H_3$.

2. Another way of performing calorimetric experiments is in a "bomb" calorimeter. A sample is placed in a "bomb," which is a stainless steel container with heavy duty walls to withstand high pressure. It is pressurized with O_2 and the sample is ignited. The temperature increase is monitored. From this the heat of reaction can be obtained. Consider the following:

A food sample (2.200 g) was burnt in an experiment with a bomb calorimeter. The heat capacity of the calorimeter was 5.754 kJ/°C. The temperature changed from 24.56 °C to 32.33 °C. What is the heat of reaction per gram of this food sample?

$$\Delta H = \frac{-\left(5.754\ \frac{\text{kJ}}{^\circ\text{C}}\right)\left(32.33\ ^\circ\text{C} - 24.56\ ^\circ\text{C}\right)}{\left(2.200\ \text{g}\right)} = -20.3\ \frac{\text{kJ}}{\text{g}}$$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Hess's Law:

A. Gives the heat of reaction for a reaction obtained by combining the heat of reaction of other reactions.

B. Provides evidence that the heat of reaction is independent of the path of the reaction.

C. Can be used to obtain the heat of reaction for reactions not possible to perform.

D. All of the above.

2. The heat capacity of the calorimeter is:

- **A. The amount of heat necessary to increase the temperature of the calorimeter, including the solutions, 1 °C.**
- **B.** The same as the heat of reaction per mole of reactant.
- **C.** Can be obtained from the heat of reaction of the combined reactions.
- **D.** Is usually negligible.

3. The heat change that accompanies the dissolution processes can be measured with calorimetry as well. In an experiment, 5.00 g of NH_4NO_3 was dissolved in 50 mL of water in a polystyrene cup calorimeter. The temperature dropped from 23.50 °C to 17.57 °C. What is the heat of reaction for the dissolution of NH_4NO_3?

- **A.** $\Delta H = +\ 1330$ J/mol.
- **B. $\Delta H = +\ 21.3$ kJ/mol.**
- **C.** $\Delta H = -\ 21.3$ kJ/mol.
- **D.** $\Delta H = +\ 2130$ J/mol.

Extended Inquiry Suggestions

Students can perform the experiment presented in the Pre-Lab Experiment section in a calorimeter. This experiment demonstrates that the heat of reaction for unmeasurable reactions can be obtained.

Atomic and Nuclear Structure

9. Absorption Spectra

Objectives

Students learn about the composition of the electromagnetic radiation in the visible range, develop an understanding of how the interaction of objects and solutions with light result in the perception of color, and dispel their misconception of objects "having color".

Procedural Overview

Students gain experience conducting the following procedures:

- Using a simple spectrophotometer and making spectroscopic measurements
- Applying color charts to determine the wavelengths transmitted and absorbed that result in various colors

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system[1]
- Spectrometer
- Cuvette
- Sensor extension cable
- Test tubes (6), large
- Test tube rack
- Graduated cylinder, 10-mL
- 0.1 M Iron(III) chloride ($FeCl_3$), 10 mL[2]
- 0.1 M Copper(II) chloride ($CuCl_2$), 10 mL[3]
- 0.1 M Cobalt(II) chloride ($CoCl_2$), 10 mL[4]
- 0.1 M Nickel(II) chloride ($NiCl_2$), 10 mL[5]
- 0.1 M Sodium chloride (NaCl), 10 mL[6]
- Color chart[7]
- Wash bottle with distilled water
- Marking pen

[1] Use either Xplorer GLX™ or a computer with Quantum software for the Amadeus spectrometer system.

[2-6] To prepare the solutions, refer to the Lab Preparation section.

[7] To present the color chart, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Moles
- Molarity
- Ionic nomenclature
- Electrolytes
- Absorbance, Beer's Law

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Equilibrium Constant for a Chemical Reaction
- Colorimetric Analysis
- Separation by Liquid Chromatography
- Order of Reaction

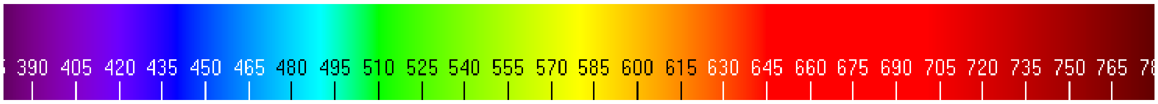
Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting sensors to the data collection system �(2.1)
- Setting up the spectrometer �(4.4)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Displaying all data runs �(7.1.3)
- Printing �(11.2)
- Saving your experiment �(11.1)

Background

It is a common misconception that the apparent color of objects is, in fact, a property of the objects themselves. The perception of the color of the object is the color of the light that is *reflected* by the object or *transmitted* by a solution. Regular white light has the full visible spectrum, approximately 380–760 nanometers (nm).



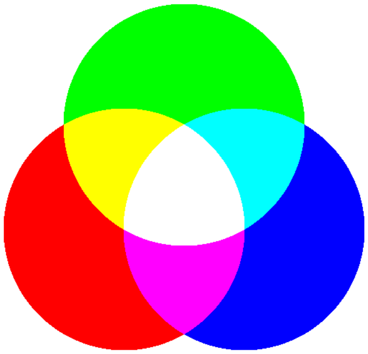
When light hits an object, the object absorbs some of the light waves and the rest of the light is reflected; this is the portion that we can see. If light is transmitted through a solution, photons with a certain wavelength can be absorbed by species in the solution, the rest of the light is transmitted through it, which we can then observe.

Pre-Lab Experiment

Setting the stage for the experiment

In actuality, it rarely happens that an object shows a color because all the other colors are absorbed. Instead, various components of the white light are absorbed to various extents, resulting in an array of visible colors. A thorough discussion of colors would be beyond this experiment; we need, however, to touch upon the topic in order to help you understand how absorption spectra are made.

There are three primary colors when discussing light: red, green, and blue. The combination of all three of these colors results in white (see the color chart). Now, if all the blue is absorbed, only the green and red light get to your eyes. As a result, you will see yellow.

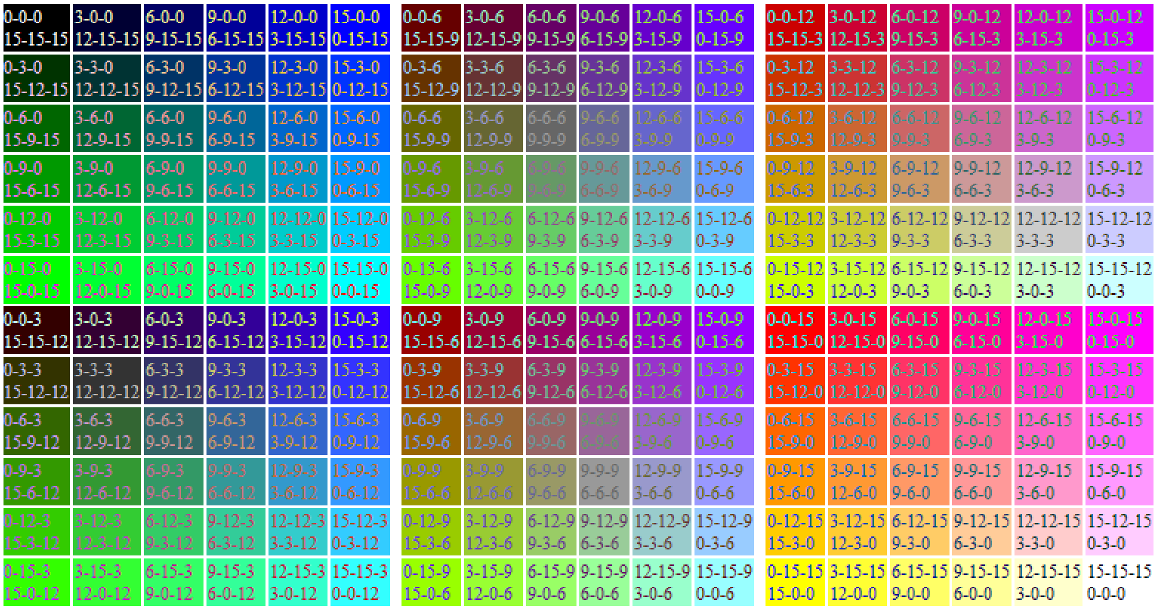


Also, if only one color is absorbed, then the mixture of the photons of the other two colors is visible. So if only the blue photons are absorbed, the red and green photons are observed as yellow. To make matters more complicated, not all the photons of a specifically-colored light necessarily have to be absorbed.

We can use a scale between 0 and 15 to describe the portion of photons of the particular color of the light that enters your eyes. For example, a light described by 15-red, 15-blue, and 15-green means that all the three colors are present in full; there was no absorption. Also, 10-red, 15-blue, and 5-green describes a light in which some of the red (5) photons and almost all of the green (10) photons were absorbed, but none of the blue photons were.

The chart below shows the different colors that result from various partial and full absorption of the primary colors. The top sequence of numbers represents (from left to right), the amount of blue, green, and red photons transmitted (present) on a 0 to 15 scale. The bottom sequence of numbers represents (from left to right) the amount of blue, green, and red photons absorbed on a 0 to 15 scale. For example, 10–15–5 in the top row means that the amount of blue present is 10, the amount of green is 15, and the amount of red is 5. The bottom set of numbers in the same block would be 5–0–10, indicating that 5 photons of blue, 0 photons of green, and 10 photons of red were absorbed.

Color chart



0-0-0 15-15-15	3-0-0 12-15-15	6-0-0 9-15-15	9-0-0 6-15-15	12-0-0 3-15-15	15-0-0 0-15-15	0-0-6 15-15-9	3-0-6 12-15-9	6-0-6 9-15-9	9-0-6 6-15-9	12-0-6 3-15-9	15-0-6 0-15-9	0-0-12 15-15-3	3-0-12 12-15-3	6-0-12 9-15-3	9-0-12 6-15-3	12-0-12 3-15-3	15-0-12 0-15-3
0-3-0 15-12-15	3-3-0 12-12-15	6-3-0 9-12-15	9-3-0 6-12-15	12-3-0 3-12-15	15-3-0 0-12-15	0-3-6 15-12-9	3-3-6 12-12-9	6-3-6 9-12-9	9-3-6 6-12-9	12-3-6 3-12-9	15-3-6 0-12-9	0-3-12 15-12-3	3-3-12 12-12-3	6-3-12 9-12-3	9-3-12 6-12-3	12-3-12 3-12-3	15-3-12 0-12-3
0-6-0 15-9-15	3-6-0 12-9-15	6-6-0 9-9-15	9-6-0 6-9-15	12-6-0 3-9-15	15-6-0 0-9-15	0-6-6 15-9-9	3-6-6 12-9-9	6-6-6 9-9-9	9-6-6 6-9-9	12-6-6 3-9-9	15-6-6 0-9-9	0-6-12 15-9-3	3-6-12 12-9-3	6-6-12 9-9-3	9-6-12 6-9-3	12-6-12 3-9-3	15-6-12 0-9-3
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0-6-3 15-9-12	3-6-3 12-9-12	6-6-3 9-9-12	9-6-3 6-9-12	12-6-3 3-9-12	15-6-3 0-9-12	0-6-9 15-9-6	3-6-9 12-9-6	6-6-9 9-9-6	9-6-9 6-9-6	12-6-9 3-9-6	15-6-9 0-9-6	0-6-15 15-9-0	3-6-15 12-9-0	6-6-15 9-9-0	9-6-15 6-9-0	12-6-15 3-9-0	15-6-15 0-9-0
0-9-3 15-6-12	3-9-3 12-6-12	6-9-3 9-6-12	9-9-3 6-6-12	12-9-3 3-6-12	15-9-3 0-6-12	0-9-9 15-6-6	3-9-9 12-6-6	6-9-9 9-6-6	9-9-9 6-6-6	12-9-9 3-6-6	15-9-9 0-6-6	0-9-15 15-6-0	3-9-15 12-6-0	6-9-15 9-6-0	9-9-15 6-6-0	12-9-15 3-6-0	15-9-15 0-6-0
0-12-3 15-3-12	3-12-3 12-3-12	6-12-3 9-3-12	9-12-3 6-3-12	12-12-3 3-3-12	15-12-3 0-3-12	0-12-9 15-3-6	3-12-9 12-3-6	6-12-9 9-3-6	9-12-9 6-3-6	12-12-9 3-3-6	15-12-9 0-3-6	0-12-15 15-3-0	3-12-15 12-3-0	6-12-15 9-3-0	9-12-15 6-3-0	12-12-15 3-3-0	15-12-15 0-3-0
0-15-3 15-0-12	3-15-3 12-0-12	6-15-3 9-0-12	9-15-3 6-0-12	12-15-3 3-0-12	15-15-3 0-0-12	0-15-9 15-0-6	3-15-9 12-0-6	6-15-9 9-0-6	9-15-9 6-0-6	12-15-9 3-0-6	15-15-9 0-0-6	0-15-15 15-0-0	3-15-15 12-0-0	6-15-15 9-0-0	9-15-15 6-0-0	12-15-15 3-0-0	15-15-15 0-0-0

To characterize the ability of solutions to absorb light we use two physical quantities: transmittance T and absorbance A. Transmittance is defined as

$$T \equiv \frac{I}{I_0}$$

where I is the number of transmitted photons (the intensity) in unit time with the absorbing species present, and I_0 is the number of transmitted photons in unit time with the absorbing species absent. As it is rather difficult to work with the number of photons, absorbance is used instead:

$$A \equiv -\log T = -\log \frac{I}{I_0}$$

It is important to keep in mind that absorption depends on wavelength, and therefore is color specific. That is, the ability of a substance to absorb light is different for photons with different wavelength.

In this experiment, you will study five solutions of different colors and predict what the absorption spectra of the five solutions looks like.

Example calculation to try

We compared three solutions: $NaNO_3$, $Cu(NO_3)_2$, and $Co(NO_3)_2$. The following table indicates the observed colors:

Table 1: Colors of various solutions

Solution	**Color**
$NaNO_3$	Colorless
$Cu(NO_3)_2$	Blue
$Co(NO_3)_2$	Pink/purple

Since all three substances are strong electrolytes, they all dissociate completely. As each solution has a different color, the color cannot be attributed to the anion, NO_3^-. Therefore, the different colors are associated with the different metal ions.

Since the $NaNO_3$ solution is colorless, we can conclude that the sodium ion does not absorb any photons in the visible spectrum. Since the $Cu(NO_3)_2$ solution is blue, we would guess that the Cu^{2+} ions don't absorb the blue photons and do absorb the red and green photons.

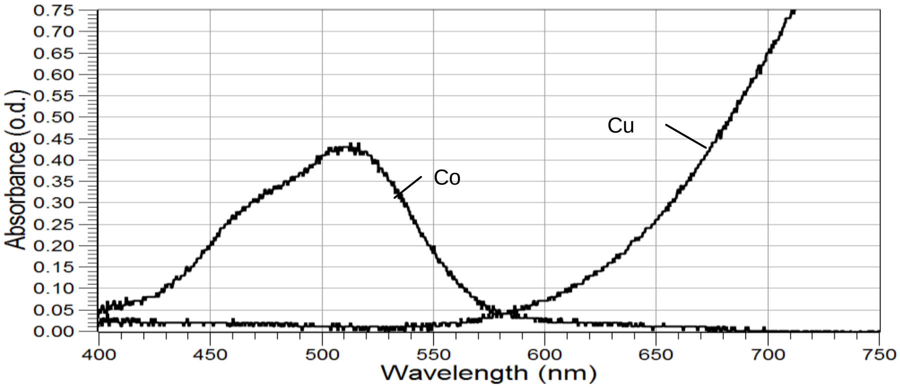
As predicted, in the absorption spectrum of the blue range (430–490 nm) we find no significant absorbance. Likewise, we assume that in the green range (510–550 nm) and in the red range (above 660 nm) there must be significant absorption. However, as you can see on the graph below, there is no significant absorption in the green range (510–550 nm), only in the red range. This means that both green and blue photons are transmitted. The green and blue photons make a color called cyan blue and indeed, the solution of $Cu(NO_3)_2$ is light green-blue.

Table 2: Wavelengths of white and the primary colors

Color Range	**Wavelength (nm)**
White	380–760
Blue	430–490
Green	510–550
Red	>660

The $Co(NO_3)_2$ solution is a dark pink or light purple. Matching the color of the solution to the color chart, the color matches the 15–0–15 block (rightmost column in the middle of the color chart) for the components transmitted. This indicates significant absorbance in the green and little or no absorbance in the red and blue areas. Indeed, the absorption spectrum below shows this behavior.

Absorption spectra



1. **If an object appears to be bright red, what wavelength range do you think it reflects? Explain!**

Bright red color suggests that only red photons are reflected. Red photons are above 600 nm in wavelength.

2. **What wavelength range do you think it absorbs? Explain!**

It must absorb the green and blue photons which have wavelengths in the range of 430–600 nm.

3. **Record in Table 3 the color of the solutions you will be working with, as well as the ions and molecules present in each solution.**

Table 3: Solution composition and color

Solution	Color	Ions, Molecules
$CoCl_2$	Pink/purple	Co^{2+}, Cl^-
$NiCl_2$	Green	Ni^{2+}, Cl^-
$FeCl_3$	Faint yellow	Fe^{3+}, Cl^-
$CuCl_2$	Cyan	Cu^{2+}, Cl^-
NaCl	Colorless	Na^+, Cl^-

4. Based on the colors of the solutions, complete the table, predicting the transmitted colors and the colors and corresponding wavelength ranges of the light absorbed.

Table 4: Solution color predictions

Solution	Visible Color	Transmitted Primary Colors	Absorbed Primary Colors	Wavelength Ranges Absorbed
$CoCl_2$	Purple/pink	Blue and Red	Some blue, all green and some red	380–500 nm (blue), some 500–550 nm (green), all 650–750 nm (red) a some
$NiCl_2$	Green	Much green and a little blue	Some of blue, all of red	380–500 nm (some blue) 650–750 nm (all red)
$FeCl_3$	Yellow	Some green, some red	All blue, some red	380–500 nm (most blue) 650–750 nm (some red)
$CuCl_2$	Blue	Much blue, some green	All red, some green	650–750 nm (all red) 500–550 nm (some green)
NaCl	Clear	All	None	None

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.10 M $FeCl_3$***: Dissolve 13.51 g of $FeCl_3 \cdot 6H_2O$ in some water in a 500-mL volumetric flask and fill the flask to the mark.
2. ***0.10 M $CuCl_2$:*** Dissolved 8.52 g of $CuCl_2 \cdot 2H_2O$ in some water in a 500-mL volumetric flask and fill the flask to the mark.
3. ***0.10 M $CoCl_2$:*** Dissolve 11.89 g of $CoCl_2 \cdot 6H_2O$ in some water in a 500-mL volumetric flask and fill the flask to the mark.
4. ***0.10 M $NiCl_2$:*** Dissolve 11.88 g of $NiCl_2 \cdot 6H_2O$ in some water in a 500-mL volumetric flask and fill the flask to the mark.
5. ***0.10 M NaCl:*** Dissolve 2.92 g of NaCl in some water in a 500-mL volumetric flask and fill the flask to the mark.
6. Print or project the color images from the last page of the experiment in the PDF file contained in the accompanying CD.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Set up the spectrometer. �(4.4.2)

2. Add about 10 mL of each of the 5 solutions into separate, labeled test tubes.

3. Are the solutions strong electrolytes, weak electrolytes, or non-electrolytes? List the ions and molecules present in the solutions.

The solutions are made from ionic compounds which are strong electrolytes; upon solution they dissociate to form ions. In this solution the ions formed are Fe^{3+}, Cu^{2+}, Ni^{2+}, Na^{+}, Co^{+}, and Cl^{-}. Of course, water molecules are present as well.

4. Observe the color of the solutions. Based on your observation and on your answer to the previous question, what ions do you think are responsible for the colors of the solutions?

Since every solution is a different color and every solution has H_2O and Cl^{-} ions, those species cannot be responsible for the color difference. Therefore, the colors have to be determined by the cations.

Collect Data

5. Display Absorbance on the y-axis of a graph with Wavelength on the x-axis. �(7.1.1)

6. Start data recording. �(6.2)

Instructor Tip: If necessary adjust the signal-to-noise ratio of the spectrometer �(4.4.3)

7. Measure the absorbance of the five solutions following the steps below.

a. Rinse the cuvette with a small portion of the first solution and fill the cuvette two-thirds full. Wipe the cuvette clean and dry and place it into the spectrometer.

b. Why do you have to rinse the cell with some of the solution?

If there is any residual water in the cuvette, it will dilute the concentration of the solution and falsify the data.

c. Dispose of the solution and rinse the cell thoroughly with water.

d. Why do you think it is important to rinse the cell thoroughly between measurements?

You need to rinse the cell to avoid contamination of the solutions.

8. Stop data recording. �(6.2)

9. Display all data runs. �(7.1.3)

10. Print the graph. �(11.2)

11. Save your experiment �(11.1) and clean up according to your instructor's instructions.

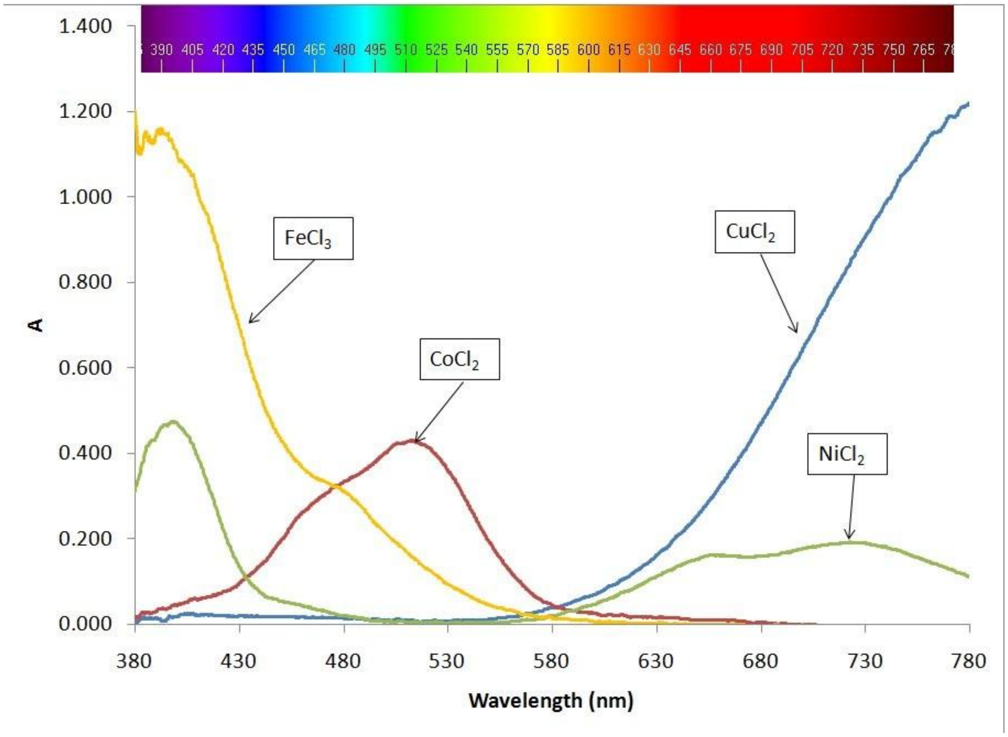
Data Analysis

1. Summarize your data in the table below.

Table 5: Absorption data

Solution	Visible Color	Predicted Absorption Wavelength Ranges	Wavelength Ranges Absorbed
$CoCl_2$	Red	380–500 nm (some blue) 500–550 nm (all green) 650–750 nm (some red)	380–600 nm (blue, green)
$NiCl_2$	Green	380–500 nm (some blue) 650–750 nm (all red)	380–475 nm (some blue) 575–750 nm (red all)
$FeCl_3$	Yellow	380–500 nm (most blue) 650–750 nm (some red)	380–575 nm (all blue and green)
$CuCl_2$	Blue	650–750 nm (all red) 500–550 nm (some green)	575–750 nm (all red)
NaCl	Clear	none	none

2. Sketch or paste the spectrum curves for the five solutions.



Analysis Questions

1. Find the color of the FeCl$_3$ solution on the color chart. What portions of the red, green, and blue photons are absorbed? Does it match with the absorption spectrum of your solution?

The best matching color shows the presence of blue 0, green 12, and red 15. The absorbed blue is 15, green is 3 and red is 0. This absorption pattern represents high absorption in the blue, some absorption in the green and no absorption in the red range. The absorption spectrum for the solution is in agreement with this.

2. Find the color of the NiCl$_2$ solution on the color chart. What portions of the red, green, and blue photons are absorbed? Does it match with the obtained absorption spectrum?

The absorbed blue is 12, green is 3 and red is 12. This absorption pattern represents high absorption in the blue, no absorption in the green and significant absorption in the red range. The absorption spectrum obtained is in agreement with this.

Synthesis Questions

Use available resources to help you answer the following questions.

1. The solution of KMnO$_4$ is purple. Describe the absorption spectrum of KMnO$_4$.

The purple color is most likely a blend of red and blue light suggesting the absorption of green. Therefore it is most likely that there will be little or no absorption in the blue and red range and significant absorption in the green range.

2. An absorption spectrum shows significant absorption in the blue and little or no absorption in the green and red range. What color do you think the solution is?

The remaining green and red make some shade of yellow.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. A colorless solution:

- **A. Absorbs no photons from the white light.**
- **B.** Emits photons to make up white light.
- **C.** Absorbs all photons; therefore we cannot observe any colors.
- **D.** Cannot transmit light.

2. $MnSO_4$ has a very faint yellow color. Which color of photons do you think are *not* absorbed?

- **A.** Blue and green
- **B.** Red and blue
- **C. Red and green**
- **D.** Blue and red

3. The Liquid Chromatography experiment analyzes grape Kool-Aid. The analysis shows both a red and a light blue component. Which statement cannot be correct regarding the two colored components?

- **A. The red and light blue, once mixed, gives a colorless solution.**
- **B.** The red component has significant absorbance in the green and blue range
- **C.** The mix of the red and blue components will not contain green photons.
- **D.** The blue component has significant absorbance in the red range.

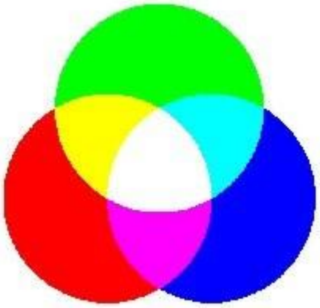
Extended Inquiry Suggestions

The eluent solution from the Liquid Chromatography experiment can be analyzed with the spectrometer. Since the red component absorbs the green and blue ranges, and the blue component absorbs in the red and green ranges, the process can be followed by monitoring the absorption spectrum of the eluent leaving the column.

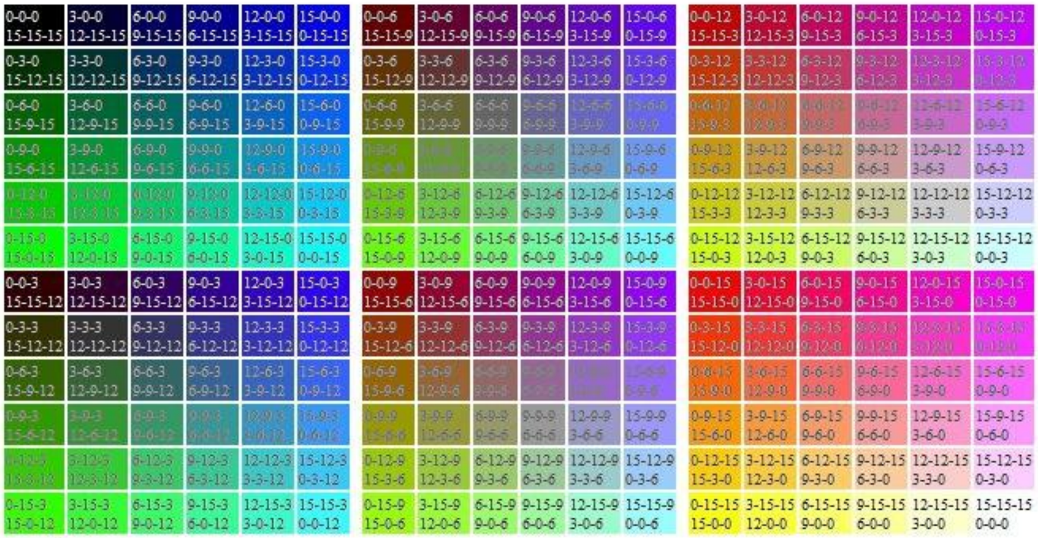
Eluent aliquots of ~0.5mL can be collected and analyzed. The reconstructed graph of absorbance versus time (or volume) represents the chromatogram. This process demonstrates how High Performance Liquid Chromatography (HPLC) works with an absorbance detector. HPLC is one of the most commonly used techniques today. For details, please refer to the experiment "Lab 18: Separation by Liquid Chromatography".

Absorption Spectra Color Images

The three primary colors and the various color combinations



The color chart



0-0-0 15-15-15	3-0-0 12-15-15	6-0-0 9-15-15	9-0-0 6-15-15	12-0-0 3-15-15	15-0-0 0-15-15
0-3-0 15-12-15	3-3-0 12-12-15	6-3-0 9-12-15	9-3-0 6-12-15	12-3-0 3-12-15	15-3-0 0-12-15
0-6-0 15-9-15	3-6-0 12-9-15	6-6-0 9-9-15	9-6-0 6-9-15	12-6-0 3-9-15	15-6-0 0-9-15
0-9-0 15-6-15	3-9-0 12-6-15	6-9-0 9-6-15	9-9-0 6-6-15	12-9-0 3-6-15	15-9-0 0-6-15
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0-3-6 15-12-9	3-3-6 12-12-9	6-3-6 9-12-9	9-3-6 6-12-9	12-3-6 3-12-9	15-3-6 0-12-9
0-6-6 15-9-9	3-6-6 12-9-9	6-6-6 9-9-9	9-6-6 6-9-9	12-6-6 3-9-9	15-6-6 0-9-9
0-9-6 15-6-9	[illegible]	[illegible]	9-9-6 6-6-9	12-9-6 3-6-9	15-9-6 0-6-9
0-12-6 15-3-9	3-12-6 12-3-9	6-12-6 9-3-9	9-12-6 6-3-9	12-12-6 3-3-9	15-12-6 0-3-9
0-15-6 15-0-9	3-15-6 12-0-9	6-15-6 9-0-9	9-15-6 6-0-9	12-15-6 3-0-9	15-15-6 0-0-9
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0-12-15 15-3-0	3-12-15 12-3-0	6-12-15 9-3-0	9-12-15 6-3-0	12-12-15 3-3-0	15-12-15 0-3-0
0-15-15 15-0-0	3-15-15 12-0-0	6-15-15 9-0-0	9-15-15 6-0-0	12-15-15 3-0-0	15-15-15 0-0-0

Example:

9-3-12
6-12-3

9 of blue, 3 of green and 12 of red is left
6 of blue, 12 of green and 3 of red is absorbed

10. Determining the Half-Life of an Isotope

Objectives

Students investigate the radioactive decay and half-life of an isotope.

Procedural Overview

Students gain experience conducting the following procedures:

- Measuring the radioactive decay of barium-137m
- Calculating the decay constant and half-life of an isotope

Time Requirement

♦ Preparation time	10 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	25 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Alpha beta gamma radiation sensor [1]
- Barium-137m solution[2]
- Aluminum plate

[1] The alpha beta gamma radiation sensor is also referred to as the G-M counter.

[2] To prepare the barium-137m solution using the isotope generator kit, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- First-order kinetics
- Logarithmic representation of data
- Radioactivity

Related Labs in This Guide

Labs conceptually related to this one include:

- Determination of the Rate of the Decomposition of Hydrogen Peroxide
- Order of Reaction

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to your data collection system �(2.1)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Finding the slope and intercept of a best-fit line �(9.6)
- Creating calculated data set �(10.3)
- Save your experiment �(11.1)
- Printing �(11.2)

Background

A nuclear reaction in which an unstable isotope of an element emits radiation spontaneously is called “radioactive decay.” There are three basic types of radiation that can be emitted during a decay process: alpha “α” (essentially the nucleus of He atoms, ${}_{2}^{4}\mathrm{He}^{2+}$), beta “β” (made up of electrons), and gamma ”γ” (high energy electromagnetic radiation).

Radioactive (or nuclear) decay is a *random* process, yet it is somewhat predictable. It is not possible to predict when a particular radioactive atom will decay, but it is safe to say that the more unstable an isotope is, the more it will decay within a period of time; that is, the number of decaying radioactive atoms within a period of time is proportional to the amount of radioactive atoms present:

$$\frac{\Delta N}{\Delta t} = -kN$$

where

ΔN = number of radioactive atoms that decays within the set time Δt

Δt = time of observation (s)

k = decay constant (the fraction of the radioactive atoms that decays per unit time), different for each isotope (s^{-1})

N = number of radioactive atoms present

Mathematically, this equation takes the following form as a function of time:

$$N(t) = N_0 e^{-kt} \qquad (1)$$

where

N_0 = number of radioactive atoms at time $t = 0$

$N(t)$ = number of radioactive atoms after time t

A concept that originated from the study of radioactive decay is “half-life.” The half-life $t_{½}$ of a radioactive isotope is the time it takes for half of the original atoms to decay:

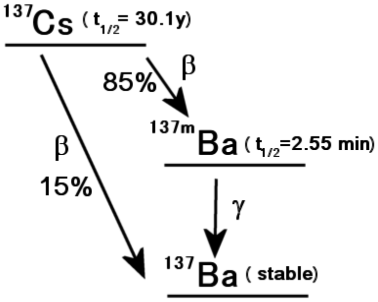
$$\begin{aligned} \frac{N_0}{2} &= N_0 e^{-kt_{1/2}} \\ \ln\frac{N_0}{2} &= \ln N_0 - kt_{1/2} \\ \ln N_0 - \ln 2 &= \ln N_0 - kt_{1/2} \\ \ln 2 &= kt_{1/2} \\ t_{1/2} &= \frac{\ln 2}{k} = \frac{0.693}{k} \end{aligned}$$

Half-lives can be as short as a fraction of a second or as long as a billion years, depending on the isotope.

Pre-Lab Experiment

Setting the stage for the experiment

In this experiment, your instructor will use an isotope generator to provide you with a small quantity of the short-lived barium-137m isotope. The barium-137m isotope is a product of the decay of the cesium-137 isotope:



In the isotope generator, the cesium-137 radioactive atoms are bound on a special matrix. When a washing solution (eluent) is forced through the generator, the product (barium-137m) is washed off the matrix and collected in the washing solution (eluate). As the barium-137m decays to its ground state by emitting γ radiation, it forms the stable barium-137 isotope.

You will use a G-M counter to monitor the decay of the barium-137m in order to calculate the decay constant and half-life of the isotope. The G-M counter will provide the rate of decay data (the number of atoms that decayed during one second). To use that data, you need to substitute the equation for $N(t)$ into the rate expression:

$$\frac{\Delta N}{\Delta t} = -kN$$

Substituting $N_0 e^{-kt}$ for N (from Equation 1):

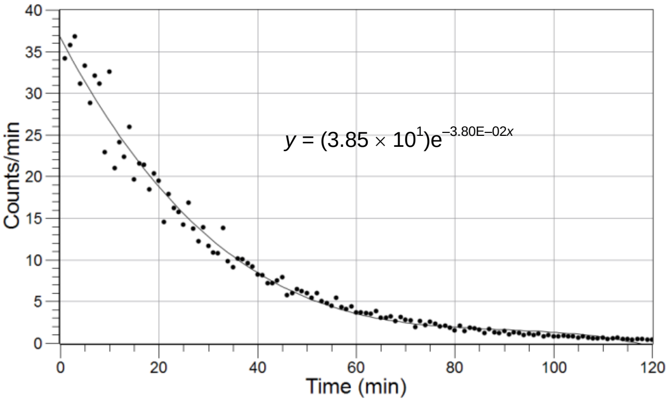
$$\frac{\Delta N}{\Delta t} = -kN_0 e^{-kt}$$

$$\ln\frac{\Delta N}{\Delta t} = -\ln(kN_0) - kt$$

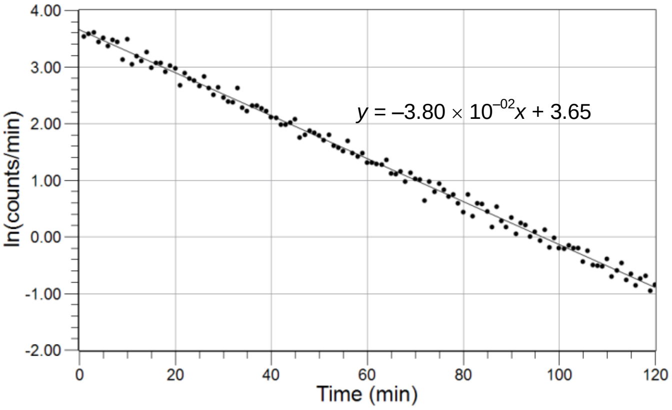
Therefore, if you plot $\ln(\Delta N/\Delta t)$ versus t, the slope gives you the decay constant. Once you know the decay constant, you can calculate the number of radioactive atoms present at $t = 0$ from the y-intercept [$\ln(kN_0)$].

Example calculation to try

In an experiment, the decay of barium-141 was studied. The following graphs, showing the rate of decay, were obtained with a G-M counter:



To determine the decay constant, the logarithm of the rate as a function of time was plotted:



The value of the decay constant k, obtained from the slope, is $3.80 \times 10^{-2}\ \text{min}^{-1}$. From that, the half-life of the barium-141 isotope was calculated:

$$t_{1/2} = \frac{0.693}{3.80 \times 10^{-2}\ \text{min}^{-1}} = 18.2\ \text{min}$$

1. Does the half-life depend on the initial number of radioactive atoms?

No, the half-life depends only on the value of the decay constant.

2. How would you obtain the initial number of radioactive atoms from the logarithmic graph?

The y-intercept is $\ln(kN_0)$:

$$\ln(kN_0) = 3.65$$

$$kN_0 = e^{3.65}$$

$$N_0 = \frac{e^{3.65}}{k} = \frac{38.47}{3.80 \times 10^{-2}\,\text{min}^{-1}} = 1.01 \times 10^3$$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. To prepare the solution with the barium-137m isotope, draw some eluting solution into the syringe, mount the isotope generator onto the tip of the syringe and squeeze the solution through the isotope generator. The solution dripping from the generator (the eluate) contains the barium-137m radioactive atoms. Collect the eluate into small aluminum plates and distribute them to students for immediate analysis.

Safety

Add these important safety precautions to your normal laboratory procedures:

- ♦ Gloves and lab coats should be worn when working with all liquid radioisotopes.
- ♦ As always, wash your hands thoroughly before leaving the lab, and then check for possible contamination.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students..

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect an alpha beta gamma radiation sensor to the data collection system. �(2.1)

3. Display Counts/sec on the y-axis of a graph with Time on the x-axis. �(7.1.1)

4. Obtain the barium-137m solution from your instructor on a small aluminum plate.

Collect Data

5. Start data recording. �(6.2)

6. Why do you have to start the data recording immediately?

Data recording has to be started because the barium-137m isotope has a very short half life.

7. Collect data for 20 minutes.

Note: After 20 minutes the rate should decline to nearly zero.

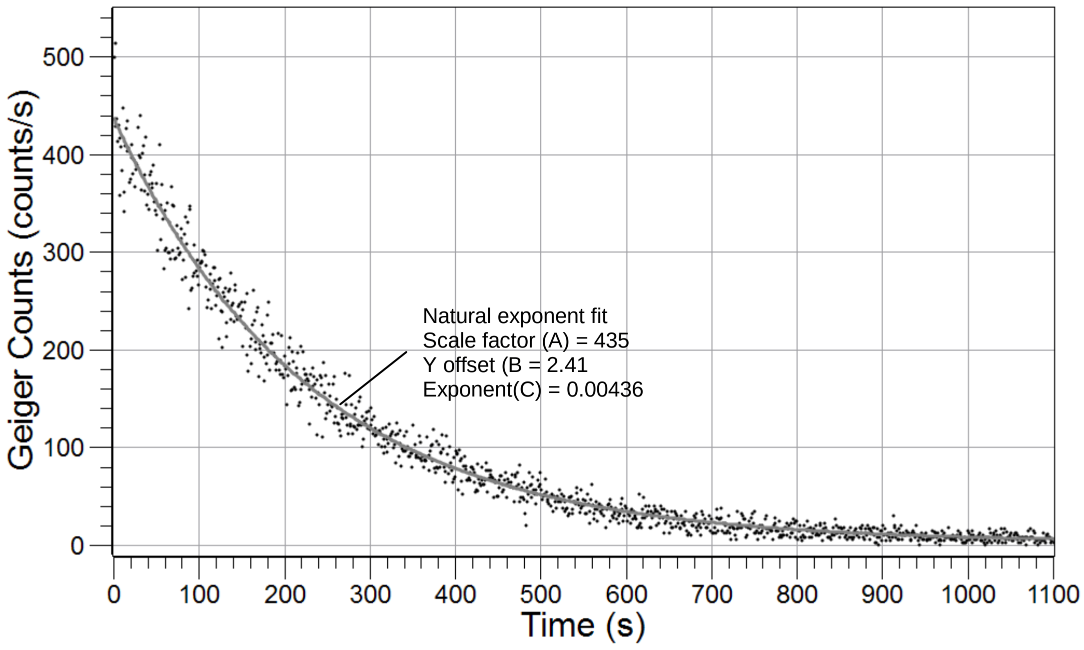
8. Stop data recording. �(6.2)

9. Print the graph. �(11.2)

10. Save your experiment �(11.1) and clean up according to your instructor's instructions.

Data Analysis

1. ☐ Sketch or attach the Counts versus Time graph below.



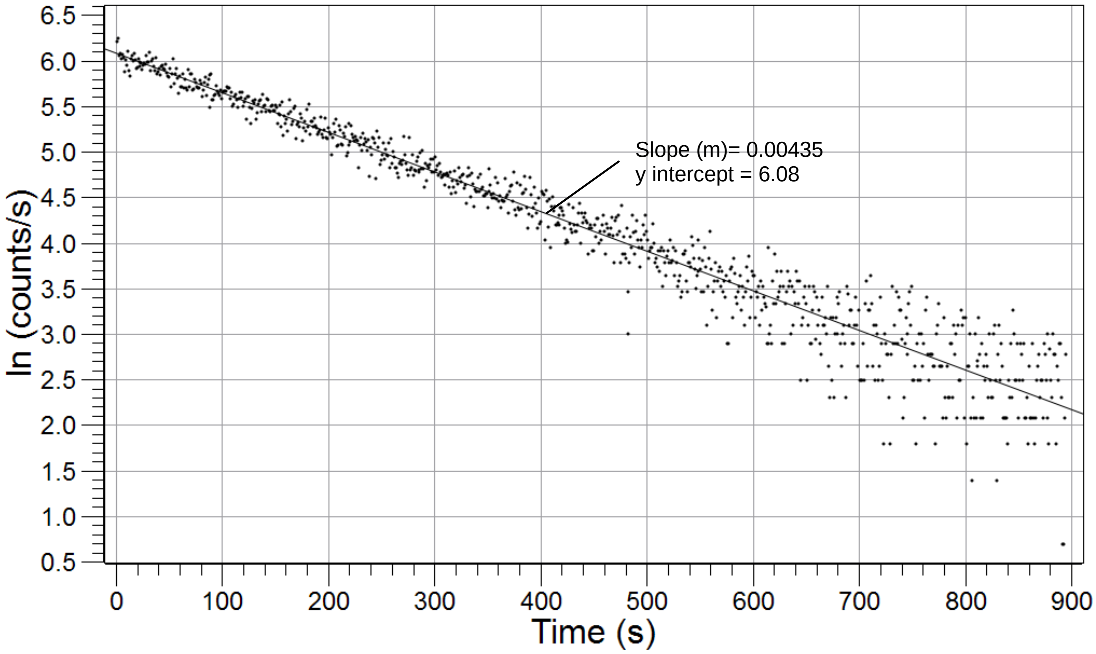
2. Create a calculated data set of ln(counts/s). �(10.3)

3. Display the data set on the y-axis with Time on the x-axis. �(7.1.1)

4. Find the slope and y-intercept of the best-fit line. �$^{(9.6)}$

5. Print the graph. �$^{(11.2)}$

6. Sketch or attach the ln(counts/sec) versus Time graph below.



7. Record the slope and y-intercept in Table 1.

The slope of the graph is -4.35×10^{-3}. The y-intercept is 2.41.

8. Convert the value of the slope from per second to per minute. Record the value in Table 1.

$$\left(-4.35 \times 10^{-3}\ \mathrm{s}^{-1}\right) \times 60\ \frac{\mathrm{s}}{\mathrm{min}} = 0.261\,\mathrm{min}^{-1}$$

9. What is the decay constant? Record the value in Table 1.

The decay constant is the slope, $0.261\ \mathrm{min}^{-1}$.

10. Calculate the initial amount of barium-137m. Record the value in Table 1.

The y-intercept is $\ln(kN_0)$:

$$\ln\left(kN_0\right) = 6.08$$

$$kN_0 = e^{6.08}$$

$$N_0 = \frac{e^{6.08}}{k} = \frac{437}{4.35 \times 10^{-3}\,\mathrm{min}^{-1}} = 1.00 \times 10^{5}$$

11. Calculate the half-life of barium-137. Record the value in Table 1.

$$t_{1/2} = \frac{0.693}{0.261\ \text{min}^{-1}} = 2.65\ \text{min}$$

12. Obtain the theoretical value of the half-life of barium-137m. Record this value in Table 1.

The theoretical value is 2.55.

13. Calculate the percent error between the theoretical value and the value you calculated.

$$\text{Percent Error} = \frac{|\text{Theoretical Value} - \text{Experimental Value}|}{\text{Theoretical Value}} \times 100$$

$$\text{Percent Error} = \left|\frac{2.55 - 2.65}{2.55}\right| \times 100 = 3.92\%$$

Table 1: Determination of the half-life of barium-137m

Parameters	Values
Slope (s^{-1})	-4.35×10^{-3}
Slope (min^{-1})	–0.261
y-intercept	6.08
k (min^{-1})	0.261
N_0	1.00×10^5
$t_{1/2}$ (min)	2.65
Theoretical $t_{1/2}$ (min)	2.55
Error (%)	3.92

Analysis Questions

1. What does it mean to say that the half-life of the barium-137m isotope is 2.65 min?

It means that it takes 2.65 min for half of the material of a radioactive isotope, in this case, barium-137m, to decay.

2. How would you determine N_0 from the ln[N(t)] versus t graph?

ln (N_0) is the y-intercept.

3. How would you determine N_0 from the rate of decay versus *t* graph? (Hint: Each point represents the number of radioactive atoms decayed during that minute; sum those between 0 to 20 minutes.)

The area under the rate of decay curve is the sum of the number of the radioactive atoms that decayed each minute, which is the number of original radioactive atoms.

Synthesis Questions

Use available resources to help you answer the following questions.

1. What do you think the *N*(t) versus *t* graph looks like?

The *N*(*t*) versus *t* graph should show exponential decay.

2. Carbon dating is a method based on the radioactive dating of the carbon-14 isotope that determines the age of carbon-based matter that was once alive. It is based on the fact that as long as the matter is alive, the ratio of the radioactive carbon-14 and carbon-12 is constant. Once the material dies, the carbon-14 concentration decreases as the carbon-14 isotope decays, with the half-life of $t_{1/2} = 5700$ year.

The analysis of a fossil sample shows that 10% of the original carbon-14 isotope is present. How old was the sample?

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5700\text{ years}} = 1.22 \times 10^{-4}\text{ year}^{-1}$$

$$\ln\left(\frac{N(t)}{N_0}\right) = -kt$$

$$\ln(0.1) = -(1.22 \times 10^{-4}\text{ year}^{-1})t$$

$$t = \frac{-2.302}{-1.22 \times 10^{-4}\text{ year}^{-1}} = 1.89 \times 10^{4}\text{ years}$$

3. What other process can be described formally using the same mathematical equation as *N*(t) versus *t*? (Hint: Think kinetics.)

The *N*(*t*) versus *t* relationship is formally the same as the [A] versus *t* in a process with first order kinetics:

$$[A] = [A]_0 e^{-kt}$$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. **During radioactive decay:**

   A. Unstable molecules fall apart.
   B. Unstable nuclei fly apart.
   C. There is electron transfer between atoms.
   D. Electrons are always emitted in the form of β radiation.

2. **The half-life of the radioactive decay of an isotope depends on:**

   A. Only the amount of the radioactive isotope present.
   B. The amount of the radioactive isotope present and the decay constant.
   C. The decay constant only.
   D. The temperature.

3. **The barium-137m isotope has a half-life of 2.55 min, which means:**

   A. All radioactive material of this isotope decays in 5.30 min.
   B. Half of the radioactive material of this isotope decays after 2.55 min.
   C. There will be no decay for 2.55 min.
   D. Half of the radioactive material of this isotope turns to cesium-137.

4. **The original number of radioactive atoms can be obtained from:**

   A. The intercept of the ln[$N(t)$] versus t graph.
   B. The half-life of the reaction.
   C. The decay constant.
   D. Carbon dating.

Extended Inquiry Suggestions

A possible extension to this experiment would be the investigation of how various materials can shield radioactive radiation. Other than common materials (such as plastic, paper, and wood) some materials can be investigated that are known to be good shields, like lead. A discussion can be held on why shielding from high-energy radiation is important (for example, shielding from radiation due to a nuclear explosion or shielding from x-ray radiation with a lead apron at the dentist).

Gas Laws

11. Determine the Molar Mass of a Volatile Liquid

Objectives

Students determine the molar mass of an unknown volatile liquid at the boiling temperature of water and at atmospheric pressure.

Procedural Overview

Students gain experience conducting the following procedures:

- Using hot and cold water baths to evaporate and condense an unknown volatile liquid, measuring the mass of a flask with and without the condensed unknown liquid
- Obtaining the mass, pressure, temperature, and volume of the evaporated volatile liquid
- Using the Ideal Gas Law to calculate the molar mass of the volatile liquid

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- Absolute Pressure sensor
- Beaker (2), 400-mL
- Erlenmeyer flask, 125-mL
- Graduated cylinder, 100-mL
- Hot plate with magnetic stirrer and stir bar
- Balance (1 per class)
- Ring stand
- Clamp (2)[1]
- Unknown volatile liquid, 8 mL[2]
- Aluminum foil, about 4-cm by 4-cm
- Paper towel (2-3 sheets)
- Dropper
- Water, 600 mL

[1] To hold the Erlenmeyer flask and temperature sensor

[2] The unknown volatile liquid is acetone. Refer to the Lab Preparation section for details or for alternative liquids.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Ideal Gas Law
- Properties of gases and liquids
- Relationship between phase changes and heat

Related Labs in This Guide

Labs conceptually related to this one include:

- Molar Volume of a Gas
- Identifying an Unknown Metal
- Exploring Gas Laws

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting multiple sensors to your data collection system �(2.2)
- Changing the units of a measurement �(5.3)
- Monitoring live data without recording �(6.1)
- Displaying data in a digits display �(7.3.1)
- Adding a variable to a digits display �(7.3.2)
- Saving your experiment �(11.1)

Background

The Dumas method of molar mass determination involves measuring the mass of the condensed vapor of a volatile liquid. This is done under controlled conditions, with known volume, pressure, and temperature. A small sample of liquid with a low boiling point is added to an Erlenmeyer flask with a pre-measured mass. The Erlenmeyer flask is submerged in a hot water bath. As the sample evaporates, air is flushed from the flask. When the entire sample has evaporated, the flask contains only the vapor of the unknown substance. At that point, the flask is cooled, and the vapor condenses. Its mass may be determined by re-measuring the mass of the flask.

The Ideal Gas Law is given by the equation:

$$PV = nRT$$

where

P = the pressure of the gas (kPa)
V = the volume of the gas sample (L)
n = the number of moles of gas present (mol)
T = the temperature of the sample (K)
R = the Ideal Gas Law constant, which is $8.314\ \frac{\text{kPa}\cdot\text{L}}{\text{mol}\cdot\text{K}}$

This relationship describes the behavior of gases very well at ordinary pressures and moderate temperatures.

The number of moles of a substance is equal to the mass of the substance divided by the mass of a mole of that substance:

$$n = \frac{m}{\text{FW}}$$

where

m = the mass of the sample (g)
FW = the molar mass, or formula weight, of the substance (g/mol)

Substituting this relationship into the Ideal Gas Law:

$$PV = \frac{mRT}{\text{FW}}$$

and rearranging to isolate the molar mass yields

$$\text{FW} = \frac{mRT}{PV}$$

Pre-Lab Experiment

Setting the stage for the experiment

Review the properties of liquids and gases. Discuss how the heat gained by the system affects the motion of molecules, ultimately resulting in phase transition.

If possible, perform the following demonstration. Place an empty soda can on a hotplate and pour about 15 mL of water into it. Bring the water to boil and then quickly, with a pair of tongs, place the can into a cold water bath upside down. The can should be crushed.

The water vapor displaces air. When cooled, the water vapor molecules are removed from the gas phase instantaneously, resulting in a significantly lowered pressure in the can. The excess external pressure crushes the can.

Discuss with your instructor what happens in the can while the water is boiling and after it is suddenly cooled. The lab experiment is an analogous experiment. You will replace the air in an Erlenmeyer flask with the vapor of a volatile liquid. When cooled, the vapors will condense in the Erlenmeyer flask, and air will rush into the Erlenmeyer flask to compensate for the pressure drop. Unlike the can made of thin aluminum, the strong glass of the Erlenmeyer flask will not crush.

Example calculation to try

The mass of an empty Erlenmeyer flask is measured and found to be 25.334 g. The flask is covered with a piece of aluminum foil which has several pin holes and placed in a water bath and kept at 80.0 °C. An unknown liquid is added to the flask and boiled. Care is taken to assure that there is always liquid in the flask. Finally, after about 5 minutes of boiling, allow all the liquid to evaporate at which stage there are only molecules of the unknown substance in the gas phase and there is no liquid left. Then the flask is placed immediately into a cold water bath, wiped dry, and the mass is measured very quickly.

The Erlenmeyer flask with the condensed drops of the liquid is found to be 25.437 g. The liquid in the flask is 0.103 g (25.437 g – 25.334 g).

The flask is filled to the rim with water and the volume of the water measured. The volume of the water is found to be 65.0 mL. The pressure sensor shows 101 kPa of atmospheric pressure.

Necessary unit conversions for doing the calculations:

$$65.0\ \text{mL} = 6.50 \times 10^{-2}\ \text{L}$$

$$80.0\ ^\circ\text{C} = 353\ \text{K}$$

Applying the Ideal Gas Law:

$$PV = nRT$$

$$PV = \frac{m}{\text{FW}} RT$$

Solving that for FW:

$$\text{FW} = \frac{mRT}{PV}$$

Applying the relevant data to the equation:

$$\text{FW} = \frac{(0.103\ \text{g})\left(8.314\ \frac{\text{kPa} \cdot \text{L}}{\text{mol} \cdot \text{K}}\right)(353\ \text{K})}{(101\ \text{kPa})\left(6.50 \times 10^{-2}\ \text{L}\right)}$$

$$\text{FW} = 46.0\ \frac{\text{g}}{\text{mol}}$$

1. What happens to the molecules of a liquid if the liquid is heated?

The average velocity of the molecules increases. The average kinetic energy of the molecules also increases.

2. What happens if a molecule of liquid possesses enough kinetic energy to break the attractive forces to other molecules?

It leaves the liquid phase and enters the gas phase.

3. Under what circumstances (pressure and temperature) is the Ideal Gas Law valid?

When there is no substantial interaction between molecules, which is generally true under low pressure and high temperature conditions.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. Use acetone as the "unknown liquid." Its formula weight is 58 g/mol. Its boiling point is 57 °C (330 K). For safety reasons, if you decide to use other liquids, they should not have a boiling point lower than 40 °C.
2. Inspect the Erlenmeyer flasks for cracks or other defects.

Safety

Add these important safety precautions to your normal laboratory procedures:

- If you feel dizzy or light-headed during the lab, notify your instructor immediately.
- Under no circumstances is an open flame (such as a Bunsen burner) allowed in the lab during the experiment. Most volatile liquids are extremely flammable.
- If the skin is exposed to a volatile liquid, rinse the exposed surface thoroughly with running water. Some volatile liquids irritate the skin.
- Dispose of liquids properly. Unused liquids must not be poured down the drain.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect the stainless steel temperature sensor and the pressure sensor to the data collection system. �(2.2)

3. Display temperature and pressure in a digits display. �(7.3.1)(7.3.2)

4. Prepare a 400-mL beaker by filling it with about 300 mL of water.

5. Place the 400-mL beaker of water on the hotplate with the magnetic stirrer, and begin heating the water to 85 °C.

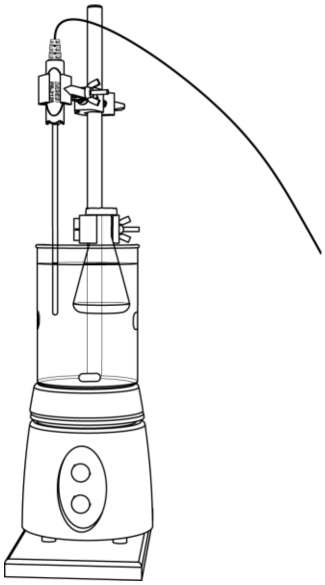
6. Clamp the stainless steel temperature sensor to the ring stand, and immerse the tip in the water.

Note: Do not allow the temperature sensor to touch the sides or bottom of the flask.

7. Place the stirring bar into the water and turn on the magnetic stirrer.

8. Place a small piece of aluminum foil over the opening of the 125-mL Erlenmeyer flask.

9. Poke a small hole in the aluminum foil.



10. Measure the mass of the empty Erlenmeyer flask and foil, and record the mass to the nearest milligram in Table 1.

11. Mount the Erlenmeyer flask on the ring stand with a clamp so that it is immersed in the water bath as far as possible without allowing water to get into the flask.

12. Why is it important to immerse the flask as far as possible into the water bath?

Because the surface of the flask exposed to air will have a lower temperature, the vapors will have a lower temperature than the known temperature of the water bath. This introduces error when using the Ideal Gas Law.

13. Fill a second 400-mL beaker with about 300 mL of cold water.

Collect Data

14. With the dropper, add 1 to 2 mL of the unknown liquid into the Erlenmeyer flask through the hole in the aluminum foil.

15. Monitor live data without recording. �(6.1)

Note: Maintain the temperature of the bath close to 85 ^{o}C.

Note: Make sure that there is always liquid in the Erlenmeyer flask.

16. When the sample is almost boiled away, use the dropper to add 1 to 2 mL more of the unknown liquid through the hole in the aluminum foil.

17. What was in the Erlenmeyer flask before the experiment and what do you think is in the Erlenmeyer flask at this point?

Before the experiment it was filled with air. At this point the air is flushed out and it is filled with the vapor of the unknown liquid.

18. After adding and evaporating 2 mL of the unknown liquid two more times, with the water bath temperature at least 85 °C, record the temperature of the bath in Table 1.

19. Change the units of the pressure measurement to kilopascal. �(5.3)

20. Measure the atmospheric pressure in the laboratory in kilopascals and record the value in Table 1.

Important: Make sure that all the liquid is evaporated inside of the Erlenmeyer flask before removing it from the hot water bath. If there is liquid left, it will add to the mass of the liquid formed from the condensed vapor, introducing error.

21. With the aluminum foil still in place, remove the Erlenmeyer flask and place it in the beaker with cold water for 15 to 20 seconds.

22. Wipe the outside of the Erlenmeyer flask completely dry with paper towels.

Important: The flask must be completely dry. Any amount of water on the flask introduces significant error.

23. Quickly measure the mass of the flask with the condensed liquid to the nearest milligram, and record it in Table 1.

24. After drying, obtain the mass of the Erlenmeyer flask and aluminum foil, immerse the Erlenmeyer flask in the hot water bath, and repeat these steps and those in the Collect Data section two more times. You should have three sets of measurements.

25. Stop monitoring live data without recording. �(6.1)

26. Fill the Erlenmeyer flask to the top with water.

27. Measure the volume of water in the Erlenmeyer flask with a graduated cylinder and record it in Table 1.

28. Save your experiment � (11.1) and clean up according to your instructor's instructions.

Data Analysis

Table 1: Measurements and calculated results

Parameters	Trial 1	Trial 2	Trial 3
Mass of dry Erlenmeyer flask and foil (g)	32.303	32.192	32.273
Mass of Erlenmeyer flask, foil and condensed vapor (g)	32.427	32.329	32.397
Mass of condensed vapor (g)	0.124	0.137	0.124
Temperature of water bath (°C)	94.3	94.0	94.0
Temperature of water bath (K)	367.5	367.2	367.2
Volume of Erlenmeyer flask (mL)	67.0	67.0	67.0
Volume of Erlenmeyer flask (L)	6.70×10^{-2}	6.70×10^{-2}	6.70×10^{-2}
Atmospheric pressure in lab (kPa)	101.176	101.168	101.188
Molar mass of unknown liquid (g/mol)	55.9	61.7	55.8
Average molar mass of unknown liquid (g/mol)	57.8		

1. Calculate the mass of the condensed vapor of the unknown volatile liquid and record the value in Table 1 for each trial.

Calculations for Trial 1:

32.427 g – 32.303 g = 0.124 g of condensed vapor

2. Convert the temperature of the water bath to Kelvin and convert the flask volume from milliliters to liters. Record the values in Table 1 for each trial.

Calculations for Trial 1:

To convert from degrees Celsius to Kelvin, add 273: 94.3 °C + 273 = 367 K

To convert from milliliters to liters, multiply by 1×10^{-3} L/mL:

$67.0\text{ mL} \times (1 \times 10^{-3}\text{ L/mL}) = 6.70 \times 10^{-2}\text{ L}$

3. Calculate the molar mass of the unknown liquid for each trial and record the values in Table 1. Calculate the average molar mass for the three trials.

Calculations for Trial 1:

$$PV = \frac{mRT}{\mathrm{FW}}$$

$$\mathrm{FW} = \frac{mRT}{PV}$$

$$\mathrm{FW} = \frac{(0.124\ \mathrm{g})\left(8.314\ \frac{\mathrm{kPa \cdot L}}{\mathrm{mol \cdot K}}\right)(367\ \mathrm{K})}{(101\ \mathrm{kPa})\left(6.70 \times 10^{-2}\ \mathrm{L}\right)}$$

$$\mathrm{FW} = 55.9\ \frac{\mathrm{g}}{\mathrm{mol}}$$

To calculate the average: (55.9 g/mol + 61.7 g/mol + 55.8 g/mol)/3 = 57.8 g/mol

Analysis Questions

1. What happens to the molecules of the unknown substance that are in the gas phase when the Erlenmeyer flask is cooling? What is going to be in the gas phase after it has cooled?

The molecules leave the gas phase and enter the liquid phase. Molecules from the air from outside the Erlenmeyer flask rush into the Erlenmeyer flask to make up for the absence of gas molecules.

2. Why is it necessary to cool the vapor?

The mass of gas molecules does not register on the balance as the atmospheric pressure is the baseline, and these molecules are at atmospheric pressure. Objects with higher density than air, such as the liquid drops of the unknown substance, will be exposed to higher gravitational pull from Earth. Therefore they will register on the balance.

3. What is the purpose of the aluminum foil?

The foil helps to keep air from getting in and molecules of the unknown substance from getting out.

4. What are some of the sources of experimental error?

Error could arise if not all of the air is flushed out of the Erlenmeyer flask, if some of the liquid evaporates after the flask is cooled but before the mass of the flask is measured, or if water is left on the outside of the Erlenmeyer flask when its mass is measured.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Why would the method in this lab experiment not work for an unknown liquid with a boiling point of 186 °C?

The liquid would not evaporate sufficiently to displace air when its temperature is raised close to the boiling point of water (100 °C).

2. How would you modify the setup of this experiment to measure the formula weight of an unknown liquid with a boiling point of 186 °C?

A liquid with a boiling point above 186 °C would be needed instead of a hot water bath.

3. Assume you have to determine the formula weight of a liquid with a boiling point slightly above room temperature. At which step in the experiment would a significant error be introduced? (Hint: Liquids with such low boiling point evaporate very quickly.)

Between cooling the Erlenmeyer flask with the condensed vapor and measuring the mass, a significant amount of liquid could evaporate at room temperature. This means a loss in the mass of the liquid, which introduces an error when measuring its mass.

4. How would you minimize the error presented in the previous question?

Cooling the Erlenmeyer flask in an ice bath lowers the temperature of the flask. Assuring a cool temperature reduces the evaporation during the time it takes to measure the mass.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. In an experiment, we obtained a *greater* formula weight than expected. Which of the following reasons can account for the error?

- **A.** Not all of the air was flushed out and replaced with molecules of the unknown substance.
- **B.** The Erlenmeyer flask was not completely dry.
- **C.** Not all of the liquid evaporated before measuring the mass.
- **D.** **Only B and C are true.**
- **E.** Only A and B are true.

2. A substance has a boiling point of 28 °C. Determination of its formula weight resulted in a significant error. What could be the most obvious reason for this error?

- **A.** Contamination of the liquid.
- **B.** Inaccuracy of the pressure and temperature sensors.
- **C.** High humidity content of the air.
- **D.** Too high a boiling point, which results in significant evaporation between cooling the Erlenmeyer flask and measuring its mass on the balance.
- **E.** **Too low a boiling point, which results in significant evaporation between cooling the Erlenmeyer flask and measuring its mass on the balance.**

3. Why is the method in this experiment unable to determine the formula weight of substances with a much higher boiling point than water?

A. Because they evaporate too quickly, introducing error.

B. Because they do not evaporate enough to flush the air out and fill the Erlenmeyer flask.

C. Because those liquids usually are contaminated.

D. The question is misleading. The formula weight of such substances can be determined very accurately with this method.

E. Because of much greater viscosity of such substances, they do not evaporate enough to flush the air out and fill the Erlenmeyer flask.

4. Does it matter how much of the liquid evaporates during the experiment and why?

A. No, what matters is that at the end, the Erlenmeyer flask is filled with vapor which will condense when cooled.

B. Yes, the mass of the liquid that was evaporated is in the Ideal Gas Law equation.

C. It depends on the liquid. Liquids with a high boiling point essentially do not evaporate at all so the loss would not matter.

D. The Ideal Gas Law does depend on the mass of the substance, which makes the amount of liquid placed into the flask important.

E. All of the above.

Extended Inquiry Suggestions

Have students determine the density of the vapor of the unknown substance given the following information:

$$PV = \frac{m}{\mathrm{FW}}RT$$

$$\frac{P \cdot \mathrm{FW}}{RT} = \frac{m}{V} = d$$

$$d = \frac{P \cdot \mathrm{FW}}{RT}$$

Density of the unknown volatile liquid vapor obtained using students' experimental results

Parameters	Trial 1	Trial 2	Trial 3
Volume of Erlenmeyer flask (L)	6.70×10^{-2}	6.70×10^{-2}	6.70×10^{-2}
Mass of condensed vapor (g)	0.124	0.137	0.124
Density (g/L)	1.85	2.04	1.85
Average density (g/L)	1.92		

12. Molar Volume of a Gas

Objectives

Students determine the molar volume of a gas by relating pressure, volume, and temperature.

Procedural Overview

Students gain experience conducting the following procedures:

- Conducting an experiment in a closed container that generates hydrogen gas while maintaining constant temperature and monitoring pressure
- Calculating the molar volume of the generated gas and converting that to standard temperature and pressure conditions

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	45 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Absolute pressure sensor with quick-release Connector, barbed connector, and plastic tubing
- Stainless steel temperature sensor
- Sensor extension cable
- Beaker, 600-mL
- Erlenmeyer flask, 250-mL
- Graduated cylinder, 10-mL or 25-mL
- Graduated cylinder, 100-mL
- Balance (1 per class)
- Rubber stopper with one hole
- 3 M Hydrochloric acid (HCl), 20 mL[1]
- Magnesium ribbon, about 0.20 g
- Water, 300 mL
- Electrical tape, roll (optional)

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[1] To prepare 3 M HCl using concentrated HCl, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Definition of an ideal gas
- Ideal Gas Law
- Relationship between temperature and pressure (Charles' Law), temperature and volume (Gay-Lussac's Law), and pressure and volume (Boyle's Law)
- Standard temperature and pressure (STP) conditions
- Avogadro's Law
- Dalton's Law
- Chemical formulas
- Balancing chemical equations
- Stoichiometric calculations

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Molar Mass of a Volatile Liquid
- Identifying an Unknown Metal
- Exploring Gas Laws

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting sensors to the data collection system �(2.2)
- Changing the units of a measurement � (5.3)
- Monitoring live data without recording � (6.1)
- Starting and stopping data recording �(6.2)

- Displaying data in a graph �(7.1.1)
- Displaying multiple graphs simultaneously �(7.1.11)
- Selecting data points in a graph �(7.2.1)

Background

The volume occupied by one mole of substance at standard temperature and pressure (STP) is known as the “standard molar volume.” According to Avogadro's hypothesis, equal volumes of gases under equal conditions of temperature and pressure contain equal numbers of molecules. It follows from this hypothesis that all gas samples containing one mole of molecules will occupy the same volume at STP.

The basis of this experiment is the following reaction, in which a known mass of magnesium (Mg) is reacted with an excess of hydrochloric acid (HCl) to yield the products shown:

$$\mathrm{Mg(s)} + 2\mathrm{HCl(aq)} \rightarrow \mathrm{MgCl_2(aq)} + \mathrm{H_2(g)} \qquad (1)$$

Inspection of this equation reveals that one mole of magnesium (24.3 g) yields one mole of hydrogen gas (2.02 g). Hydrogen gas is the product of interest in this experiment. By determining the number of moles of magnesium that react, you will indirectly determine the number of moles of hydrogen gas produced. The Ideal Gas Law is used to find the volume that the gas would occupy at STP. The number of moles and volume at STP is used to calculate the molar volume of hydrogen gas.

Pre-Lab Experiment

Setting the stage for the experiment

In order to determine the number of moles of hydrogen gas produced by the reaction of Equation 1, first calculate the number of moles of magnesium used:

$$n_{\mathrm{Mg}} = \frac{m_{\mathrm{Mg}}}{\mathrm{AW}_{\mathrm{Mg}}} \qquad (2)$$

where

n_{Mg} = number of moles of magnesium used in the experiment (mol)

m_{Mg} = mass of magnesium measured (g)

$\mathrm{AW}_{\mathrm{Mg}}$ = atomic weight of magnesium (g/mol).

Avogadro's Law states that the number of moles of an ideal gas is proportional to its volume. Therefore the volume of hydrogen gas that can be made from 1 mol of magnesium can be calculated:

$$\frac{n_{\mathrm{H_2}}}{n_0} = \frac{V_{\mathrm{E}}}{V_1}$$

where

n_{H_2} = number of moles of H_2 produced in the reaction (mol)

n_0 = 1 mol

V_E = the volume of the Erlenmeyer flask (L)

V_1 = the volume of H_2 gas produced from the reaction with 1 mol of magnesium (m^3)

Considering that 1 mol of Mg produces 1 mol of H_2

$$n_{Mg} = n_{H_2}$$

$$\frac{n_{Mg}}{n_0} = \frac{V_E}{V_1}$$

where

n_{Mg} = the number of moles of Mg that was used in the reaction (mol)

Solving for V_1:

$$V_1 = \frac{n_0}{n_{Mg}} V_E \tag{3}$$

The volume can be readily converted to STP:

$$\frac{P_1 V_1}{T_1} = \frac{P_0 V_0}{T_0}$$

Solving for V_0:

$$V_0 = \frac{P_1 T_0 V_1}{P_0 T_1} \tag{4}$$

where

the zero indices refer to the STP conditions (T_0 = 273 K, P_0 = 101.3 kPa)

P_1 = the pressure inside the Erlenmeyer flask due to the gas produced (kPa)

V_1 = the volume of H_2 gas produced from the reaction with 1 mol of magnesium (L)

T_1 = final temperature of the water bath (K)

Magnesium will instantaneously react with hydrochloric acid to form H_2 gas. The gas is captured in a closed Erlenmeyer flask. The volume of the flask will be measured at the end of the experiment. The final pressure and final temperature will be measured by the data collection system.

Example calculation to try

In an experiment, 20 mL of 3 M HCl were placed into a 125-mL Erlenmeyer flask. The atmospheric pressure was recorded as 101.5 kPa. Then 0.180 g of magnesium was measured and dropped into the hydrochloric acid. The flask was immediately sealed with a one-hole rubber stopper attached to the pressure sensor via a piece of Tygon® tubing.

The flask was placed into a water bath. The temperature of the bath and the pressure inside the flask were monitored. When the reaction was completed, the pressure was 253.0 kPa and the temperature of the bath was 25 °C. The volume of the Erlenmeyer flask was measured by filling it with water, inserting the stopper, and measuring the volume of the water, which was 141.00 mL.

The volume of the flask that the gas could occupy was 121 mL (141 mL minus the 20 mL occupied by the hydrochloric acid). The pressure of the hydrogen produced was 151.5 kPa (253.0 kPa – 101.5 kPa).

Converting the volume to liters and the pressure to pascals results in the following:

$$V_E = 121\ \text{mL}\left(\frac{1\ \text{L}}{10^3\ \text{mL}}\right) = 1.21 \times 10^{-1}\ \text{L}$$

Using Equation 2, the number of moles of magnesium used in the experiment are

$$n_{\text{Mg}} = \frac{0.180\ \text{g}}{24.3\ \frac{\text{g}}{\text{mol}}} = 7.41 \times 10^{-3}\ \text{mol}$$

From Equation 3, the volume of hydrogen formed from 1 mol of magnesium is

$$V_1 = \frac{(1\ \text{mol})}{(7.41 \times 10^{-3}\ \text{mol})}(1.21 \times 10^{-1}\ \text{L})$$

$$V_1 = 16.3\ \text{L}$$

Using Equation 4 to convert the molar volume to STP conditions yields

$$V_0 = \frac{(151.5\ \text{kPa})(293\ \text{K})(16.3\ \text{L})}{(101.3\ \text{kPa})(298\ \text{K})}$$

$$V_0 = 24.0\ \text{L}$$

The molar volume was found to be 24.0 L.

1. Why do you subtract the atmospheric pressure from the final pressure to obtain the pressure of the hydrogen gas generated?

It’s necessary to subtract atmospheric pressure from final pressure because the final pressure includes the atmospheric pressure and only the partial pressure of hydrogen is applicable for the calculations.

2. Would it matter if the volume of the Erlenmeyer flask used in the experiment was 250 mL?

The flask size would not matter because the number of moles of hydrogen depends only on the number of moles of magnesium.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***3M HCl:*** Prepare 20 mL of 3 M hydrochloric acid solution for each student group by diluting a concentrated hydrochloric acid solution 1:4 with distilled water. The exact concentration is not critical in this experiment.

CAUTION: Remember to add the concentrated acid to the water to prevent spattering.

Safety

Add these important safety precautions to your normal laboratory procedures:

- If you get hydrochloric acid on your skin, wash it off with plenty of water.
- Handle the Erlenmeyer flask very carefully when it is pressurized. Knocking on the glass can cause the glass to crack and because of the pressure, a slight explosion can occur.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

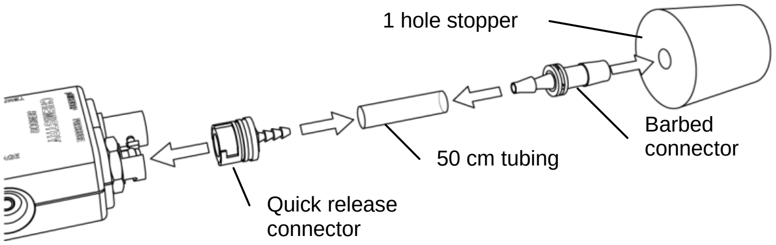
1. Start a new experiment on the data collection system. �(1.2)

2. Connect the absolute pressure sensor, using the sensor extension cable, and the temperature sensor to the data collection system. �(2.2)

3. Set up one graph to monitor the pressure and another graph to monitor the temperature as a function of time. � (7.1.11)

   Note: Change the units of the temperature measurement to Kelvin. � (5.3)

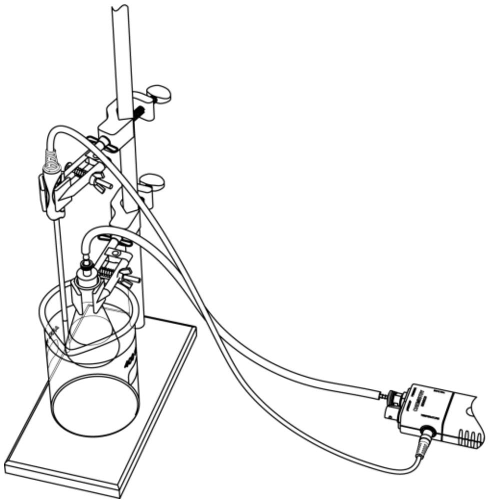
4. Place the barbed connector of the pressure sensor tightly into the rubber stopper and connect it to the pressure port of the sensor with a piece of tubing.



5. If electrical tape is available, wrap the Erlenmeyer flask with 10 to 15 rounds of electric tape. This is a preventive measure in case the flask cracks. The tape keeps the glass pieces together.

6. Fill the 600-mL beaker 3/4 full with tap water.

7. Mount the 250-mL Erlenmeyer flask in the water bath—place it inside the 600-mL beaker with water. The water should cover as much of the flask as possible. Add more water if needed.



8. Place the temperature sensor in the water bath.

9. Why do you need to immerse the flask as much as possible into the water bath?

The flask is immersed as much as possible so students know the temperature of the gas in the flask. If the flask is not completely immersed, the temperature of the gas will not be the same as the temperature of the water bath. Then students will not know what the temperature of the gas is.

Collect Data

10. Magnesium and hydrochloric acid reaction

- **a.** Measure a small piece of magnesium ribbon (between 0.150 g and 0.180 g) to the nearest milligram and record the mass in Table 1.
- **b.** Measure 20 mL of 3 M HCl solution with a graduated cylinder and transfer it into the Erlenmeyer flask.
- **c.** Start data recording. �(6.2)
- **d.** What does the pressure reading on the sensor represent at this point?

The pressure sensor shows the atmospheric pressure of air.

- **e.** Drop the pre-measured piece of magnesium into the flask and immediately insert the stopper airtight.

Important: Make sure that the stopper is sitting firmly in the flask because pressure is building in the flask and a loose stopper might pop out. If that happens, you will need to repeat the experiment.

- **f.** Continue to monitor the pressure.
- **g.** When the hissing in the flask ends and the pressure stabilizes, stop the data collection. �(6.2)
- **h.** Record the initial and final pressure during the reaction and record those values in Table 1. �(7.1.4)
- **i.** Record the initial and final temperature of the water bath and record those values in Table 1. �(7.1.4)

Note: Aside from recording this data in the table, you do not need to save your data.

- **j.** Remove the stopper carefully and dispose of the spent acid solution properly.

11. Repeat the magnesium and hydrochloric acid reaction two times.

12. What does the final pressure reading represent? (Hint: What components contribute to the final pressure?)

Both the air (initial pressure) and the hydrogen gas generated by the reaction are responsible for the pressure. In fact, the pressure increase is due to the hydrogen gas produced.

13. Fill the Erlenmeyer flask to the top with water, insert the stopper (without tubing), and then use the 100-mL graduated cylinder to measure the volume of the water, which is the volume of any gases in the flask. Record this value in Table 1.

14. Clean up according to your instructor's instructions.

Data Analysis

1. Calculate the number of moles of magnesium used for each trial and record the values in Table 1.

For Trial 1:

$$n_{\mathrm{Mg}} = \frac{0.106\ \mathrm{g}}{24.3\ \frac{\mathrm{g}}{\mathrm{mol}}} = 4.36 \times 10^{-3}\ \mathrm{mol}$$

2. Calculate the pressure due to the hydrogen gas generated and record the values in Table 1.

For Trial 1:

Pressure change due to the hydrogen gas produced: 146 kPa – 102 kPa = 44.0 kPa

3. Determine the volume the hydrogen gas can occupy in the flask and convert it from milliliters to Liters. Record the values in Table 1.

For Trial 1:

250 mL available volume – 20 mL HCl solution = 230 mL available for H_2

$$230\ \mathrm{mL}\left(\frac{1\ \mathrm{m}^3}{10^3\ \mathrm{mL}}\right) = 2.3 \times 10^{-1}\ \mathrm{L}$$

4. Determine the volume of hydrogen that would be generated by 1 mol of magnesium. Record the value in Table 1.

For Trial 1:

$$V_1 = \frac{n_0}{n_{\mathrm{Mg}}} V_{\mathrm{E}}$$

$$V_1 = \left(\frac{1\ \mathrm{mol}}{4.36 \times 10^{-3}\ \mathrm{mol\ Mg}}\right)\left(2.30 \times 10^{-1}\ \mathrm{L}\right) = 52.7\ \mathrm{L}$$

5. At standard temperature and pressure, what is the volume of 1 mol of hydrogen gas? Calculate the average volume of 1 mol of hydrogen gas at STP for all three trials. Record the values in Table 1.

For Trial 1:

$$V_0 = \frac{P_1 T_0 V_1}{P_0 T_1}$$

$$V_0 = \frac{(44.0\ \mathrm{kPa})(293\ \mathrm{K})(52.7\ \mathrm{L})}{(101.3\ \mathrm{kPa})(302\ \mathrm{K})} = 22.7\ \mathrm{L}$$

The average volume is (22.7 L + 24.3 L + 22.7 L)/3 = 23.3 L

Table 1: Molar volume of H_2 calculated from the measured values

Parameters	Trial 1	Trial 2	Trial 3
Mass of magnesium ribbon (g)	0.106	0.104	0.106
Moles of magnesium (mol)	4.36×10^{-3}	4.28×10^{-3}	4.36×10^{-3}
Initial pressure (kPa)	102	102	102
Final pressure (kPa)	146	147	149
Pressure due to hydrogen gas (kPa)	44.0	45.0	47.0
Initial temperature of water bath (K)	298.0	298.0	298.0
Final temperature of water bath (K)	302.0	302.0	302.9
Volume of flask (mL)	250		
Volume H_2 can occupy (mL)	230		
Volume of flask (L)	0.250		
Volume H_2 can occupy (L)	0.230		
Volume of H_2 generated by 1 mol of Mg (L)	52.7	53.7	52.7
Volume of H_2 generated by 1 mol of Mg (L) under STP	22.7	24.3	22.7
Average molar volume at STP (L):	23.3		

Analysis Questions

1. The accepted value for the molar volume of an ideal gas at STP is 22.4 L/mol. Calculate the percent error of your average results.

$$\left|\frac{23.3\text{ L} - 22.4\text{ L}}{22.4\text{ L}}\right| \times 100 = 4.02\%$$

2. List possible sources of error in this experiment.

Delay of putting in the stopper or a leak in the system might allow some of the hydrogen to escape, resulting in too low a final pressure. If the flask isn't completely immersed in the water bath, the recorded temperature will not accurately reflect the temperature in the flask.

3. Assume that the magnesium ribbon was covered with a thin layer of MgO which naturally forms on the surface of magnesium. Provide an equation between MgO and HCl.

$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$

4. **Does MgO generate hydrogen then (when combined with hydrochloric acid)?**

No, it does not.

5. **Does the presence of MgO introduce an error then?**

Yes, since it contributes to the mass of the sample but does not react to form hydrogen.

6. **How does the temperature change during the course of the reaction? Provide a possible explanation for the change of temperature**

The temperature goes up usually a few degrees due the fact that the reaction is highly exothermic.

Synthesis Questions

Use the available resources to help you answer the following questions.

1. **Assume we have only zinc to perform this experiment. Zinc reacts with hydrochloric acid according to the same stoichiometry as magnesium. How many grams of zinc would you need to form the same amount of hydrogen as 0.185 g magnesium?**

$$0.185 \text{ g Mg}\left(\frac{65.54 \text{ g/mol Zn}}{24.3 \text{ g/mol Mg}}\right) = 0.499 \text{ g Zn}$$

2. **Consider the following reaction, which occurs when $CaCO_3$ reacts with HCl Describe how you would utilize this process to measure the molar volume of carbon dioxide.**

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O$$

A known amount of $CaCO_3$ can be reacted with HCl solution much like in this experiment. The pressure increase is due to the CO_2 generated. This calculation is identical to the calculation in the experiment that students just performed.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. **What error would a layer of MgO on the surface of the magnesium ribbon cause?**

A. **The sample would have less magnesium that will react, which in turn would form fewer moles and a smaller volume of hydrogen.**

B. The sample would have more magnesium that will react, which in turn would form a greater number of moles and a greater volume of hydrogen.

C. The sample would have less magnesium that will react, which in turn would form greater number of moles and a greater volume of hydrogen.

D. The presence of MgO would not cause any error because it forms no hydrogen gas.

2. Would a water bath with higher temperature than room temperature cause an error?

- **A.** Yes. A higher temperature is not STP.
- **B.** Yes. A higher temperature would cause a higher pressure reading.
- **C. No. A higher temperature would proportionally increase pressure according to the gas laws, yielding the same volume.**

3. Does it matter how much hydrochloric acid was added to the flask?

- **A.** Yes. It matters because the reactants have to be present in stoichiometric quantities.
- **B.** No. It does not matter because we are interested in the amount of hydrogen made from the known amount of magnesium.
- **C. No. If there is enough to react with the magnesium, an excess amount of hydrochloric acid makes no difference.**

Extended Inquiry Suggestions

Discuss with your students how the partial pressure of water (evaporating from the hydrochloric acid) can affect the results. Students can do research to see how significant the error from water vapor is at the temperature of the experiment. Have them redo the calculations with the water vapor pressure taken into account.

Challenge students to prove that the molar volume of a gas under standard pressure and temperature conditions is the same for all ideal gases.

13. Exploring Gas Laws

Objectives

Students explore the relationship between pressure and volume, and pressure and temperature, for a gas.

Procedural Overview

Students gain experience conducting the following procedures:

- Assembling an experimental setup
- Using pressure and temperature sensors to relate the temperature and pressure of a gas (Gay-Lussac's Law)
- Using the pressure sensor to relate the pressure and volume of a gas (Boyle's Law)
- Recording pressure and temperature data

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	10 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Absolute pressure sensor with quick-release connectors and plastic tubing
- Sensor extension cable
- Stainless steel temperature sensor
- Ring stand
- Clamp, utility
- Beaker, 1500-mL
- Erlenmeyer flask, 250-mL
- Syringe, 60-mL
- Hot plate with magnetic stirrer and stir bar
- Rubber stopper, 2-hole
- Glycerin, several drops
- Electrical tape, roll
- Water, 1200 mL

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Measuring physical quantities
- Direct and inverse proportionality relationships
- Interpreting graphs

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Molar Mass of a Volatile Liquid
- Molar Volume of a Gas
- Identifying an Unknown Metal
- Molecular Interaction in Ethanol and Acetone

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting multiple sensors to your data collection system �(2.2)
- Putting the data collection system into manual sampling mode with manually entered data �(5.2.1)
- Changing the units of a measurement �(5.3)
- Starting and stopping data recording �(6.2)
- Starting a manually sampled new data set �(6.3.1)
- Recording a manually sampled data point �(6.3.2)
- Stopping a manually sampled set �(6.3.3)
- Displaying data in a graph �(7.1.1)
- Adjusting the scale of a graph �(7.1.2)

- Creating calculated data �$^{(10.3)}$
- Save your experiment �$^{(11.1)}$
- Printing �$^{(11.2)}$

Background

In solids and liquids the atoms or molecules are very close to each other, leaving no room between them. For this reason, solids and liquids cannot be measurably compressed. Gases, on the other hand, have relatively large distances between the atoms or molecules as they bounce into each other and into the walls of their container. This fact allows gases to be compressed.

Gas pressure is related to the frequency of gas molecules bouncing into surfaces. When the volume of a container of gas is changed, the distance between the walls changes and the amount of time it takes for a particle to get from one wall to another changes. This results in a different number of collisions per second which causes a different pressure. Decreasing the volume, therefore, increases the pressure and vice versa. This relationship was discovered by Robert Boyle in 1661.

If a gas is allowed to expand, increasing the temperature will force the gas to expand, maintaining constant pressure. This relationship was discovered by Jacques Charles in 1789. Also, if the temperature of a gas increases, the average kinetic energy of the molecules increases and results in 1) more energetic collisions between molecules and 2) more energetic collisions between the molecule and the wall of the container, which results in higher pressure if the gas is not allowed to expand. This relationship was discovered by Joseph Gay-Lussac in1802.

Since temperature is a measure of the average kinetic energy (and therefore the average speed) of gas molecules, a change in temperature will change the time it takes for molecules to move from wall to wall in a container. This implies that if the molecules stopped moving, they would no longer hit the walls and the pressure would be zero. The colder something becomes, the slower the molecules move, thus the temperature at which all motion stops must be the coldest temperature possible. This temperature is called "absolute zero".

In this lab you will study the relationship between the pressure and volume (Boyle's Law) at constant temperature and the relationship between the pressure and temperature (Gay-Lussac's Law) at constant volume.

Pre-Lab Experiment

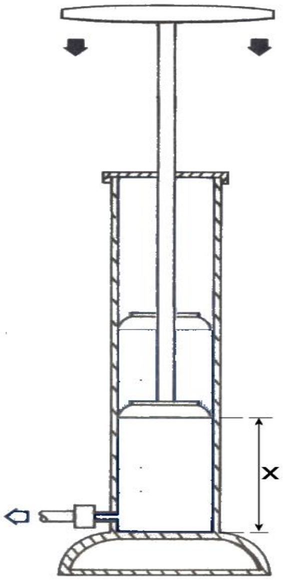
Setting the stage for the experiment

In this experiment, you will perform experiments to study the properties of gases. In the first experiment, you will relate the pressure to the volume of gases at room temperature. Connecting a syringe to a pressure sensor, you will monitor pressure changes as the volume of the captured gas changes (the plunger is pushed in, decreasing the volume). In the second experiment, you will keep the volume of a gas sample constant and monitor the change in the pressure of the gas as the temperature is increased.

Example calculation to try

Boyle's Law

We used to use hand-driven pumps to inflate tires on bicycles and cars. An average car tire requires 33.0 psi pressure. The pump we are using has an inner diameter of 1.00 inch and the length of 0.700 cm.



How far from the top of the pump must the piston be pushed in to build enough pressure to force the air into a tire with 33 psi pressure?

We will employ Boyle's Law, which states that the pressure is inversely proportional to the volume while the number of molecules and the temperature are kept constant. For example, reducing the volume by half will double the pressure. This also means that the product of pressure and volume will always be constant:

$$P_1V_1 = P_2V_2 = \text{a constant value}$$

The necessary conversions are

$$1 \text{ atm} = 14.5 \text{ psi} = 101.3 \text{ kPa}$$

$$1 \text{ inch} = 2.54 \text{ cm}$$

$$(33.0 \text{ psi})\left(\frac{1 \text{ atm}}{14.5 \text{ psi}}\right)\left(\frac{101.3 \text{ kPa}}{1 \text{ atm}}\right) = 231 \text{ kPa}$$

The area of the base of the piston is

$$\left(\frac{2.54 \text{ cm}}{2}\right)^2\left(\frac{1 \text{ m}}{100 \text{ cm}}\right)^2(3.14) = 5.07 \times 10^{-4} \text{ m}^2$$

The volume of the pump is

$$V_1 = \Delta l\, A$$

where

Δl = displacement of the piston (m)

A = surface area of the piston (m^2)

Substituting the appropriate values yields:

$$V_1 = (0.700 \text{ m})\left(5.07 \times 10^{-4} \text{ m}^2\right) = 3.55 \times 10^{-4} \text{ m}^3$$

The initial pressure is the atmospheric pressure (P_1 = 101.3 kPa). In order to achieve the desired pressure of 33 psi, the final volume should be:

$$P_1V_1 = P_2V_2$$

$$V_2 = \frac{P_1V_1}{P_2}$$

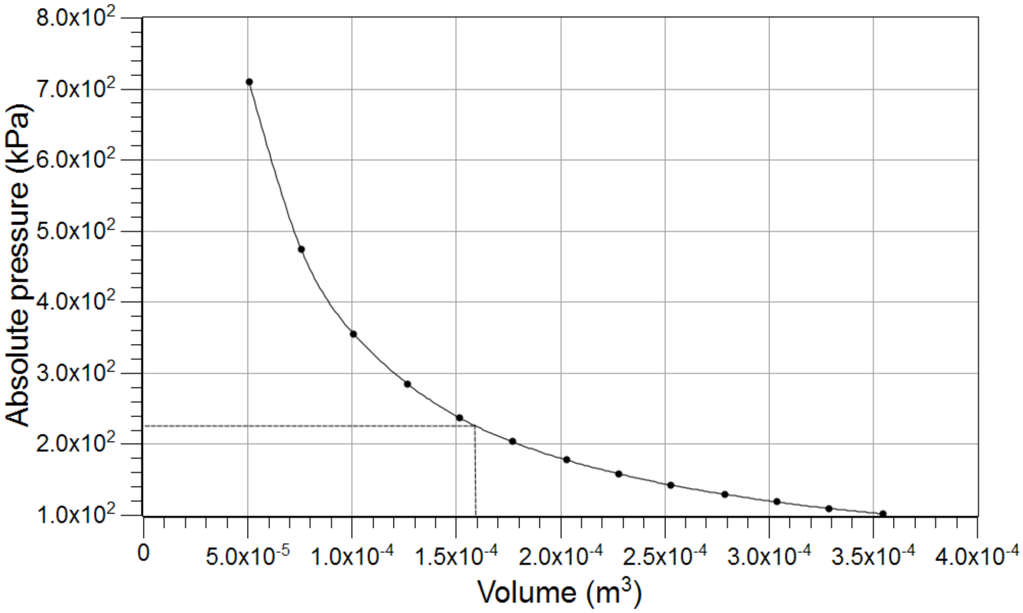
$$V_2 = \left(\frac{(101.3\ \text{kPa})(3.55 \times 10^{-4}\ \text{m}^3)}{(231\ \text{kPa})}\right) = 1.55 \times 10^{-4}\ \text{m}^3$$

The distance x of the piston from the bottom is

$$x = \frac{(1.55 \times 10^{-4}\ \text{m}^3)}{(5.07 \times 10^{-4}\ \text{m}^2)} = 0.308\ \text{m}$$

Therefore, the pump has to be pushed down until it is at least 0.308 m from the bottom—a little more than halfway down. We can actually push the piston in much further, which is why we can build much higher pressure to drive air into the tire effectively.

If you monitor the increase in pressure as the volume is decreasing, you obtain the following graph:



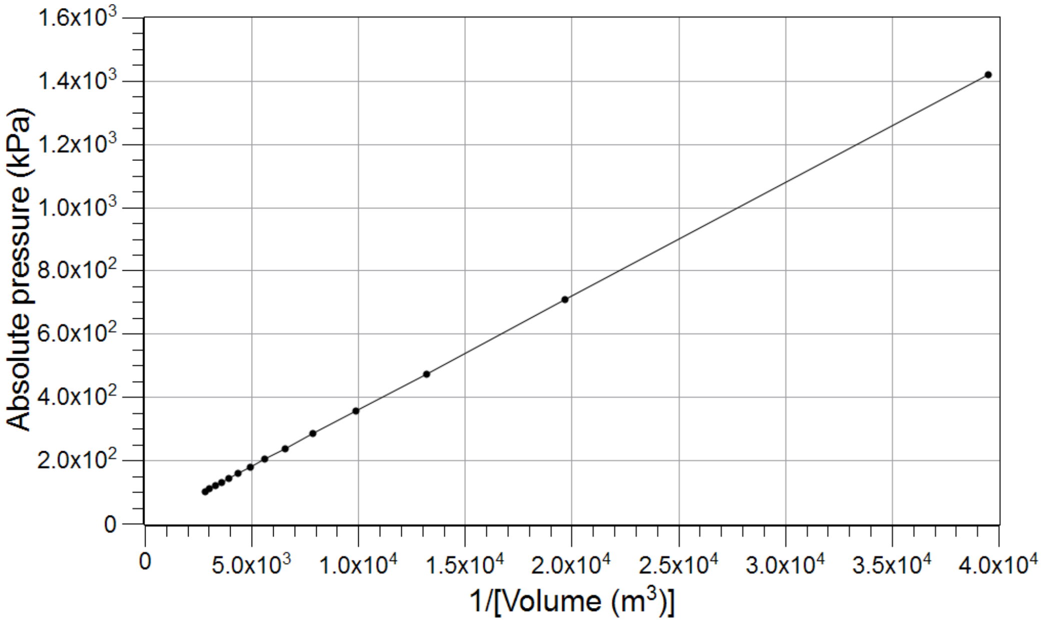
Notice that the pressure necessary to drive air into the tire is marked on the graph with the corresponding volume. The inverse relationship can be shown more clearly if we consider that an inverse relationship means that one quantity is directly proportional to the inverse of the other quantity:

$$PV = \text{constant}$$

$$P = \frac{\text{constant}}{V}$$

$$P \propto \frac{1}{V}$$

Therefore, the plot of P versus $1/V$ is linear:



Gay-Lussac's Law

In another example, a 50-m^3 gas container is pressurized with methane gas at room temperature (T_1 = 25 °C) to an initial pressure (P_1 = 50 atm). To what value would the safety valve be set in order to release the gas if the temperature rises above a critical value (T_2 = 40 °C)?

To solve this example we have to employ Gay-Lussac's Law. This law states that the pressure of a gas with a constant number of molecules and constant volume is proportional to the temperature:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

The necessary conversions are

$$T_1 = 25\ ^{\circ}\text{C} = 298\ \text{K}$$

$$T_2 = 40\ ^{\circ}\text{C} = 313\ \text{K}$$

$$P_1 = 50\ \text{atm} = 5.07 \times 10^3\ \text{kPa}$$

The critical pressure will be

$$P_2 = \frac{\left(5.07 \times 10^3 \text{ kPa}\right)\left(313 \text{ K}\right)}{\left(298 \text{ K}\right)} = 5.32 \times 10^3 \text{ kPa} = 52.5 \text{ atm}$$

(The conversion to kil0pascals turns out not to have been necessary, as long as the pressure units are constant.)

1. Explain why the decreasing volume results in higher pressure.

A decreasing volume increases the frequency of the collisions among the molecules as well as of the collisions between molecules and the wall of the container. In this case, the increased number of collisions between the molecules and the container wall is responsible for the increasing pressure.

2. Explain why increasing temperature increases the pressure.

Higher temperature will increase the average kinetic energy which will increase the average speed of molecules. Higher speed results in more energetic and more frequent collisions with the wall and with other molecules, which results in higher pressure.

Lab Preparation

Although this experiment requires no specific lab preparation, allow 10 minutes to assemble the equipment needed to conduct the lab.

Safety

Add these important safety precautions to your normal laboratory procedures:

- Organic solvents are extremely flammable; have no open flames in the lab during the experiment.
- Do not inhale the fumes of volatile organic liquids.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Part 1 – Boyle's Law

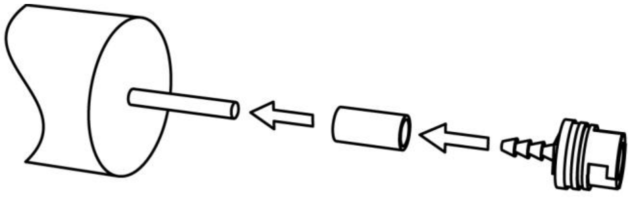
Set Up

1. Start a new experiment on the data collection system. �$^{(1.2)}$

2. Connect the absolute pressure sensor to the data collection system using a sensor extension cable. �$^{(2.2)}$

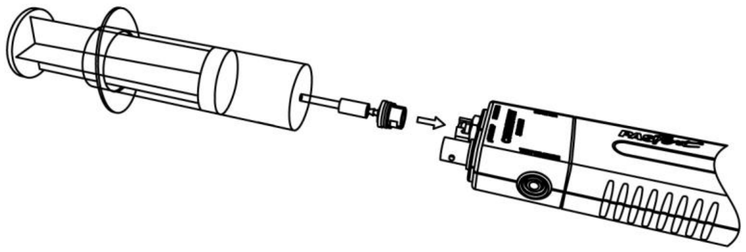
3. Put a drop of glycerin on the barbed end of a quick-release connector and put that end into one end of a short piece (about 2.5 cm) of plastic tubing that comes with the sensor.

4. Put a drop of glycerin on the end of the syringe. Connect the end of the syringe to the other end of the small piece of plastic tubing.



5 Adjust the plunger so there is 60.0 mL of air in the syringe.

6. Align the quick-release connector on the end of the plastic tubing with the pressure port of the absolute pressure sensor. Push the connector onto the port, and then turn the connector clockwise until it clicks (about one-eighth turn).



7. Configure the data collection system to manually collect pressure and volume. Define "volume" as a manually entered data set with units of milliliters. �$^{(5.2.1)}$

8. Change the units of the pressure measurement to kPa. �$^{(5.3)}$

9. What is the pressure at this time in the syringe?

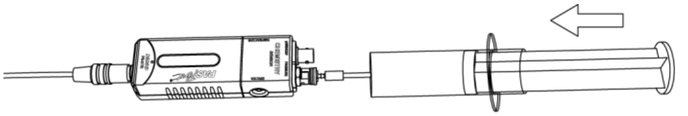
The pressure is the same as the atmospheric pressure.

Collect Data

10. Start a new, manually sampled data set. �$^{(6.3.1)}$

11. Before pushing the plunger (set at 60 mL), record the pressure and enter the volume. �$^{(6.3.2)}$

12. One student should push the plunger in 5 mL at a time while another student records the pressure and manually enters the volume. �$^{(6.3.2)}$



13. Continue to take readings at 5 mL intervals. Stop the data set when the pressure exceeds 4 atm (404 kPa). � $^{(6.3.3)}$

CAUTION: To minimize the risk of injury or damage to the equipment, avoid over-compressing the air in the syringe.

14. Display Pressure on the y-axis of a graph and Volume on the x-axis. � $^{(7.1.1)}$

15. Print the graph. � $^{(11.2)}$

16. Save your experiment. �$^{(11.1)}$

17. How does it feel to push the plunger in as the volume decreases?

It becomes increasingly more difficult to push the plunger in as the volume decreases.

18. Can you push the plunger in all the way? Explain your answer.

No, because the volume of the gas molecules cannot be zero. Mathematically, as the volume approaches zero, the pressure will approach infinity.

Part 2 – Guy-Lussac's Law

Set Up

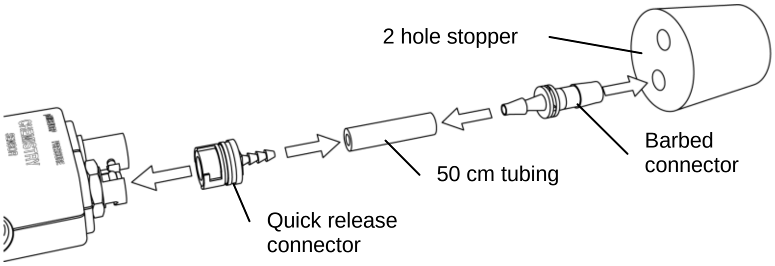
19. Start a new experiment on the data collection system. �(1.2)

20. Connect the pressure sensor and the temperature sensor to the data collection system. �(2.2)

21. Display Pressure on the y-axis and Temperature on the x-axis. � (7.1.1)

Note: Change the units of the temperature measurement to Kelvin. � (5.3)

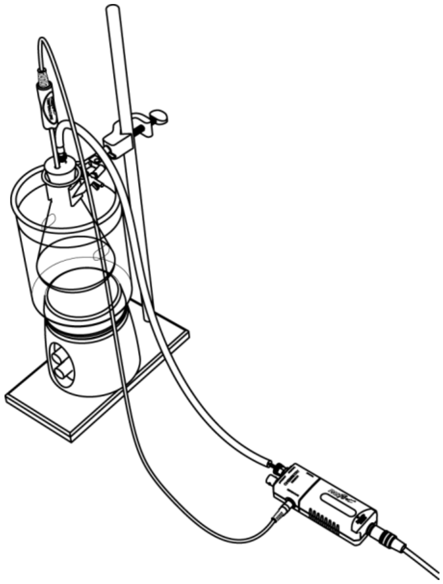
22. Place the barbed connector of the pressure sensor tightly into one hole of the rubber stopper and connect it to the pressure port of the sensor with a piece of tubing. Use a drop of glycerin if necessary.



23. Insert the temperature sensor into the other hole in the rubber stopper. If necessary, add a drop of glycerin. Wrap the 250-mL flask 15 to 20 times with electric tape if available.

24. Set a 1500-mL beaker, 3/4 full with water, on the hot plate with magnetic stirrer on the ring stand.

25. Place the stirring bar in the beaker.



26. Mount the 250-mL Erlenmeyer flask in the water so that it is covered with water as much as possible.

27. Why is it essential to immerse the Erlenmeyer flask as far as possible into the water bath?

The temperature of the glass wall of the flask will be the temperature of the gas inside the flask, which is needed for calculations. If the temperature of the wall is not homogenous, we will not know the temperature of the gas inside of the flask.

28. Place the stopper tightly into the Erlenmeyer flask.

Collect Data

29. Start recording data. �(6.2)

30. Turn on the hot plate.

31. Monitor the pressure as a function of temperature until the water bath temperature reaches 80 °C.

32. Stop recording data. �(6.2)

33. Print the graph. � (11.2)

34. Save your experiment. �(11.1)

35. What is the highest temperature you could achieve with this setup? Explain your answer.

The highest temperature would be the boiling point of water, 100 °C.

36. How does the pressure change as the temperature increases?

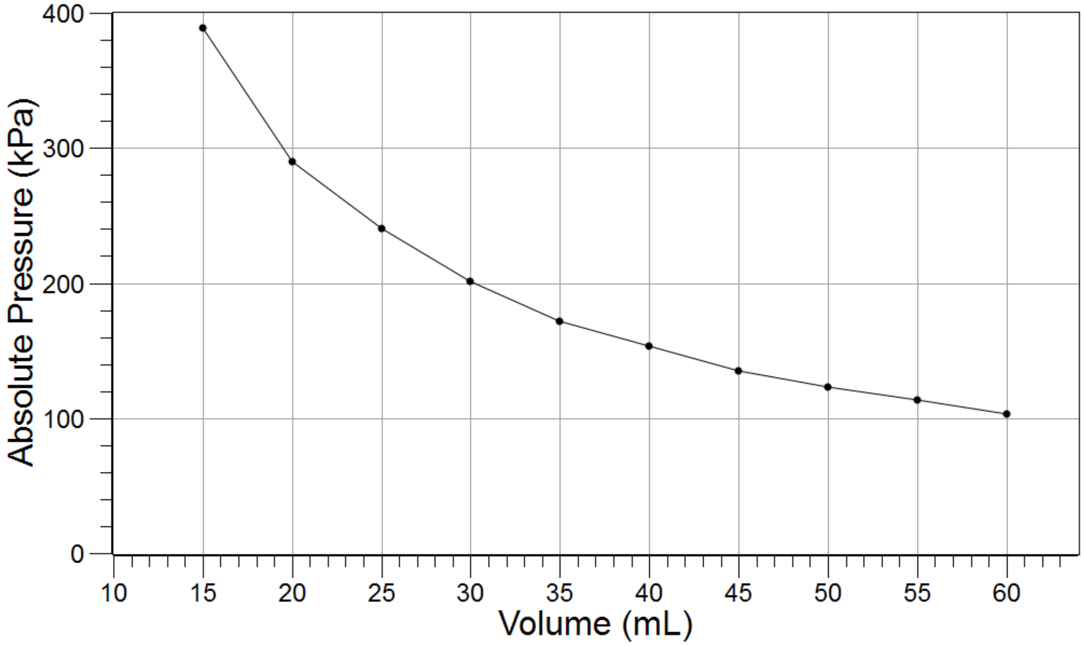
The pressure increases as the temperature increases.

Data Analysis

Part 1 – Boyle's Law

1. Open the file that you saved earlier in Part 1 of the procedure. �(1.1)

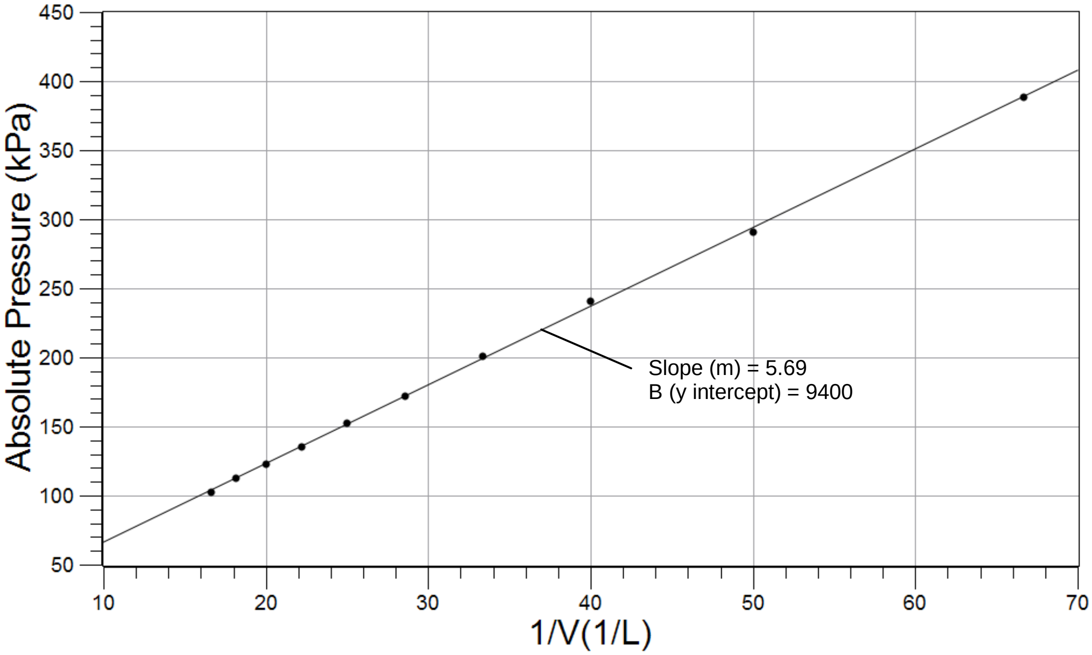
2. Sketch or attach the Pressure versus Volume graph below.



3. Load the data set of pressure versus volume and create a calculated data set of 1/*V* using the volume data. �(10.3)

4. Display Pressure on the y-axis and 1/*V* on the x-axis. � (7.1.1)

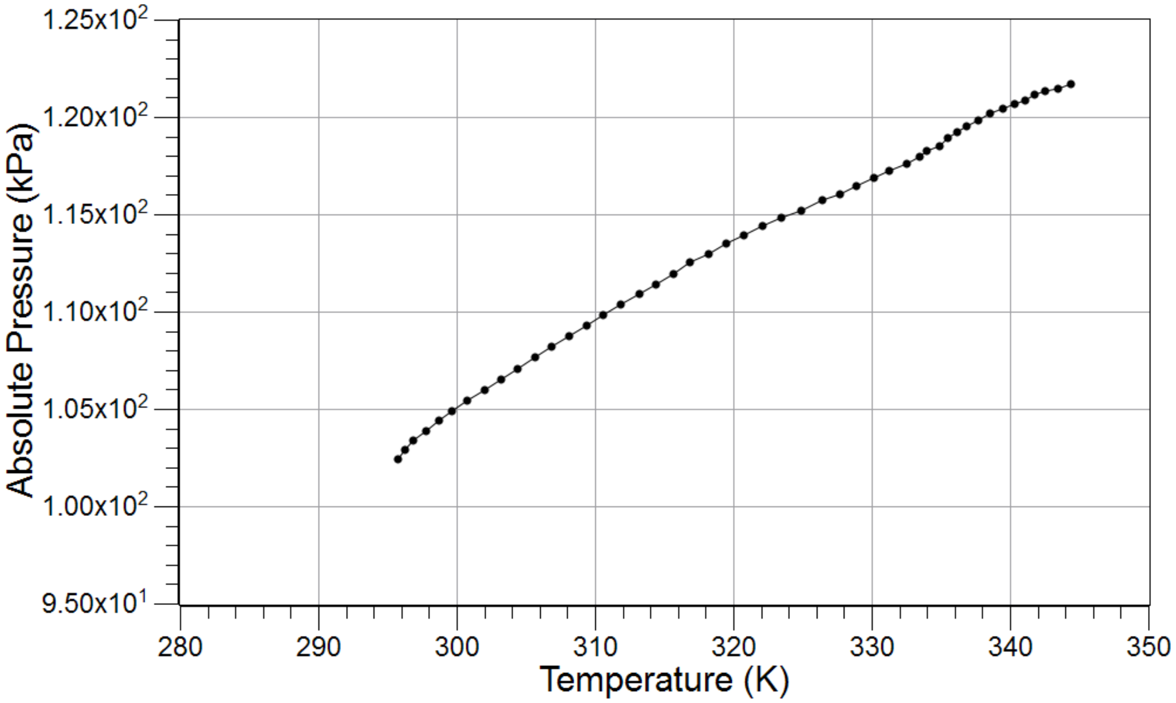
5. Sketch or attach the pressure versus inverse volume graph below.



Part 2 – Gay-Lussac's Law

6. Open the file you saved earlier in Part 2 of the procedure. �$^{(1.1)}$

7. Sketch or attach the Pressure versus Temperature graph below.



Analysis Questions

1. Did the pressure change as expected as you pushed the plunger in? How did the pressure change influence how hard you were pushing the plunger?

The pressure increased as the plunger was pushed in. The increasing pressure increased the resistance, making it harder to push the plunger further into the syringe.

2. Did you find the pressure directly proportional or inversely proportional to the volume based on the graph?

Inversely proportional.

3. What kind of relationship did you find based on the graph between the pressure and inverse volume? Express this relationship mathematically!

Pressure was directly proportional to the inverse volume: $P \propto \frac{1}{V}$

4. What kind of relationship did you find between the pressure and temperature based on the graph? Express this relationship mathematically!

Pressure was directly proportional to the temperature: $P \propto T$

5. **Combine the two equations into one. (Hint: If a quantity is proportional to two other quantities, it is proportional to their products as well.)**

$$P \propto \frac{T}{V}$$

6. **Predict what the intercept should be on the vertical axis of the Absolute pressure versus time graph and explain your prediction.**

The pressure should be zero at 0 K. That is where theoretically molecules have no kinetic energy and therefore their velocity is zero. Since molecules do not move, the pressure should be zero.

Synthesis Questions

Use available resources to help you answer the following questions.

1. **Consider the Erlenmeyer flask with the stopper tightly inserted. How do you think the pressure would change if you doubled the number of molecules (moles) in the flask? Explain your prediction!**

Doubling the number of molecules increases the number of collisions, resulting in an increase of pressure.

2. **Based on your answer to the previous question, what kind of mathematical relationship is there between the pressure and number of moles *n* of a gas? What is the mathematical representation of that relationship?**

Direct proportionality

$$P \propto n$$

3. **Combine the relationship between pressure and the number of moles of the gas with the relationship you obtained for pressure, temperature, and volume.**

$$P \propto n\frac{T}{V}$$

4. **Direct proportionality can be turned into an equation by using a constant. For example, if $A \propto B$, then with a constant, for example, *k*, the relationship turns into a mathematical equation: $A = kB$. Using the constant R, turn the proportionality relationship between *P*, *n*, *T*, and *V* into an equation!**

$$P = R\frac{nT}{V}$$

5. **The equation you just derived is referred to as the "Ideal Gas Law" which relates pressure, temperature, number of moles, and volume for gases. The constant R is referred to as the universal gas constant and has the value of 8.314 (L kPa)/(mol K). Arrange the Ideal Gas Law so you have *P* and *V* on the left and the other terms on the right. This is a more common form of this law.**

$$PV = nRT$$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Assume that the plunger of the syringe is at the 30 mL mark. Close the tip of the syringe with your thumb and pull the plunger to the 60 mL mark. How will the pressure change in the syringe?

- **A.** The pressure will not change.
- **B.** The pressure will double.
- **C.** **The pressure will be half of the original value**.
- **D.** We need the temperature to be able to calculate it.

2. The pressure and volume are inversely proportional to each other, which means:

- **A.** They are also directly proportional to each other.
- **B.** **Pressure is directly proportional to the inverse volume**.
- **C.** The pressure is proportional to the temperature.
- **D.** The pressure is proportional with the number of moles of gas molecules.

3. The relationship between the pressure and temperature is such that:

- **A.** **Increasing temperature will yield increasing pressure.**
- **B.** Increasing temperature will yield decreasing pressure.
- **C.** Increasing temperature will yield increasing inverse pressure.
- **D.** They are inversely proportional to each other.

4. Increasing the number of moles of gas two-fold in the Erlenmeyer flask will:

- **A.** Double the volume.
- **B.** Double the temperature.
- **C.** Double the gas constant.
- **D.** **Double the pressure**.

Extended Inquiry Suggestions

As an extended inquiry, students can determine the theoretical values of the slope of the "*p* versus 1/*V*" and "*P* versus *T*" graphs, based on the Ideal Gas Law, and compare them with the experimental values.

To determine the theoretical value of the slope of the *p* versus 1/*V* graph, we need to rearrange the Ideal Gas Law:

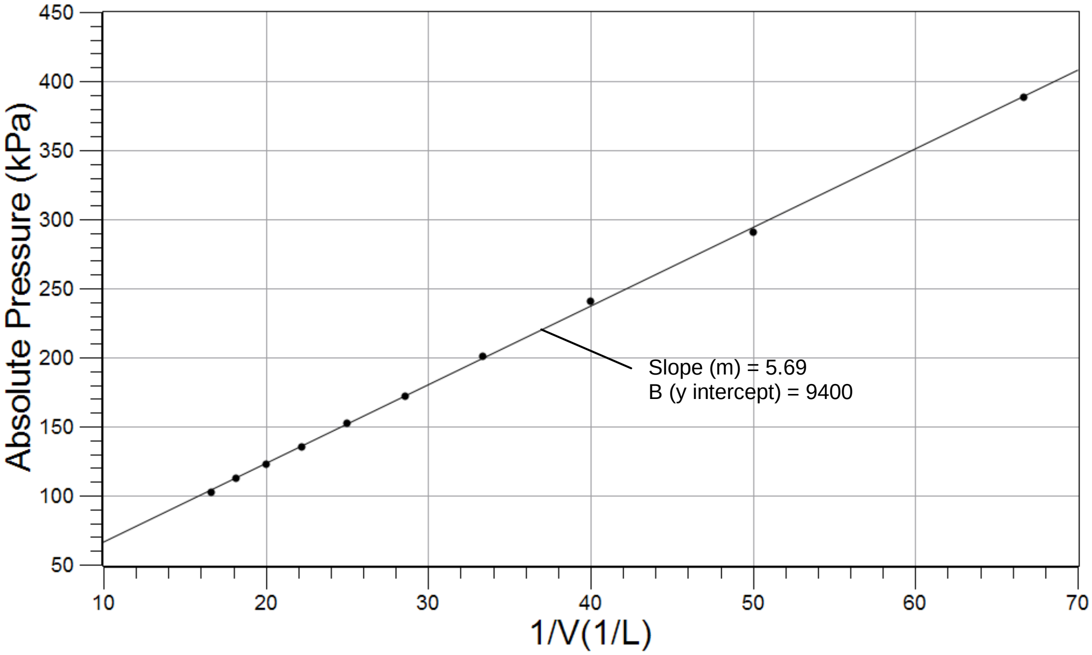
$$P = nRT\frac{1}{V}$$

The value of n can also be calculated from the Ideal Gas Law, based on the initial conditions:

$$n = \frac{PV}{RT} = \frac{(101.3\text{kPa})(6.00 \times 10^{-2}\ \text{L})}{\left(8.314\ \frac{\text{L kPa}}{\text{mol K}}\right)(298\ \text{K})} = 2.45 \times 10^{-3}\ \text{mol}$$

The theoretical value of the slope, then, is:

$$nRT = (2.45 \times 10^{-3}\ \text{mol})\left(8.314\ \frac{\text{J}}{\text{mol K}}\right)(298\ \text{K}) = 6.08\ \text{J}$$



The experimental value from the equation from the graph is 5.69 J; therefore, the error is:

$$\left|\frac{6.08\ \text{J} - 5.59\ \text{J}}{6.08\ \text{J}}\right| \times 100 = 8.1\%$$

To calculate the theoretical value of the slope of the Pressure versus Temperature graph, the Ideal Gas Law has to be rearranged as follows:

$$P = \frac{nR}{V}T$$

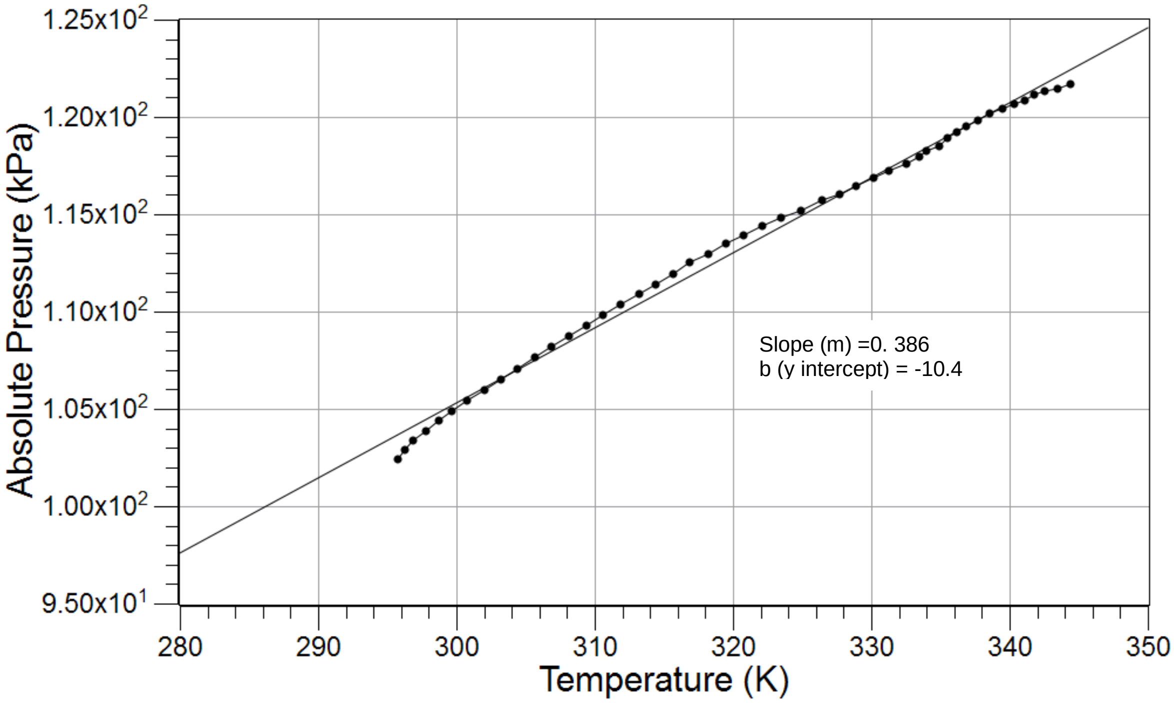
Students have to realize that along with n, they need the volume of the Erlenmeyer flask. The total volume of a 250-mL flask is more than 250 mL. Students must measure the entire volume (by filling it with water).

In this experiment, $V = 256$ mL. When calculating n, they have to realize that after the stopper is placed in the flask, n doesn't change:

$$n = \frac{PV}{RT} = \frac{(101.3\ \text{kPa})(2.56 \times 10^{-1}\ \text{L})}{\left(8.314\ \frac{\text{L kPa}}{\text{mol K}}\right)(298\ \text{K})} = 1.05 \times 10^{-2}\ \text{mol}$$

Therefore, the value of the slope should be

$$\frac{nR}{V} = \frac{(1.05 \times 10^{-2}\ \text{mol})\left(8.314\ \frac{\text{L kPa}}{\text{mol K}}\right)}{(2.56 \times 10^{-1}\ \text{L})} = 3.40 \times 10^{-1}\ \frac{\text{kPa}}{\text{K}}$$



The experimental value from the equation from the graph appears to be 386.0 N/(m^2K). The error is

$$\left| \frac{0.386\,\frac{\text{kPa}}{\text{K}} - 0.340\,\frac{\text{kPa}}{\text{K}}}{0.340\,\frac{\text{kPa}}{\text{K}}} \right| \times 100 = 13.5\%$$

Intermolecular Forces and States of Matter

14. Molecular Interaction in Ethanol and Acetone

Objectives

Students determine and relate the heat of vaporization of substances to the interactions between molecules.

Procedural Overview

Students gain experience conducting the following procedures:

- Studying the molecular interaction of ethanol and of acetone by monitoring their vapor pressure as a function of temperature
- Using pressure and temperature sensors

Time Requirement

♦ Preparation time	10 minutes
♦ Pre-lab discussion and experiment	10 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- Absolute pressure sensor with quick-release connectors and plastic tubing
- Sensor extension cable
- Beaker, 1500-mL
- Beaker, 50-mL
- Erlenmeyer flask, 250-mL
- Graduated cylinder, 50-mL
- Hot plate with magnetic stirrer and stirring bar
- Clamp, utility
- Ring stand
- 100% Ethanol (C_2H_5OH), 50 mL
- Acetone [$(CH_3)_2CO$], 50 mL
- Rubber stopper, 2-hole
- Glycerin, 2 drops
- Water, 1200 mL

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Molar volume of a gas
- Molar mass
- Gas laws
- Intermolecular interactions

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Molar Mass of a Volatile Liquid
- Molar Volume of a Gas
- Identifying an Unknown Metal
- Exploring Gas Laws

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a temperature sensor and a pressure sensor to your data collection system �(2.2)
- Starting and stopping data recording �(6.2)
- Displaying data on a graph �(7.1.1)
- Displaying two data runs on a graph �(7.1.3)
- Creating calculated data �(10.3)
- Printing �(11.2)

Background

Many of the physical properties of substances and solutions are determined by the nature of the interactions between molecules. There are three fundamental interactions which collectively are known as “van der Waals” interactions: dipole-dipole (DD), ion-dipole (ID), and London-type dispersion forces (LD).

The DD forces exist between two dipole molecules—for example, between the water molecules and the polar ethanol molecule. A special type of DD interaction is the hydrogen bond which exists between a partially negatively-charged atom (usually oxygen or nitrogen) and a hydrogen atom which is attached to an atom with high electronegativity. Hydrogen bonds are relatively strong; for example, hydrogen bonding is responsible for the very high boiling point of water.

The ion-dipole forces exist between ions and polar molecules, such as Na^+ ions and water molecules in a NaCl solution. The LD forces are rather weak and based on temporary, induced polarity between two otherwise non-polar molecules—CCl_4 and I_2 molecules, for example.

The strength of the bonds between molecules determines the melting point, boiling point, and vapor pressure of a substance at a given temperature. Greater bond strength results in higher melting and boiling points as more thermal energy is needed to break the bonds. Also, greater strength between molecules results in lower vapor pressure at a given temperature as fewer molecules will possess the necessary kinetic energy to escape into the gas phase.

Another factor in molecular interactions is the size of the molecules. Larger molecules need more thermal energy to be able to escape, therefore, the vapor pressure of larger molecules at a given temperature is less. For the same reason, the melting and boiling points of substances with larger molecules are higher. The greater amount of energy needed for molecules to escape from liquid phase to gas phase is reflected by the heat of vaporization.

Heat of vaporization is the energy required for a known amount of substance to escape from the liquid to gas phase. The mathematical relationship between the heat of vaporization and the temperature is given by the Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H_{\text{vap}}}{R}\frac{1}{T} + C \qquad (1)$$

where

P = vapor pressure of the substance (kPa)

ΔH_{vap} = heat of vaporization (J/mol)

T = temperature (K)

C = a constant

R = 8.314 J/(mol K)

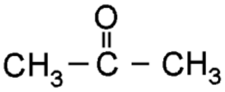
Equation 1 shows that a plot of ln P versus 1/T should give a straight line with a slope of $-(\Delta H_{\text{vap}}/R)$.

Pre-Lab Experiment

Setting the stage for the experiment

In this experiment, you will compare the molecular interactions between ethanol molecules and then between acetone molecules. Their formulas and properties are listed in Table 1.

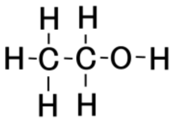
Table 1: Properties of acetone and ethanol

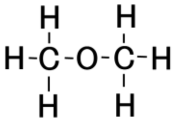
Properties	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$ **Acetone**	CH_3-CH_2-OH **Ethanol**
Possible interactions	London-type of dispersion	Hydrogen bond
Strength of strongest interactions	Weak	Strong
Formula weight (g/mol)	58.0	46.0
Boiling point (°C)	56.5	78.4

The ethanol molecule is much lighter and its boiling point is much higher than the boiling point of acetone because of the existing hydrogen bond between the ethanol molecules.

Example calculation to try

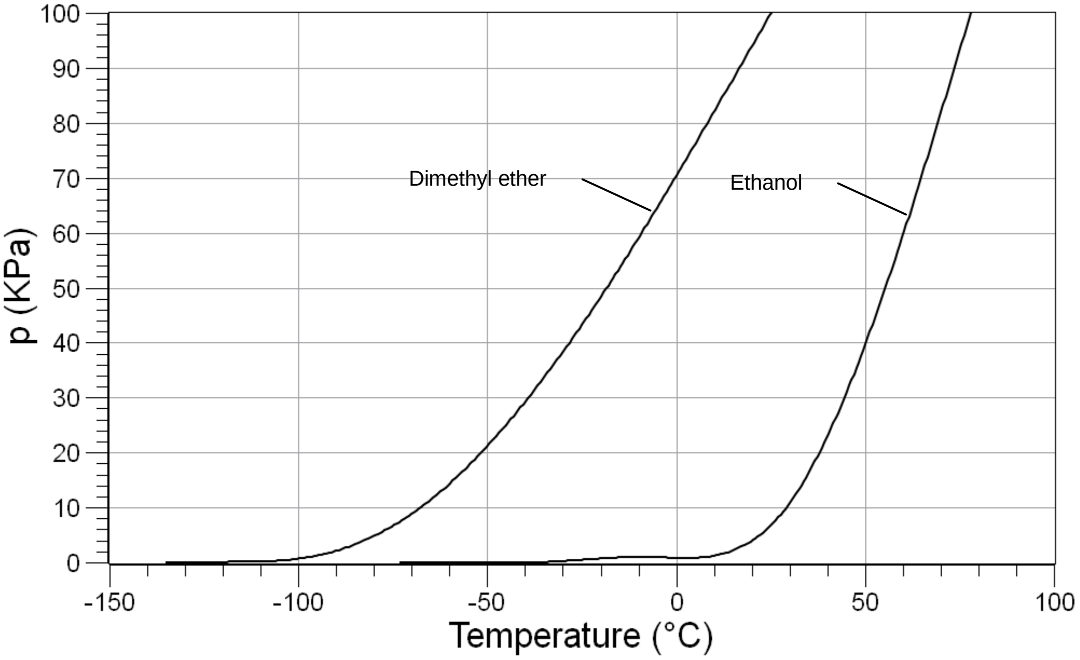
In an experiment, the molecular interactions between ethanol and dimethyl ether were compared. They have the same formula but different molecular structures:





	Ethanol	**Dimethyl ether**
Boiling point:	78.4 °C	–23.6 °C

Ethanol molecules can form hydrogen bonds between the oxygen and the hydrogen atoms of other ethanol molecules. This explains its relatively high boiling point. Dimethyl ether, on the other hand, can form only weak London-type interactions between molecules, which explains its low boiling point. The following data was obtained as the vapor pressures of these two substances were compared:



As you can see, at any given temperature where both compounds are in the liquid phase more of the dimethyl ether molecules escape to the gas phase, building higher pressure than ethanol molecules, due to the weaker interactions between dimethyl ether molecules. The heat of vaporization of ethanol, therefore, is higher than it is for dimethyl ether. The heat of vaporization can be calculated from the data above with the Clausius-Clapeyron equation:

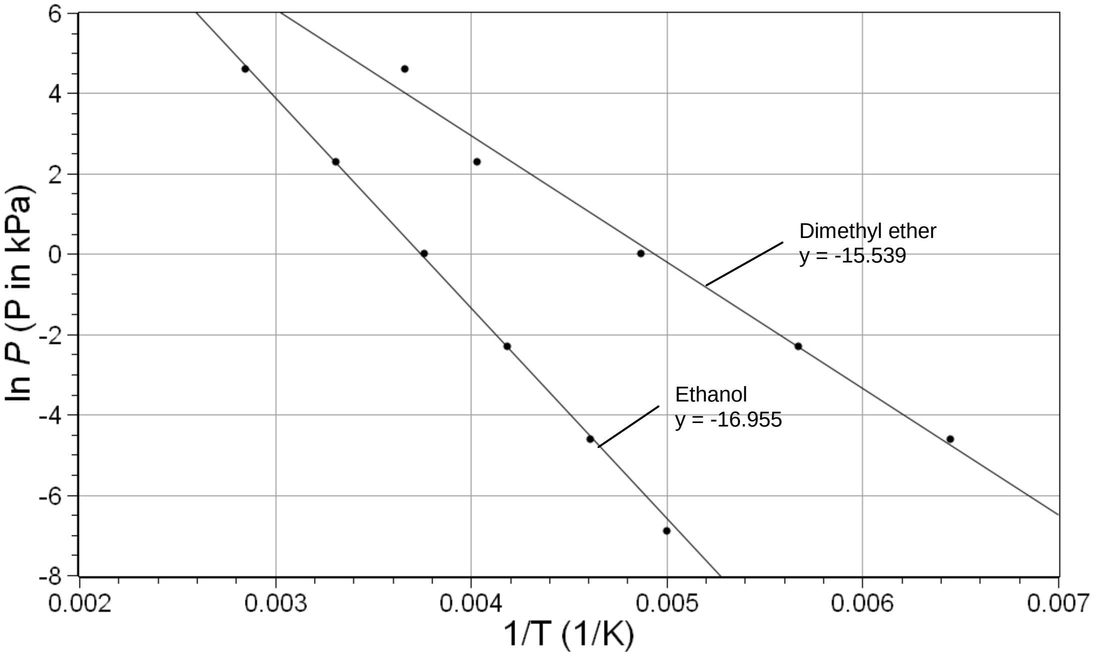


Table 2: Determination of the heat of vaporization

Substance	Slope (K)	Heat of Vaporization (J/mol)
Ethanol	–5341.1	44,406
Dimethyl ether	–3146.5	26,160

Calculation of the heat of vaporization for ethanol from the slope:

$$(\text{slope}) = -\frac{\Delta H_{\text{vap}}}{R}$$

$$\Delta H_{\text{vap}} = -(\text{slope})R = -(5341.1\,\text{K})\left(8.314\frac{\text{J}}{\text{mol K}}\right) = 44{,}406\frac{\text{J}}{\text{mol}}$$

The same calculation applies for the dimethyl ether.

The lower heat of vaporization for dimethyl ether demonstrates the weaker intermolecular interactions between the dimethyl ether molecules.

1. Explain how the boiling point and heat of vaporization are related.

They both depend on intermolecular interactions. They both increase with the increase in the strength of the intermolecular interaction.

2. Explain how the vapor pressure of a liquid is related to its boiling point and its intermolecular interactions.

Stronger intermolecular interactions result in higher boiling points because molecules need higher thermal energy to escape into the gas phase. It also results in fewer molecules in the gas phase, which means that the vapor pressure will be lower.

Lab Preparation

Although this experiment requires no specific lab preparation, allow 10 minutes to assemble the equipment needed to conduct the lab.

Safety

Add these important safety precautions to your normal laboratory procedures:

- ♦ Organic solvents are extremely flammable; have no open flame in the lab during the experiment.
- ♦ Do not inhale the fumes of volatile organic liquids.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Set a 1500-mL beaker, 3/4 full with water, on the hot plate with magnetic stirrer and gently place a stirring bar in the beaker.

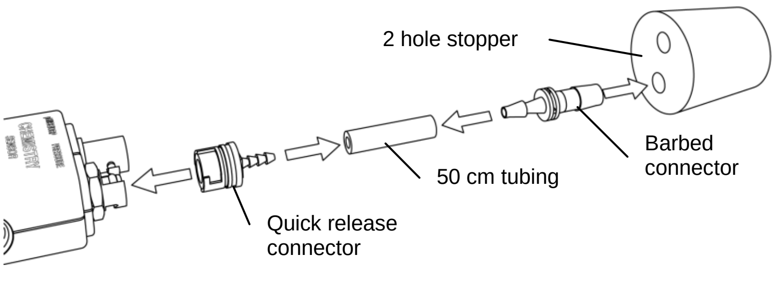
2. Use the ring stand and utility clamp to mount a 250-mL Erlenmeyer flask in the water bath so it is immersed as much as possible without allowing water to enter in the top.

3. Turn on the hot plate. Heat the water bath until the temperature is about 80°C (bubbles start to form on the bottom of the beaker)

4. Start a new experiment on the data collection system. �(1.2)

5. Place the barbed connector of the absolute pressure sensor tightly into the rubber stopper and connect it to the pressure port of the sensor with a piece of tubing.

Note: If necessary, add a drop of glycerin onto the end of the connector that goes into the hole in the rubber stopper.



6. Insert the temperature sensor into the other hole in the rubber stopper. If necessary, add a drop of glycerin.

7. Connect the absolute pressure sensor to the data collection system using a sensor extension cable. �(2.2)

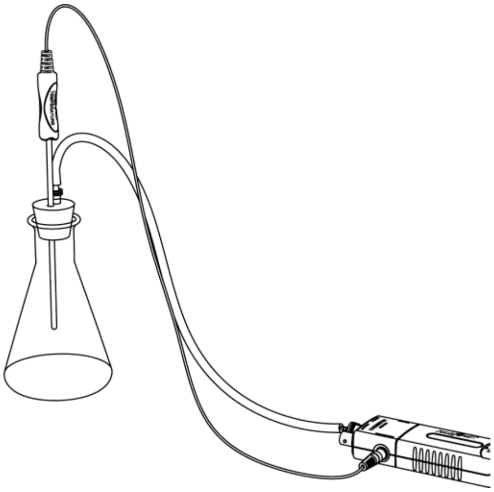
8. Display Pressure on the y-axis with Temperature on the x-axis. �(7.1.1)

9. Place the stopper into the Erlenmeyer flask to test for a tight fit.

10. Remove the stopper.

11. Transfer 50 mL of ethanol into the Erlenmeyer flask in the water bath.

Collect Data



12. Once the ethanol starts to boil, allow a few minutes for the ethanol fumes to fill the flask.

13. What is going to fill the flask at this point?

The air is replaced by ethanol molecules.

14. Remove the flask from the water bath and immediately insert the stopper tightly.

15. Start recording data. �(6.2)

16. Continue the data collection until the temperature drops to about 30 °C.

17. Stop recording data. �(6.2)

18. How do you predict the pressure will change? Explain your answer.

The pressure will decrease as the temperature decreases; the vapor pressure at lower temperature is lower.

19. Discard the ethanol as instructed by your instructor and rinse the flask.

20. Repeat the procedure with a 60 °C water bath and 50 mL of acetone. Allow the flask to cool to about 25 °C.

21. Why do you think 60 °C is a sufficiently high temperature for the water bath for acetone?

Acetone has a boiling point at about 56 °C.

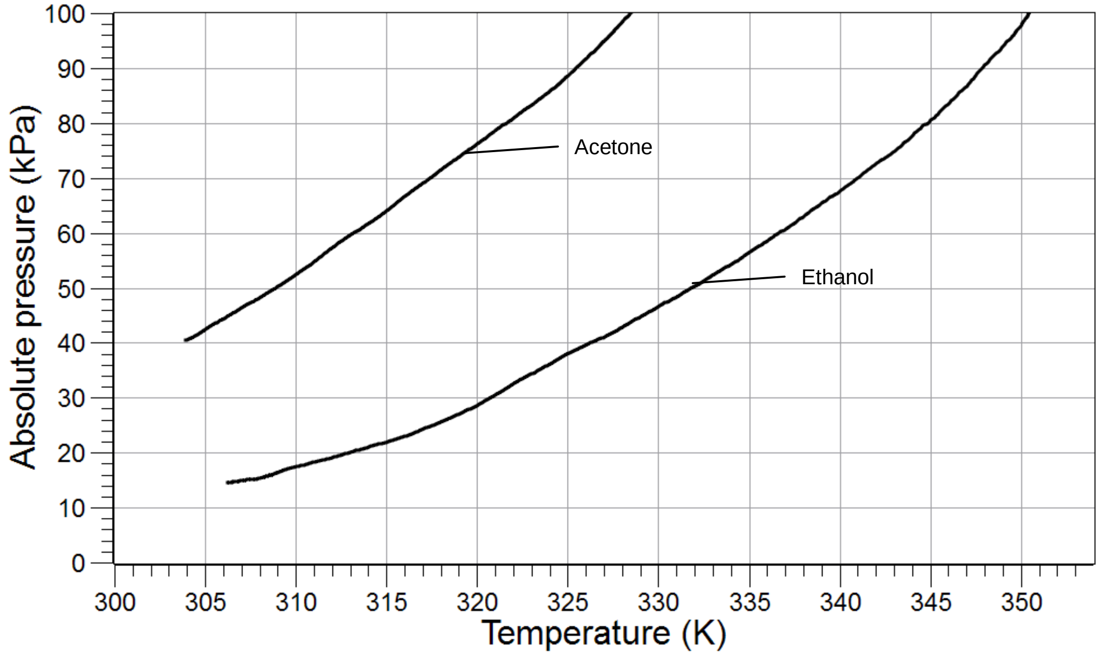
22. Display both data runs. �(7.1.3)

23. Print the graph. �(11.2)

24. Save your experiment �(11.1) and clean up according to your instructor's instructions.

Data Analysis

1. Sketch or attach the Pressure versus Temperature graph below.

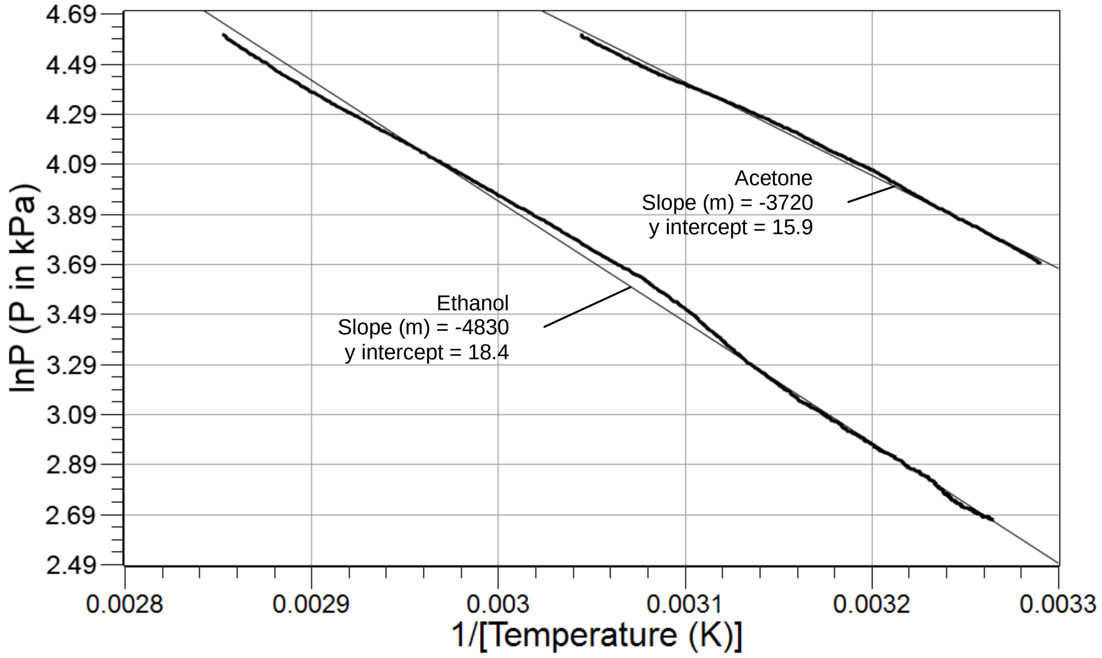


2. Generate the Clausius-Clapeyron plot: Generate two calculated datasets: one for ln P and one for $1/T$. �(10.3)

3. Display ln P on the y-axis of a graph with $1/T$ on the x-axis. �(7.1.1)

4. Print the graph. �(11.2)

5. Sketch or attach the graph of ln P versus $1/T$).



6. Calculate the heat of vaporization for both substances from the slope of the Clausius-Clapeyron plot.

Using the results for ethanol:

$$(\text{slope}) = -\frac{\Delta H_{\text{vap}}}{R}$$

$$\Delta H_{\text{vap}} = -(\text{slope})\,R = -(-4830\ \text{K})(8.314\ \tfrac{\text{J}}{\text{mol K}}) = 4.016 \times 10^{4}\ \tfrac{\text{J}}{\text{mol}} = 40.16\ \tfrac{\text{kJ}}{\text{mol}}$$

Table 3: Heat of vaporization determined for ethanol and acetone

Substance	Slope (K)	Heat of Vaporization (J/mol)
Ethanol	–4830	4.016×10^{4}
Acetone	–3720	3.093×10^{4}

Analysis Questions

1. Did it matter how much of the liquid phase was present? Explain your answer!

The actual amount present is not relevant as long as there was enough to establish the vapor pressure.

2. Compare the curves of the pressure versus temperature graph for ethanol and acetone. Compare the pressures at 35 °C and 50 °C. What conclusions can you draw about the intermolecular interactions between the ethanol and acetone molecules?

At both temperatures the vapor pressure of acetone is significantly higher, which means that there are more acetone molecules than ethanol molecules in the gas phase. More molecules in the gas phase at the same temperature indicate weaker intermolecular interactions.

3. Compare the slopes of the Clausius-Clapeyron curves for ethanol and acetone. What conclusion can you draw from the difference between the slopes?

The line for ethanol is steeper, indicating a higher heat of vaporization.

4. Compare the calculated heats of vaporization. Do your results support your predictions?

The significantly larger heat of vaporization for ethanol supports the assumption that the ethanol molecules have much stronger intermolecular interactions than the acetone molecules.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Knowing the heat of vaporization for ethanol and acetone, predict how the heat of fusion (the amount of heat necessary to melt 1 mol of substance) of ethanol and acetone would compare.

Because of the stronger interactions between the ethanol molecules, the heat of fusion for ethanol would be significantly more than for acetone.

2. Based on what you have learned, predict the heat of vaporization for ethylene glycol (HO–CH_2–CH_2–OH), a common ingredient of car coolant liquids. Explain your predictions!

Since there are two polar hydrogen atoms and two oxygen atoms in each ethylene glycol molecule, each molecule can form two hydrogen bonds. A higher number of hydrogen bonds will most likely result in a higher heat of vaporization for ethylene glycol. Indeed, the heat of vaporization for ethylene glycol is 63,200 J/mol.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. High vapor pressure at room temperature is an indication of:

- **A.** High heat of vaporization.
- **B.** High heat of fusion.
- **C.** Strong intermolecular interactions.
- **D.** **Weak intermolecular interactions**.

2. The vapor pressure of acetone was:

- **A.** **Higher at any temperature than the vapor pressure of ethanol**.
- **B.** Lower at any temperature than the vapor pressure of ethanol.
- **C.** Not significant below 30 °C.
- **D.** About the same at any temperature as the vapor pressure of ethanol.

3. The heat of vaporization is greater for ethanol than for dimethyl ether because:

- **A.** There are stronger intermolecular interactions between the dimethyl ether molecules.
- **B.** **There are weaker intermolecular interactions between the dimethyl ether molecules.**
- **C.** The ethanol molecule is larger.
- **D.** The dimethyl ether molecule is larger.

4. The heat of vaporization of methanol (CH_3–OH) is most likely:

- **A.** **Less than the heat of vaporization of ethanol because the molecule is smaller**.
- **B.** Greater than the heat of vaporization of ethanol because the molecule is smaller.
- **C.** Less than the heat of vaporization of acetone because the molecule is smaller.
- **D.** The same as the heat of vaporization of ethanol because there are hydrogen bonds in methanol just like in ethanol.

Extended Inquiry Suggestions

A modeling experiment could be performed by students to "study" the molecular interactions between ethylene glycol molecules. The actual experiment is not easily done since ethylene glycol does not have significant vapor pressure below 100 °C and at higher temperatures safety becomes a concern. Instead, provide students with a set of vapor pressure versus temperature data. The data can be readily generated from the Antoine equation for ethylene glycol:

$$\ln(P) = A - \frac{B}{T} + C\ln(T) + DT^{E}$$

where

$A = 84.09$

$B = 10411$

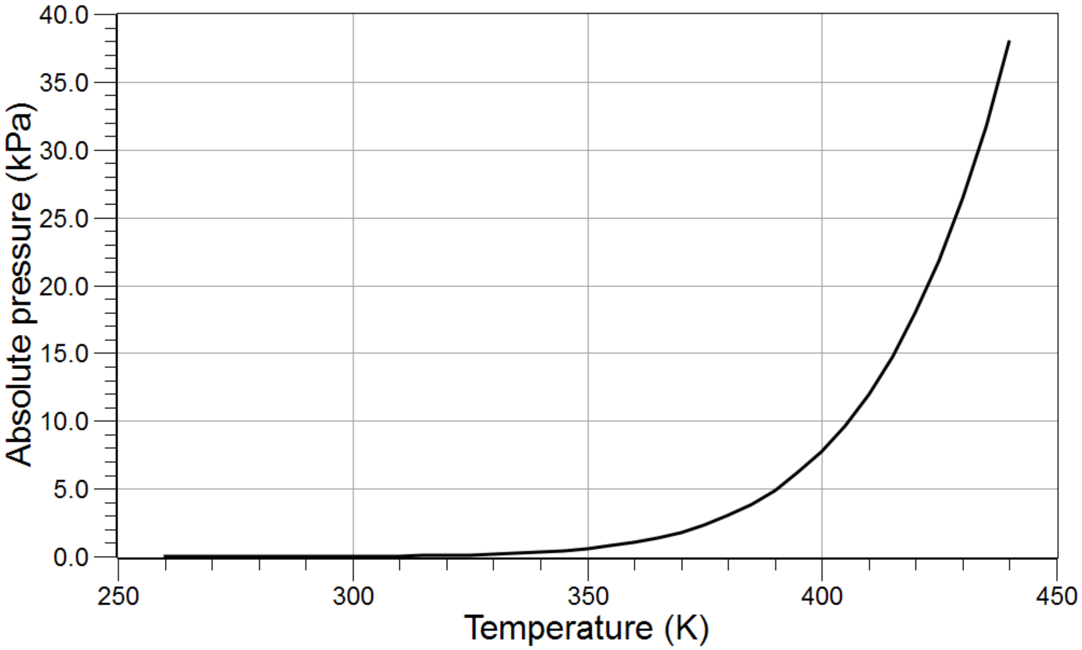
$C = -8.1976$

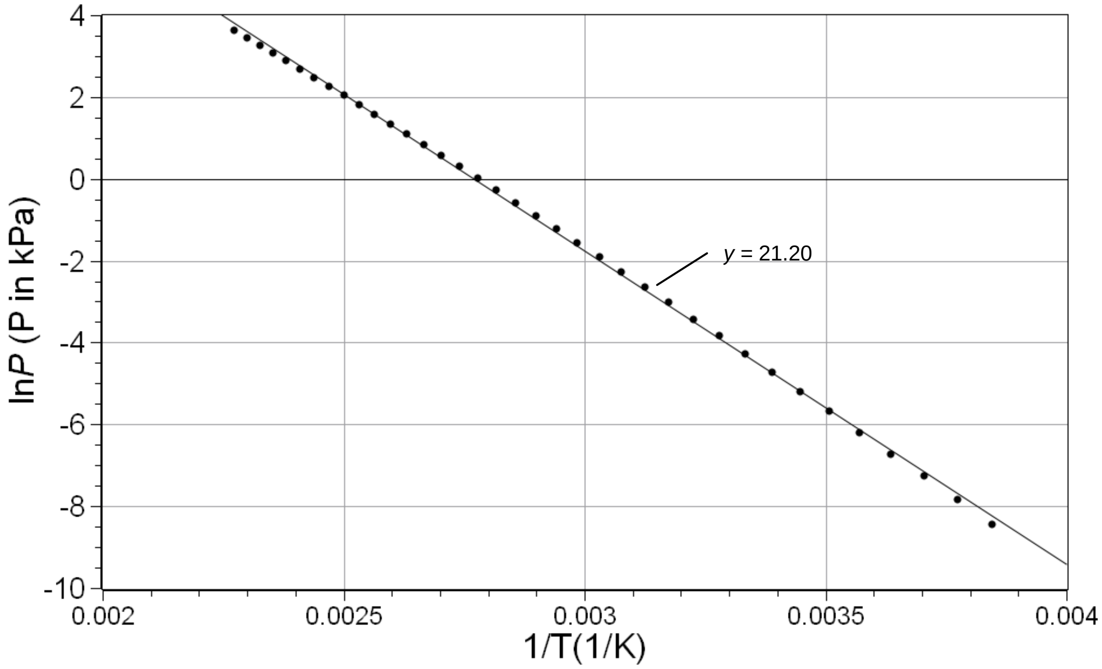
$D = 1.6536 \times 10^{-18}$

$E = 6$

Please note, no units are provided.

The pressure versus temperature graph and the Clausius-Clapeyron plot can be obtained from the modeled data, shown below, clearly demonstrating a higher heat of vaporization than that of ethanol. Hold a discussion to relate the high heat of vaporization (higher than water) to the fact that ethylene glycol is used as a major ingredient in various automotive systems for two reasons: high boiling point (heat of vaporization) and low freezing point.





Determination of the heat of vaporization

Substance	Slope (1/K)	Heat of vaporization (J/mol)
Ethylene glycol	–7657.0	63,660

Solutions and Solubility

15. Molecular Weight by Freezing Point Depression

Objectives

Students determine the molecular weight of a compound by measuring the freezing point depression of a solution.

Procedural Overview

Students gain experience conducting the following procedures:

- Measuring the freezing point of a solvent
- Making a solution with a solvent that has a higher freezing point than room temperature
- Using phase diagrams and obtaining freezing point curves

Time Requirement

♦ Preparation time	20 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- Erlenmeyer flask, 250-mL
- Beaker, 400-mL
- Test tube, 20-mL
- Copper wire coil[1]
- Ring stand
- Hot plate
- Stirring bar
- Clamp (2), utility
- Lauric acid, $CH_3(CH_2)_{10}COOH$, 8 g
- Unknown solute, 0.5 g[2]
- Water, 300 mL

[1] To prepare the copper wire coil, refer to the Lab Preparation section.

[2] To prepare the unknown solute sample, which is benzoic acid, C_6H_5COOH, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Colligative properties

- Definition of electrolytes
- Molality concentration
- Phase diagrams, heat of vaporization, heat of fusion

Related Labs in This Guide

There are no labs conceptually related to this one.

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system �(2.1)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Adjusting the scale of the graph �(7.1.2)
- Display two data runs in a graph. �(7.1.3)
- Print the graph. �(11.2)
- Saving your experiment �(11.1)

Background

Understanding the process by which solutions are made helps one understand colligative properties. The solution process involves breaking attractive forces and forming new attractive forces. The attractive forces between ions and molecules in solid phase have to be broken (ionic bonds in ionic lattices, or intermolecular forces between molecules in molecular compounds) and some attractive forces among the solvent molecules have to be broken to accommodate the dissolved particles. These steps require energy.

The ions formed or molecules freed form new attractions with the free solvent molecules. This process releases energy. The result of these three energy changes is the “heat of solution,” which can be positive or negative. A positive energy change indicates an endothermic solution process; a negative energy change indicates an exothermic process.

Because of the attractions formed between the solute and solvent molecules, a solution has fewer "free" solvent molecules available to escape from the liquid phase into the gas phase. This important consequence means that the vapor of the solvent builds a lower vapor pressure over the solution. Use the phase diagram to understand the effect of the lower vapor pressure.

The top diagram applies to the states of matter of a substance in general. The bottom diagram compares the freezing and boiling points of a solution and the pure solvent.

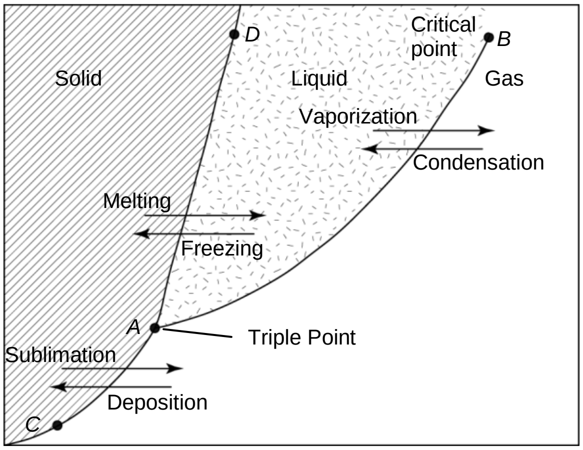


Figure 1: Phase diagram

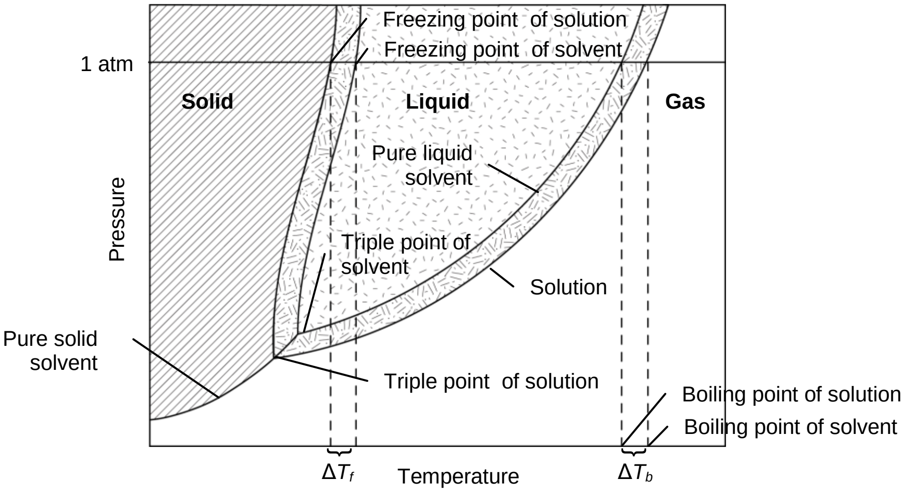


Figure 2: Phase diagram comparing a solution to the pure solvent

The phase diagram shows how the vapor pressure over a solution is lower at any given temperature compared with the solvent. Because of the lower vapor pressure over solutions, the vapor pressure reaches the atmospheric pressure at a higher temperature than the boiling point and at a lower temperature than the freezing point of the pure solvent. Compared with pure solvent, the freezing point of solutions is lower and the boiling point of solutions is higher.

Note that the standard freezing point phase transition occurs at atmospheric pressure and the standard boiling point phase transition occurs at atmospheric pressure.

The respective temperature changes are referred to as the freezing point depression (ΔT_f) and boiling point elevation (ΔT_b).

Another concept to understand is the effects of heat on substances. This can be observed on the heating curve below.

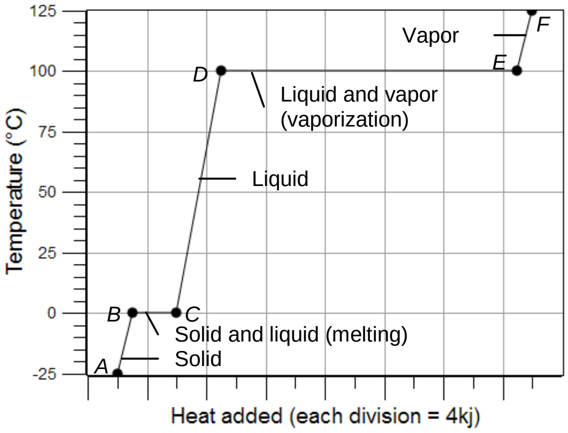


Figure 3: Heating curve

The temperature of solid (AB), liquid (CD), and gas (EF) phases increases as heat is absorbed. However, at the freezing point and boiling point the temperature remains constant while the heat of fusion (BC) and heat of vaporization (DE) are absorbed.

In this experiment students will perform the process in the reverse direction: instead of heating, they will cool a liquid solvent and solution until it freezes.

Pre-Lab Experiment

Setting the stage for the experiment

As a solute is added to a solvent, the freezing point of the resulting solution is lowered. The freezing point depression of the solution is dependent on two things: the solvent and the amount of solute added. However, it does not depend on the nature of the solute. The following equation describes this relationship:

$$\Delta T_f = K_f m$$

where

ΔT_f = the freezing point depression (K)
K_f = the freezing point depression constant for a particular solvent (K kg mol^{-1})
m = the molality of the solution (mol/kg)

Stated another way:

$$\Delta T_f = K_f \frac{n_s}{m_{\text{solvent}}}$$

where

n_s = number of moles of solute (mol)

m_{solvent} = mass of solvent (kg)

Moles of solute can be determined from the following equation:

$$n_s = \frac{m_s}{\text{FW}_s}$$

where

m_s = mass of solute (g)

FW_s = formula weight of solute (g/mol)

Replacing n_s with this expression yields

$$\Delta T_f = K_f \frac{\left(\frac{m_s}{\text{FW}_s}\right)}{m_{\text{solvent}}} = K_f \frac{m_s}{m_{\text{solvent}}\ \text{FW}_s}$$

Rearranging, the molecular weight of the solute is

$$\text{FW}_s = K_f \frac{m_s}{\Delta T_f\ m_{\text{solvent}}}$$

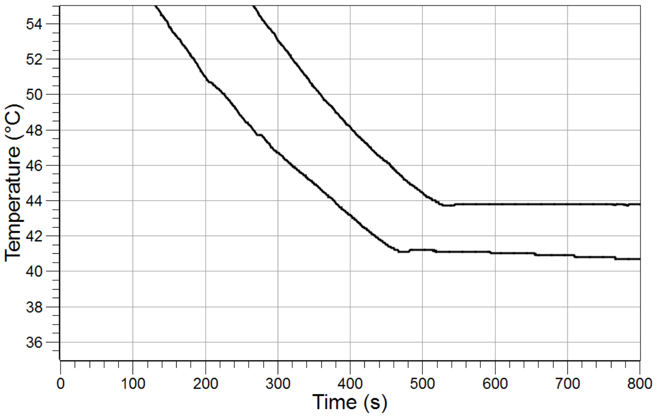
In this experiment, you will measure the freezing point of a pure solvent, lauric acid (dodecanoic acid). You will measure the freezing point of a mixture of lauric acid and an unknown solute. From the freezing point change, the formula weight of the solute can be calculated.

To obtain the cooling curve, the melted solvent or the melted solution must be cooled very slowly. During this time, the temperature of the system is monitored and the contents of the test tube are continuously mixed.

Example calculation to try

In an experiment, the formula weight of an unknown organic substance is determined. First, the freezing point is determined for 8.50 g (0.00850 kg) of solvent placed in a test tube. Then the contents of the test tube are melted and 0.9407 g of the unknown substance is dissolved in the liquid. As the graph shows, the freezing point of the solution is also measured.

K_f for the solvent is 3.90 K kg mol^{-1}.



The freezing point of the pure solvent is 43.8 °C. The freezing point of the solution is 41.2 °C. Therefore the freezing point depression is 2.60 °C, or 2.60 K.

Substituting these values into the relevant equation to find the formula weight:

$$\mathrm{FW_s} = \left(3.90\ \frac{\mathrm{K\,kg}}{\mathrm{mol}}\right)\frac{(0.9407\ \mathrm{g})}{(2.60\ \mathrm{K})(0.00850\ \mathrm{kg})} = 166\ \frac{\mathrm{g}}{\mathrm{mol}}$$

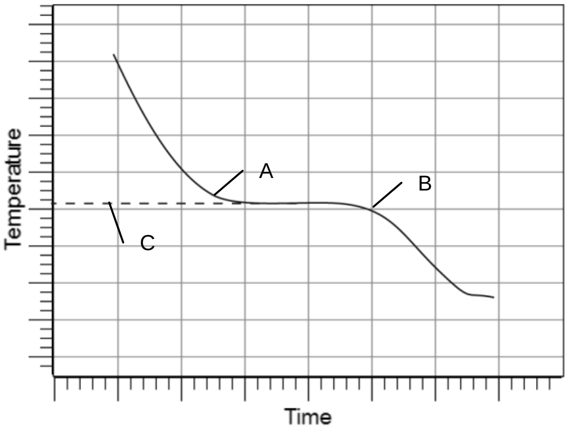
1. Why is the vapor pressure lower over solutions than over the pure solvent?

The solute species bind solvent molecules. Therefore there are fewer "free" solvent molecules available to escape into the gas phase.

2. How does a lower vapor pressure result in standard boiling point elevation?

Standard boiling point is defined as the temperature where the vapor pressure reaches the atmospheric pressure (1 atm). Since the vapor pressure over a solution at any temperature is less than the vapor pressure over a pure solvent, solutions must be heated to a higher temperature to reach that atmospheric pressure. So the boiling point of solutions is higher than the boiling point of solvents.

3. Knowing how the heating curve looks, sketch a graph of the cooling curve starting from the liquid phase and ending with the solid phase. Label the axes, the points where freezing starts, freezing ends, and label the freezing point.



A: freezing starts
B: freezing ends
C: freezing point

4. Why does the temperature remain constant at the freezing point?

The temperature remains constant because the heat is used for the heat of fusion rather than for heating the system.

5. Using the fact that the temperature remains constant at the freezing point for an interval of time, how would you measure the freezing point change of a solution relative to the freezing point of a pure solvent?

Because the temperature remains constant for a while at the freezing point, that temperature can be measured very accurately. We can measure the freezing point of the solvent and then the freezing point of the solution made from a known amount of solvent and solute. The difference in the freezing points can be calculated easily.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. For stirring purposes, loosely wrap copper wire around the stainless steel sensor so it can easily slide up and down on the sensor. Make one coil for each group.

2. Place an appropriate amount of the benzoic acid (C_6H_5COOH) in a container labeled “Unknown Solute” for students to use.

3. For cleaning, use an organic solvent, such as toluene or xylene. The coil is disposable.

Safety

Add these important safety precautions to your normal laboratory procedures:

♦ Handle the hot water bath carefully while mounting and removing the test tube.

♦ Upon completion, wash all equipment properly with the assigned solvent for cleaning.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system �$^{(1.2)}$

2. Connect the stainless steel temperature sensor to the data collection system. �$^{(2.1)}$

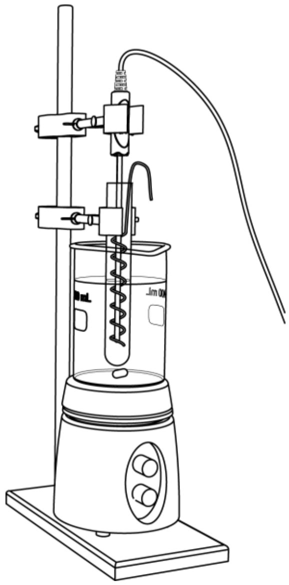
3. Display data on the graph to show Temperature versus Time. �$^{(7.1.1)}$

4. Measure about 8 g of lauric acid and record the mass of this solvent to the nearest 0.01 g in Table 1.

5. Place a 400-mL beaker 3/4 full of water on a hotplate.

6. Place a stirring bar into the beaker.

7. Use a clamp to connect the test tube to the ring stand so it is immersed in the water as far as possible. If necessary, add more water to the beaker.



8. Wrap the copper wire coil around the stainless steel sensor. Clamp it to the ring stand.

Collect Data

9. Carefully transfer the solvent into the test tube.

Important: Make sure there is no loss of the sample when doing a transfer.

10. Turn on the hotplate and the stirring bar.

11. When the crystals melt, place the stainless steel sensor with the copper coil wrapped around it into the melted crystals as shown in the illustration.

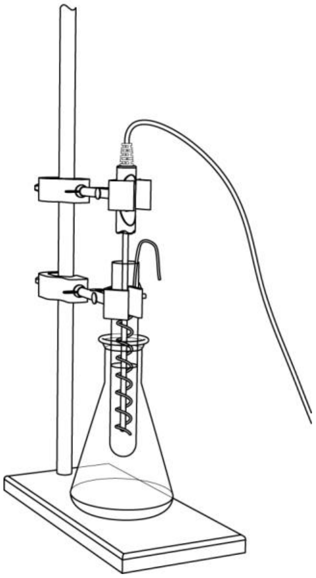
Note: Observe the white deposit on the surface of the sensor.

12. What is the white deposit and why does it appear on the sensor?

Because the sensor is cold, the lauric acid freezes temporarily on the surface of the sensor. It melts when the sensor warms up to the temperature of the liquid**.**

13. Once the test tube is clear (the crystals are melted), remove the test tube from the water bath, with the sensor and coil still in it, and clamp it in the empty Erlenmeyer flask.

Important: Do not stop stirring while collecting data. Even a few seconds without stirring can affect your graph.



14. Start data recording �(6.2) and start stirring the contents of the test tube by moving the copper coil up and down.

15. Adjust the scale of the graph. �(7.1.2)

16. Once the contents of the test tube are completely solidified, stop data recording. �(6.2)

17. Mount the test tube into the water bath again and allow the contents of the test tube to melt.

18. Measure about 0.5 g of the unknown sample to the nearest 0.01 g and record the mass in Table 1.

19. ☐ Carefully transfer the solute into the test tube.

Important: Make sure there is no loss of the sample when making the transfer.

20. What happens if you lose some of the sample during the transfer?

The measured freezing point depression is going to be less, but it will be attributed to the mass that was measured, resulting in a higher formula weight than should be obtained.

21. Once the test tube is clear (the crystals are melted), remove the test tube from the water bath, with the sensor and coil still in it, and clamp it in the empty Erlenmeyer flask.

Important: Do not stop stirring while collecting data. Even a few seconds without stirring can affect your graph.

22. Start the data recording �(6.2) and start stirring the contents of the test tube by moving the copper coil up and down.

23. Once the contents of the test tube are completely solidified, stop data recording. �(6.2)

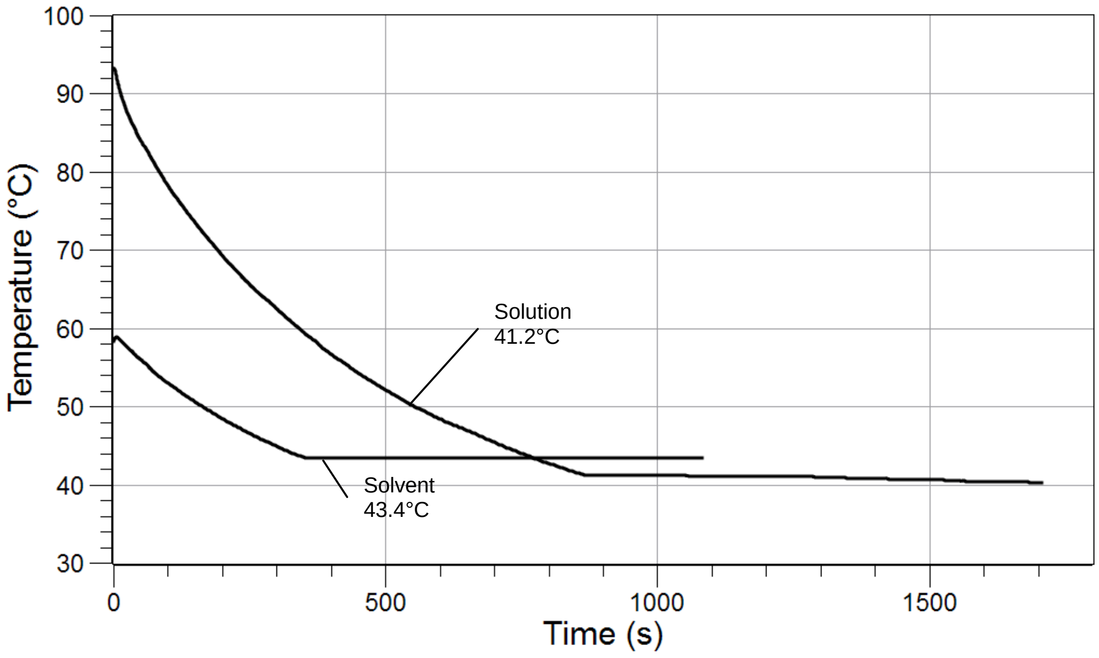
24. Display both data runs in the graph. �(7.1.3)

25. From the curves, locate the freezing points of the pure solvent and the solution. Record these in Table 1.

26. Melt the contents of the test tube again and dispose of the chemicals into the designated waste container.

27. Save your experiment �(11.1) and clean up according to your instructor's instructions.

28. Sketch the graph or print the graph �(11.2) and paste it below.



Data Analysis

Table 1: Freezing point depression measurements and calculations

Parameter	Value
Mass of the lauric acid (g)	7.96
Mass of the unknown sample (g)	0.500
Freezing point of lauric acid (°C)	43.5
Freezing point of lauric acid mixed with the unknown solute (°C)	41.3
Change in freezing point (°C)	2.20
Molar mass (experimental) of unknown solute (g/mol)	111.35
Molality of the solution (mol/kg)	0.566
Moles of the unknown sample (mol)	4.49×10^{-3}
Possible solute	Benzoic acid
Molar mass (from Table 2) of possible solute (g/mol)	122.4
Percentage of error (%)	9.31

1. Calculate the formula weight of the solute.

Note: K_f for lauric acid is 3.90 K kg mol^{-1}.

$$\text{FW}_s = K_f \frac{m_s}{\Delta T_f\, m_{\text{solvent}}}$$

$$\text{FW}_s = \left(3.90\ \frac{\text{K kg}}{\text{mol}}\right)\frac{(0.500\ \text{g})}{(2.20\ \text{K})(0.00796\ \text{kg})} = 1.11 \times 10^2\ \frac{\text{g}}{\text{mol}}$$

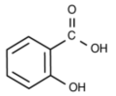
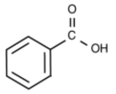
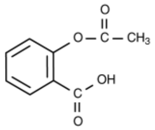
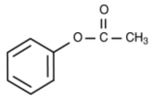
2. Calculate the number of moles of the solute used, based on the calculated formula weight and determine the molality of the solution.

$$\frac{0.50\ \text{g solute}}{1.11 \times 10^2\ \text{g/mol solute}} = 0.00450\ \text{mol solute}$$

$$\frac{0.00450\ \text{moles solute}}{0.00796\ \text{kg lauric acid}} = 0.566\ \text{mol/kg}$$

3. Based on the formula weights of the compounds in Table 2, what solute have you been using? Record it and its formula weight in Table 1.

Table 2: Formula weights of different compounds

Name	Formula	Formula Weight (g/mol)
Salicylic acid		138.1
Benzoic acid		122.4
Acetylsalicylic acid (aspirin)		180.2
Acetyl phenol		136.1

4. Determine the percent error between the experimental molar mass and the molar mass from Table 2.

$$\text{Percent Error} = \left|\frac{\text{Actual Value} - \text{Experimental Value}}{\text{Actual Value}}\right| \times 100$$

$$\text{Percent Error} = \frac{122.4 - 1.11 \times 10^2}{122.4} \times 100 = 9.31\%$$

5. What are the sources of error?

The loss of material during the mixing is one source of error. Also, reading the freezing point from the graph might be difficult because sometimes the portion of the cooling curve that is supposed to be horizontal is not, making it difficult to determine the freezing point exactly.

Analysis Questions

1. Why is lauric acid the solvent in this experiment, even though lauric acid is solid at room temperature and solvents are usually liquids at room temperature?

Lauric acid was present in greater quantity than the unknown sample. It is considered by definition as the solvent.

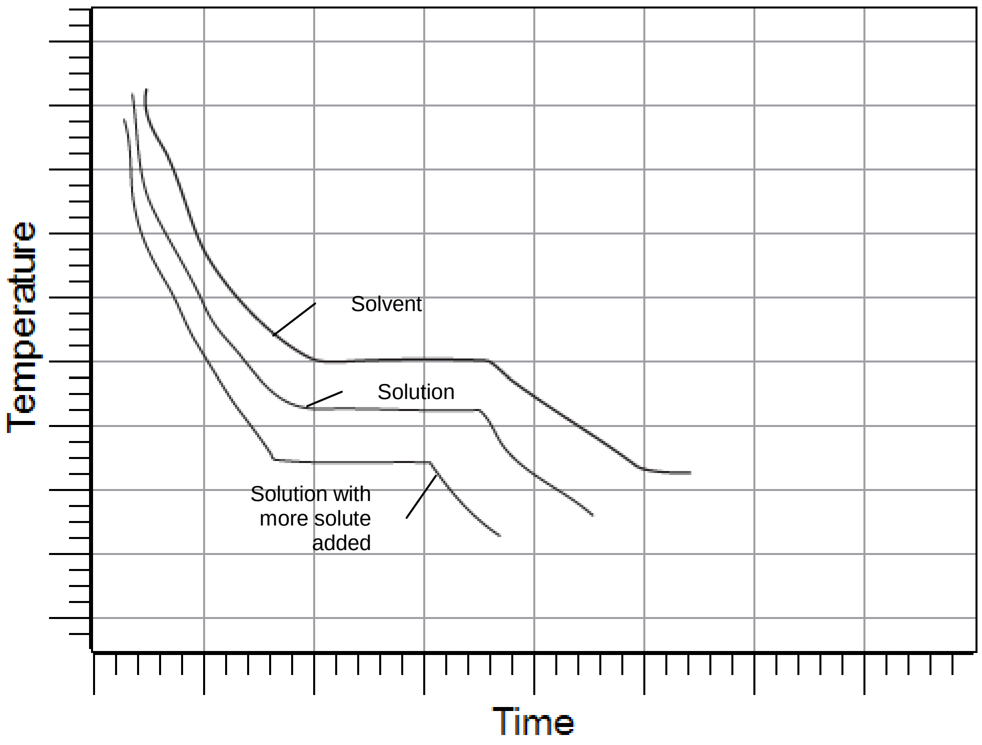
2. How would the error show itself if the test tube was dirty?

The contamination would lower the freezing point because of the increased number of non-solvent particles. This would result in a lower calculated formula weight.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Suppose you collected data for an additional cooling curve, adding additional unknown sample to the solution; sketch a graph with the three cooling curves and label each curve.



2. Why would you collect data for an additional cooling curve with additional unknown sample?

It would give an additional measured value for the formula weight. Then you could average the values to reduce experimental error.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Which of the following statements is *not* correct regarding colligative properties?

- **A.** Vapor pressure over solutions is lower than the vapor pressure of pure solvent.
- **B.** The freezing point of solutions is lower than that of a pure solvent.
- **C.** The boiling point is elevated by solutes.
- **D.** **All the statements are correct.**

2. Consider two unknowns, A and B. We measure the same mass for each to determine the formula weight for each. We measure the same mass of the solvent to mix with the two unknowns. The freezing point depression for unknown A is significantly greater than for unknown B. What does this say about the formula weights of unknowns A and B?

- **A. Assuming the same mass of unknown A and B (m_s) and the same mass of solvent ($m_{solvent}$) are used, a greater freezing point depression with A would mean that A has a smaller formula weight than B.**
- **B.** Assuming the same mass of unknown A and B (m_s) and the same mass of solvent ($m_{solvent}$) are used, a greater freezing point depression with A would mean that A has a greater formula weight than B.
- **C.** Assuming the same mass of unknown A and B (m_s) and the same mass of solvent ($m_{solvent}$) are used, a greater freezing point depression with A would mean that B has a smaller formula weight than A.
- **D.** Not enough information

Extended Inquiry Suggestions

The freezing points of electrolytes are larger than expected because they dissociate, producing more species in solution.

Use this information to discuss colligative properties with students, that they depend on the number of species only and not on the nature of the solute, more species yields larger effect. Quantitatively this effect is taken into account with the coefficient *i,* the so called van't Hoff coefficient:

$$\Delta T_f = iK_f m$$

For substances that do not dissociate, $i = 1$, resulting in the original equation for the freezing point depression. For electrolytes, the limiting value of i is the number of species resulting from the dissociation. For example, $MgCl_2$ yields three ions. Therefore, the limiting value of i is 3.

This "limiting" nature comes from the fact that at higher concentration there is no complete dissociation. Therefore the ion concentration is somewhat less than the predicted value.

Discuss, as well, how electrolytes have a much larger effect than non-electrolytes.

In a separate discussion, ask why the Department of Public Works uses $CaCl_2$ and $MgCl_2$ to de-ice roads instead of NaCl.

16. Colorimetric Analysis

Objectives

Students learn how the factors of concentration and path length affect the absorbance of a colored solution.

Procedural Overview

Students gain experience conducting the following procedures:

- Diluting a copper(II) sulfate solution of known concentration in order to create five calibration standards
- Creating a calibration curve of the absorbance of 660 nanometers of light versus the concentration of the five $CuSO_4$ standards
- Determining the concentration of a sixth copper(II) sulfate solution using the calibration curve and the equation of the slope of the best-fit line of the calibration curve

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Colorimeter
- Cuvette
- Sensor extension cable
- Beakers (2), 100-mL
- Test tubes (6), large
- Test tube rack
- Graduated cylinder, 50-mL
- Pipet with pump or bulb, 10-mL
- Glass stirring rod
- 0.40 M copper(II) sulfate ($CuSO_4$), 30 mL[1]
- Distilled water, 30 mL
- Marking pen
- Wash bottle with distilled water

[1] For the preparation of 0.40 M copper (II) sulfate solution, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

♦ Moles

♦ Using linear graphs and equations

♦ Molarity

♦ Ionic nomenclature

Related Labs in This Guide

Labs conceptually related to this one include:

♦ Determine the Equilibrium Constant for a Chemical Reaction

♦ Absorption Spectra

♦ Order of Reaction

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

♦ Starting a new experiment on the data collection system �(1.2)

♦ Connecting sensors to the data collection system �(2.1)

♦ Calibrating the colorimeter �(3.2)

♦ Using the colorimeter to collect data with red light �(4.1)

♦ Putting the data collection system into manual sampling mode with manually entered data �(5.2.1)

♦ Starting a manually sampled new data set �(6.3.1)

♦ Recording a manually sampled data point �(6.3.2)

♦ Stopping a manually sampled data set �(6.3.3)

♦ Displaying data in a graph �(7.1.1)

♦ Adjusting the scale of the graph �(7.1.2)

- Finding the slope and intercept of a best-fit line �$^{(9.6)}$
- Creating calculated data �$^{(10.3)}$
- Saving your experiment �$^{(11.1)}$
- Printing the graph �$^{(11.2)}$

Background

To characterize the ability of solutions to absorb light, we use two physical quantities: transmittance T and absorbance A. Transmittance is defined as

$$T \equiv \frac{I}{I_0}$$

where

I = the number of transmitted photons (the intensity) per unit time with the absorbing species present

I_0 = the number of transmitted photons per unit time with the absorbing species absent

Transmittance multiplied by 100 gives the percentage of the photons that can pass through a solution. It is rather difficult to work with the number of photons, so “absorbance” is used instead. Absorbance is defined as follows:

$$A \equiv -\log T = -\log \frac{I}{I_0}$$

where

I = the number of transmitted photons (the intensity) per unit time with the absorbing species present

I_0 = the number of transmitted photons per unit time with the absorbing species absent

It is important to keep in mind that absorption depends on wavelength, and therefore is color specific. That is, the ability of a substance to absorb light is different for photons with different wavelengths.

The wavelength dependence of absorbance is expressed by Beer's Law:

$$A = \varepsilon\, l\, c \qquad (1)$$

where

A = absorbance
ε = absorptivity coefficient ($M^{-1}cm^{-1}$)
l = path length that light travels through the solution (cm)
c = molar concentration of the absorbing species (M).

Note: Equation 1 can also be written as "A = $a\ b\ c$" where a and b correspond to ε and l, respectively.

In this experiment, you will prepare five solutions of $CuSO_4$ of different concentrations. Since $CuSO_4$ is blue, it absorbs light in the visible wavelength region. You will measure the absorbance of the five solutions and construct a calibration curve. Based on the calibration curve and the absorbance obtained of a $CuSO_4$ solution with unknown concentration, you will determine the concentration of that solution.

Pre-Lab Experiment

Setting the stage for the experiment

When light interacts with light-absorbing particles, some of the light is removed. Consequently, objects with many light-absorbing particles appear darker than objects with fewer light-absorbing particles. The ability to absorb color, as well as what color is to be absorbed, depends on the type of particle present.

One can vary the number of particles with which light interacts in two ways. If you compare two solutions of the same colored substance with different concentrations, you see that the one with the higher concentration appears darker because it has more absorbing particles and it absorbs more of the incident light. Also, if you pour the same solution into a test tube and a 100-mL beaker, the solution in the beaker appears darker. Even though the concentration in the two solutions is the same, the light has to travel a longer path in the beaker. Therefore, photons have a higher probability of being absorbed so less light will leave the beaker and the solution appears darker.

Next, if you pour a little bit of the 1 M copper(II) sulfate solution into a 1-L beaker nearly full with water, why is the original beaker so much darker? It is darker because the "light catching" particles in the more diluted solution are much farther apart. From this we see that concentration is another variable to consider when looking at absorbed light.

To measure the amount of light absorbed, we use a colorimeter. Like all electronic measuring devices, the colorimeter produces a voltage based on the amount of light that hits it. The voltage is converted to an absorbance level in optical density units (o.d.).

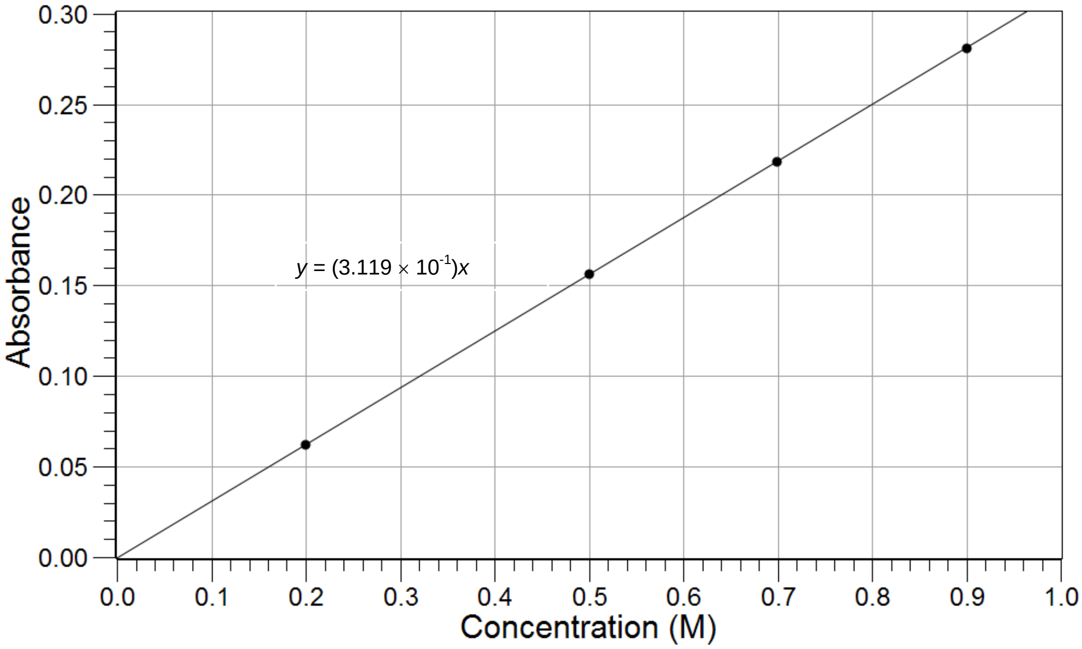
Example calculation to try

In an experiment, four calibrating solutions are used to determine the concentration of a $CuSO_4$ solution with unknown concentration. Given the following data, create a calibration graph, find the equation, and use the equation to solve for the concentration of the unknown solution.

Table 1: Concentration and absorbance calibration data

Sample	Concentration (M)	Absorbance
1	0.20	0.062
2	0.50	0.156
3	0.70	0.218
4	0.90	0.281

The graph of these calibrating solutions:



The absorbance A of the solution of unknown concentration is 0.200.

The concentration c of the unknown can be found on the graph, which looks to be between 0.63 M and 0.64 M or calculated from the obtained equation:

The equation of the line is

$$y = 0.3119x$$

Solving for the concentration:

$$A = \left(0.3119\ \mathrm{M}^{-1}\right)\mathrm{c}$$

$$0.200 = \left(0.3119\ \mathrm{M}^{-1}\right)\mathrm{c}$$

$$\mathrm{c} = \frac{0.200}{0.3119\ \mathrm{M}^{-1}} = 0.641\ \mathrm{M}$$

It is worth mentioning that the equation provides a more accurate estimate of the unknown concentration, since the graph-based estimate can be subjective.

1. The $CuSO_4$ solution is blue. Which photons are absorbed and which ones are transmitted through the solution?

The blue photons are transmitted (they reach our eyes, which is why we can see them) and the red and green photons are absorbed.

2. Explain why the transmitted light intensity depends on the path length of the solution.

As light is transmitted through the solution, photons are absorbed. The longer the path is, the more light-absorbing particles the photons encounter, and the greater the probability that a particular photon is absorbed. In general, fewer photons exit a solution in a wider container than those exiting a solution in a narrow container, as indicated by their respective light intensities.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.40 M $CuSO_4$:*** Dissolve 49.93 g of $CuSO_4{\cdot}5H_2O$ in some water in a 500-mL volumetric flask. Fill the flask to the mark and mix the solution well.
2. An unknown can be produced by taking a sample of the stock solution and diluting it.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

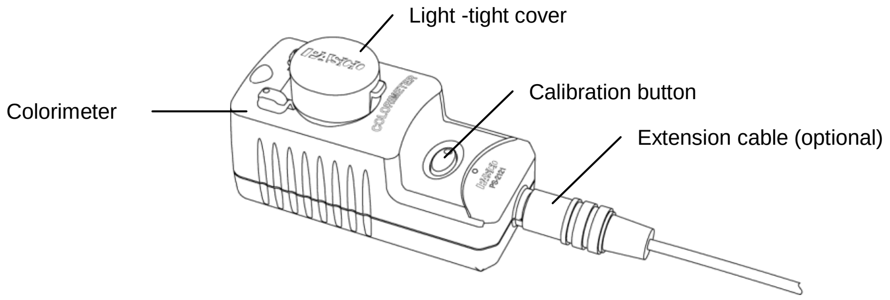
1. Start a new experiment on the data collection system. �(1.2)

2. Connect the colorimeter to the data collection system using the extension cable. �(2.1)

3. Configure the data collection system to manually collect Absorbance of orange (610 nm) light and the Concentration in a table. Define the concentration as a manually entered data set with units of molarity. �(5.2.1)

4. Throughout this experiment, collect data using orange light (610 nm) in the colorimeter. �(4.1)

5. Calibrate the colorimeter with the blank solution (use distilled water for the blank). �(3.2)



Collect Data

6. Water absorbs a small amount of light. Explain why not calibrating with distilled water causes a systematic error in your data.

Since water absorbs light, each absorbance value for the $CuSO_4$ solutions would be a little greater, but they would all be greater by about the same amount because of the additional absorbance due to the water. The calibration graph would be shifted upwards.

7. Measure 30 mL of 0.40 M copper(II) sulfate stock solution into a 100-mL beaker.

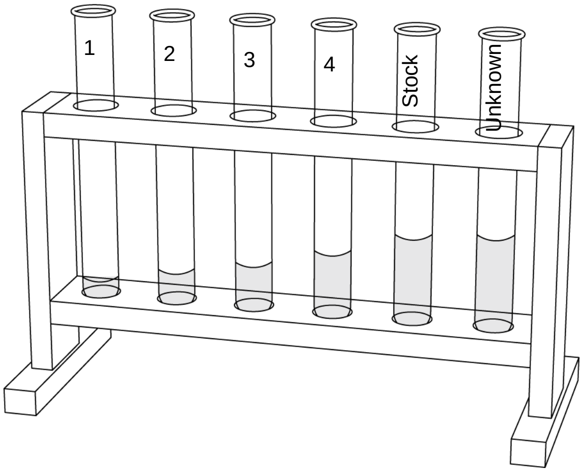
8. Measure 30 mL of distilled water into another 100-mL beaker.

9. Label four clean, dry test tubes “1” through “4” and place them into a test tube rack. Label a fifth test tube "Stock" and the sixth test tube "Unknown".

10. Why do the test tubes need to be dry? What error would be caused by wet test tubes?

Wet test tubes would change the molarity of the standards, making our calibration graph incorrect.

11. Pipet 2.0, 4.0, 6.0, and 8.0 mL of the 0.40 M copper(II) sulfate solution into test tubes 1 through 4, respectively.



12. Wash the pipet and use it to deliver 8.0, 6.0, 4.0, and 2.0 mL of distilled water into test tubes 1 through 4 so that each test tube has 10.0 mL of solution.

13. Thoroughly mix each solution with a stirring rod.

Note: Clean and dry the stirring rod before stirring a different solution.

14. Pour the remaining 0.40 M copper(II) sulfate solution into the "Stock" test tube to use as the fifth data point for your calibration graph.

15. Put ~10 mL of a solution of unknown concentration, obtained from your instructor, in your test tube labeled "Unknown".

Table 2: Volumes and concentrations for the calibration solutions

Trial #	0.40 M $CuSO_4$ (mL)	H_2O (mL)	Concentration (M)
1	2.0	8.0	0.08
2	4.0	6.0	0.16
3	6.0	4.0	0.24
4	8.0	2.0	0.32
5	~10	0	0.40
6	~10	0	Unknown

Collect Data

16. Start a new, manually sampled data set. �(6.3.1)

17. Measure the absorbance of the five known solutions following the steps below.

a. Rinse the cuvette twice with a small portion of the first solution and then fill the cuvette two-thirds full. Wipe the cuvette clean and dry and place it into the colorimeter.

b. Why do you have to rinse the cell with some of the solution?

If there is any residual water in the cuvette, it will dilute the concentration of the solution and falsify the data.

c. After the reading stabilizes, record a data point. �(6.3.2)

d. Dispose of the solution appropriately and rinse the cell thoroughly with water.

e. Why do you think it is important to rinse the cell thoroughly between measurements?

You need to rinse the cell to avoid contamination of the solutions.

f. When you have recorded all of your data, stop the data set. �(6.3.3)

Note: The data for test tube 6 is not yet recorded because it has an unknown molarity and it will not be part of the standardization curve.

18. Save your experiment. �(11.1)

Data Analysis

1. Record your data in the table below.

Table 3: Concentration and absorbance data

Test Tube	Concentration (M)	Absorbance
1	0.08	0.402
2	0.16	0.620
3	0.24	1.099
4	0.32	1.470
5	0.40	1.680
6	Unknown	0.956

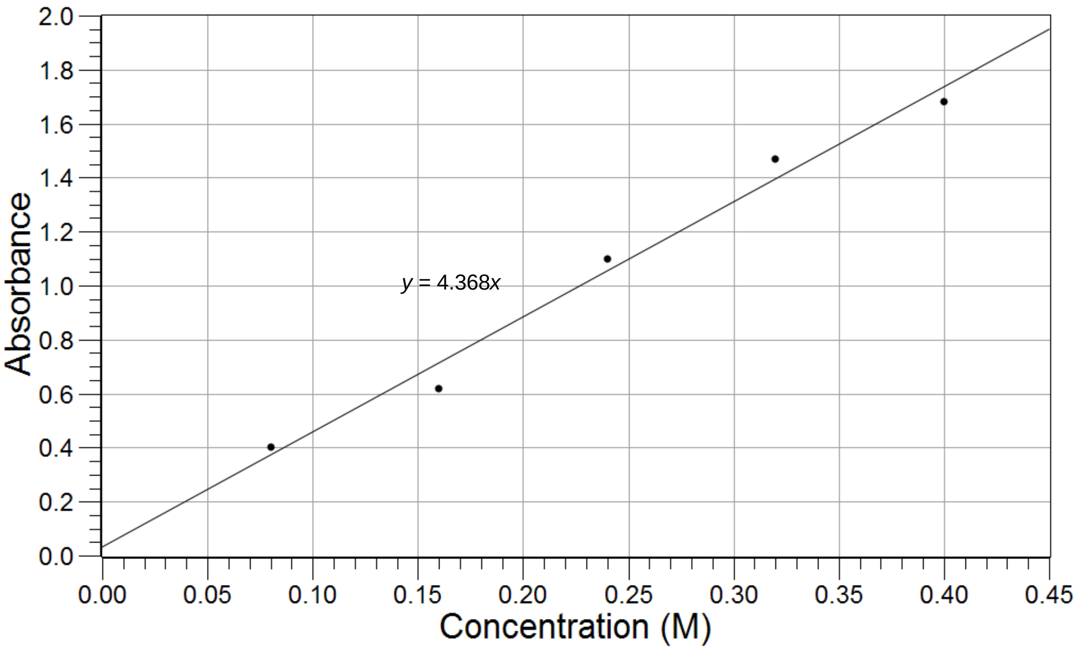
2. Display Concentration on the x-axis and Absorbance on the y-axis. �(7.1.1)

3. Adjust the scale of the graph to show all data. �(7.1.2)

4. Find the slope of the best-fit line. �(9.6)

5. Print the graph. �(11.2)

6. Sketch or attach your graph of Concentration versus Absorbance.



7. Using your understanding of dependent and independent variables, explain why concentration should be on the horizontal (x) axis for this graph.

The concentration is varied and the absorbance was a response to the concentration. That makes absorbance the dependent variable and concentration the independent variable, which should be on the x-axis.

8. Monitor Orange (610 nm) Absorbance data in a digits display. �(6.1)

9. Measure the absorbance of the sixth solution. Record the Orange (610 nm) Absorbance in Table 3 and clean up according to your instructor's instructions.

10. Use the equation for the line to calculate the concentration of the unknown. Show all of your work.

The equation of the line is:

$$y = 4.368x$$

$$x = \frac{y}{4.368}$$

Solving for the concentration:

$$c = \frac{A}{\varepsilon l} = \frac{0.956}{4.368\ \mathrm{M}^{-1}} = 0.219\ \mathrm{M}$$

11. Use the calibration curve to estimate the concentration of the unknown.

The concentration that corresponds to *A* = 0.956 is about 0.213 M.

Analysis Questions

1. Does using the graph or using the equation give a more accurate value of the concentration of the unknown?

The equation relies on the best-fit line of all five points so is more reliable than estimating the value from the graph.

2. Beer's law states that absorbance is proportional to concentration. How does your data support this statement?

For two variables to be proportional, a graph must be linear and may go through the origin. The graph from the data was linear and did go through the origin.

3. Why would one or more dirty cuvettes cause error in the data?

The absorbance readings would be incorrect for individual samples because some light would be absorbed by the dirt.

Synthesis Questions

Use available resources to help you answer the following questions.

1. In a copper(II) sulfate solution, copper(II) ions cause the blue color. Sulfate ions have no color. Sodium sulfate solution has no color because neither ion has color. Could you use Beer's law to find the concentration of a sodium sulfate solution?

No. The absorbance would not change with the concentration of sodium sulfate.

2. Hypothetically, how would you modify the experiment if the measured absorbance of the unknown was too low to measure?

Increasing the path length would increase the absorbance. Therefore, using a cell with a longer path length would work.

3. How would you modify your experiment if the measured absorbance of the unknown was too high to measure?

Making a proportional dilution of the solution would decrease the absorbance.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Which of the following variables affects the absorbance of light in a solution?

A. The distance the light must travel through the solution (path length)
B. The amount of solute in each volume (concentration)
C. The wavelength of the light that is interacting with the solution
D. **All of the above**

2. A sample of 0.10 M copper(II) chloride is placed into a cuvette with a 1.00-cm path length. The solution has a measured absorbance of 2.000. What would you expect the absorbance of a 0.05 M copper(II) chloride solution to be?

- **A.** 2.000
- **B.** **1.000**
- **C.** 4.000
- **D.** Not enough information.

Extended Inquiry Suggestions

Many water quality studies are done using colorimetric techniques. PASCO offers water quality test kits for use with the water quality colorimeter. The kits allow rapid testing of water for specific ions as the calibration curves are stored in the device. Have students analyze a nearby stream, taking advantage of the learning from this lab.

17. Separation by Liquid Chromatography

Objectives

Students use liquid chromatography to separate the ingredients of a mixture.

Procedural Overview

Students will gain experience conducting the following procedures:

- Separation processes
- Practicing basic principles of liquid chromatography
- Calculating the effectiveness of the column and its ability to separate the compounds of the mixture

Time Requirement

♦ Preparation time	20 minutes
♦ Pre-lab discussion and experiment	20 minutes
♦ Lab experiment	120 minutes

Materials and Equipment

For each student or group:

- C18 Sep-Pak® cartridge
- Syringe, 1-mL
- Syringe, 10-mL, or dropper bottle or wash bottle
- Graduated cylinder, 10-mL
- 18% Isopropanol, 100 mL[1]
- Unsweetened Kool-Aid® drink, 10 mL[2]
- Distilled water

[1-2] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Interaction between molecules
- Polarity of molecules
- Basic separation principles

Related Labs in This Guide

Labs conceptually related to this one include:

- Molecular Interaction in Ethanol and Acetone

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Note: As this lab experiment does not use a data collection system, no Tech Tips (indicated by the symbol "�" and a superscripted number following a step) are needed.

Background

Chromatography is a separation method that exploits the differences in the behavior of substances between a mobile phase (solvent or eluent) and a stationary phase (substrate), to separate the components of a mixture. The stationary phase may interact with the substances in the mixture based on charge, relative solubility, or adsorption. The mobile phase carries each substance along at a rate that depends on the attraction of the substance to the stationary phase. The components of the mixture will separate if their interactions with the substrate and solvent are significantly different.

Pre-Lab Experiment

Setting the stage for the experiment

In this experiment, you will separate the dyes: FD&C Blue and FD&C Red, from the other ingredients in grape-flavored Kool-Aid®. You will use a C18 Sep-Pack® chromatography column. The column contains a silica matrix with a non-polar substrate consisting of a C18 hydrocarbon bonded to the silica. The C18-coated surface can bind non-polar molecules, particularly organic molecules with a carbon chain with London dispersion forces. The more polar a molecule is, the less it is bound to the C18-coated matrix.

If a mixture of molecules with different polarity is put through the column, the ones with greatest polarity will bind the least to the C18-coated surface. Therefore, they will move to the end of the column first. The molecules with the least polarity will be trapped at the beginning of the column, on the C18-coated surface. Therefore, they will be "retained" and show up last at the end of the column.

The separation of the molecules can be improved by using a polar solvent (or solvent mixture, the eluent) to promote the removal (elution) of the more polar molecules first and less polar molecules last. In a more sophisticated setting, the polarity of the eluting solvent can be changed continuously during the course of the experiment.

Example calculation to try

A sample of unsweetened, grape-flavored Kool-Aid was analyzed for two major coloring ingredients. The Sep-Pak column used for the analysis was flushed with 10 mL of 26% isopropanol solution and then 10 ml of water. A 1.00 mL sample of Kool-Aid was loaded into the column and eluted with 26% isopropanol from a 10-mL syringe at the rate of 10 mL/min into a 10-mL graduated cylinder. The red coloring agent started to elute after 0.8 mL of the mobile phase was completely eluted after 1.7 mL of eluent was collected in the graduated cylinder.

At this point the blue coloring agent started to come out. The blue component was completely eluted after a total of 4.1 mL of eluent was collected. The data obtained was collected in the table below. The bandwidth, W_{red}, can be calculated for the red compound as follows:

$$W_{\mathrm{red}} = V_{\mathrm{R(end,red)}} - V_{\mathrm{R(start,red)}} = 1.7\text{ mL} - 0.8\text{ mL} = 0.9\text{ mL}$$

where

$V_{\mathrm{R(end,\ red)}}$ = volume of eluent collected by the time all red dye left the column

$V_{\mathrm{R(start,\ red)}}$ = volume of eluent collected by the time the red dye starts to show up in the eluent

Note: The “R” subscript means “retention,” common terminology in chromatography.

For the blue compound the same calculation applies:

$$W_{\mathrm{blue}} = V_{\mathrm{R(end,blue)}} - V_{\mathrm{R(start,blue)}} = 4.1\text{ mL} - 1.7\text{ mL} = 2.4\text{ mL}$$

The center of both bands can be obtained:

$$V_{\mathrm{R(avg,red)}} = V_{\mathrm{R(start,red)}} + 0.5\,W_{\mathrm{red}} = 0.8\text{ mL} + (0.5)(0.9\text{ mL}) = 1.2\text{ mL}$$

$$V_{\mathrm{R(avg,blue)}} = V_{\mathrm{R(start,blue)}} + 0.5\,W_{\mathrm{blue}} = 1.7\text{ mL} + (0.5)(2.4\text{ mL}) = 2.9\text{ mL}$$

where

$V_{\mathrm{R(avg,red)}}$ = volume of eluent collected by the time half of the red dye left the column

$V_{\mathrm{R(avg,blue)}}$ = volume of eluent collected by the time half of the blue dye left the column

The length L of the column was 1.25 cm and the radius r of the column was 0.50 cm. The mobile phase volume, V_{M}, was

$$V_{\mathrm{M}} = 0.5\pi r^2 L = (0.5)(3.14)(0.50\text{ cm})^2(1.25\text{ cm}) = 0.49\text{ cm}^3 = 0.49\text{ mL}$$

The retention factors, k_{blue}' and k_{red}', which are the measure of how much the stationary phase can "retain" the two components, were:

$$k_{\text{red}}' = \frac{V_{\text{R(avg,red)}} - V_{\text{M}}}{V_{\text{M}}} = \frac{(1.2\text{ mL}) - (0.49\text{ mL})}{(0.49\text{ mL})} = 1.4$$

$$k_{\text{blue}}' = \frac{V_{\text{R(avg,blue)}} - V_{\text{M}}}{V_{\text{M}}} = \frac{(2.9\text{ mL}) - (0.49\text{ mL})}{(0.49\text{ mL})} = 4.9$$

The separation, α, can be obtained:

$$\alpha = \frac{k_{\text{blue}}'}{k_{\text{red}}'} = \frac{4.9}{1.4} = 3.5$$

The theoretical plate number, N, which characterizes the number of interactions between the stationary phase and mobile phase (calculated from the last eluted component) is:

$$N = 16\left(\frac{V_{\text{R(end,blue)}}}{W_{\text{blue}}}\right)^2 = 16\left(\frac{4.1\text{ mL}}{2.4\text{ mL}}\right)^2 = 46.7$$

The most important factor, the resolution (R) for the two ingredients is:

$$R = \frac{2(V_{\text{R(avg,blue)}} - V_{\text{R(avg,red)}})}{W_{\text{red}} + W_{\text{blue}}} = \frac{(2)(2.9\text{ mL} - 1.2\text{ mL})}{2.4\text{ mL} + 0.9\text{ mL}} = 1.0$$

The numerator is the volume between the center of the bands made by the two dyes in the column, which is related to the selectivity factor α. The denominator is the sum of the bandwidths. R is proportional to the efficiency of the column. As the value of R increases above 1 there is greater separation of the dyes.

Table 1: Effectiveness of the separation of the red and blue dyes in Kool-Aid

Parameters	Red Dye	Blue Dye
$V_{\text{R (start)}}$ (mL)	0.8	1.7
$V_{\text{R (end)}}$ (mL)	1.7	4.1
W (mL)	0.9	2.4
$V_{\text{R(avg)}}$ (mL)	1.25	2.9
L (cm)	1.25	1.25
r (cm)	0.50	0.50
V_{M} (mL)	0.49	0.49
k'	1.4	4.9
α	3.5	
N	46.7	
R	1.0	

1. The greater the resolution *R*, the better the column separates the two different components. What can you tell about the column for this particular separation process based on the obtained resolution factor?

The conditions are not ideal as $R = 1.0$, indicating a small degree of separation.

2. Based on the process described above, can you propose a modification that might improve the resolution?

Changing the polarity of the eluent or increasing the column length (that is, using two columns connected) might improve the separation process.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***18% Isopropanol:*** Combine 260 mL of 70% isopropanol with some water in a 1-L volumetric flask and fill it to the mark.
2. ***Unsweetened Grape Kool-Aid:*** Prepare as instructed on the package without the sugar.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: This experiment does not use a data collection system, so there are no Tech Tips (indicated by the symbol "�" and a superscripted number following a step).

Set Up

1. Cut off the exit tube of the C18 Sep-Pack chromatography cartridge (see Figure 1).

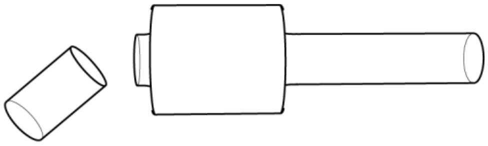


Figure 1: Cutting the Sep Pak to size

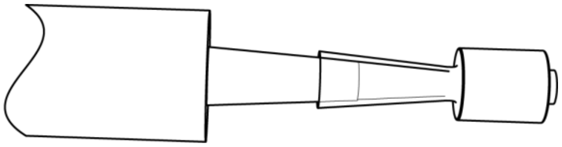


Figure 2: Mounting the Sep Pak on a syringe

Collect Data

Perform the following steps three times and record your data for each trial in Table 2.

2. Use a 10-mL syringe (see Figure 2), a dropper bottle, or a wash bottle as a solvent pump to flush the C18 Sep-Pack cartridge with 10 mL of undiluted 18% isopropanol at a rate of 5 to 10 mL per minute.

3. Collect the eluate in a 10-mL graduated cylinder to monitor the flow rate of the isopropanol.

4. Using the 10-mL syringe, flush the Sep-Pack cartridge with 10 mL of distilled water.

5. Draw up 1 mL of the grape Kool-Aid sample with the 1-mL syringe.

6. Slowly inject the Kool-Aid sample into the Sep-Pack cartridge.

7. Collect and discard the effluent that washes out of the column as you inject the sample.

8. Fill the solvent pump (10-mL syringe, dropper, or wash bottle) with 18% isopropanol solution.

9. Which is the most and which is the least polar solvent of the following: pure isopropanol, 18% isopropanol solution, and water?

Water is the most polar and pure isopropanol is the least polar.

10. Pump the solvent through the Sep-Pack cartridge at a steady rate of 5 to 10 mL per minute.

11. Collect the eluent in the 10-mL graduated cylinder.

12. What do you think will happen if you pump the eluent at too high a rate?

The separation of the two components will be reduced.

13. Record (in Table 2) the volume of liquid in the graduated cylinder when the red or blue dye is first observed in the eluent from the Sep-Pak column ($V_{R(start)}$) and when that color is no longer observed ($V_{R(end)}$).

Note: If the red and blue bands are not completely separated, the overlapping region will be purple. Use the center of the purple band as the end of the first band and the beginning of the second band.

14. Clean up according to your instructor's instructions.

Data Analysis

1. For each trial, calculate V_M, the mobile phase volume. This factor represents about half of the empty column volume. The unit for V_M is cm^3 (mL) if the values of r and L are used in the calculations in centimeters. Record these values in Table 2.

$$V_M = 0.5\pi r^2 L = 0.5(3.14)(0.5\text{ cm})^2(1.25\text{ cm}) = 0.49\text{ cm}^3 = 0.49\text{ mL}$$

2. For each trial, calculate the bandwidth for the two components. Record these values in Table 2.

Performing the calculations for Trial #1:

$$W_{red} = V_{R(end,red)} - V_{R(start,red)} = 2.00\text{ mL} - 1.50\text{ mL} = 0.50\text{ mL}$$

$$W_{blue} = V_{R(end,blue)} - V_{R(start,blue)} = 3.40\text{ mL} - 2.10\text{ mL} = 1.30\text{ mL}$$

3. For each trial, calculate the center of the bands for the two components. Record these values in Table 2.

Performing the calculations for Trial #1:

$$V_{R(avg,red)} = V_{R(start,red)} + 0.5\,W_{red} = 1.50\text{ mL} + (0.5)(0.50\text{ mL}) = 1.75\text{ mL}$$

$$V_{R(avg,blue)} = V_{R(start,blue)} + 0.5\,W_{blue} = 2.1\text{ mL} + (0.5)(1.30\text{ mL}) = 2.75\text{ mL}$$

4. For each trial, calculate the retention factor *k'* for both components, which is the measure of how much the stationary phase can "retain" the two components. Record these values in Table 2. (Optimum values of *k'* are commonly between 1 and 10, where 10 indicates the greatest retention.)

Performing the calculation for Trial #1:

$$k_{red}' = \frac{V_{R(avg,red)} - V_M}{V_M} = \frac{(1.75\text{ mL}) - (0.49\text{ mL})}{(0.49\text{ mL})} = 2.57$$

$$k_{blue}' = \frac{V_{R(avg,blue)} - V_M}{V_M} = \frac{(2.75\text{ mL}) - (0.49\text{ mL})}{(0.49\text{ mL})} = 4.61$$

5. For each trial, calculate the selectivity, or separation factor, α. Record these values in Table 2. (The value of α is always larger than 1, and the larger it is, the greater the separation of the eluates.)

Performing the calculation for Trial #1:

$$\alpha = \frac{4.61}{2.57} = 1.79$$

6. For each trial, calculate the number of theoretical plates, *N,* in the column. Think of *N* as the number of times a dye molecule is exchanged between the stationary phase and the mobile phase. The value of *N* is generally based on the dye which is eluted last. A large value of *N* means that the column is more efficient. (The range of *N* is normally between 20 and 200).

Record these values in Table 2.

Performing the calculations for Trial #1:

$$N = 16\left(\frac{V_{\mathrm{R(end,blue)}}}{W_{\mathrm{blue}}}\right)^2 = 16\left(\frac{3.40}{1.30}\right)^2 = 109$$

7. For each trial, calculate the resolution *R,* the major objective of a chromatographic separation. *R* measures how well the two dyes were separated by the Sep-Pack cartridge. Record these values in Table 2.

Performing the calculations for Trial #1:

$$R = \frac{2(V_{\mathrm{R(avg,blue)}} - V_{\mathrm{R(avg,red)}})}{W_{\mathrm{red}} + W_{\mathrm{blue}}} = \frac{2(2.75\ \mathrm{mL} - 1.75\ \mathrm{mL})}{0.50\ \mathrm{mL} + 1.30\ \mathrm{mL}} = 1.11$$

8. Calculate the average values for α, N, and R. Record these values in Table 2.

α: (1.79 + 1.76 + 1.75)/3 = 1.64

N: (109.4 + 90.9 + 111.2)/3 = 103.8

R: (1.11 + 1.00 + 1.00)/3 = 1.04

Table 2: Effectiveness of the separation of the red and blue dyes in Kool-Aid

Parameters	Trial #1		Trial #2		Trial #3		Average
	Red Dye	Blue Dye	Red Dye	Blue Dye	Red Dye	Blue Dye	▨
$V_{R\text{ (start)}}$ (mL)	1.50	2.10	1.40	1.80	1.30	1.80	
$V_{R\text{ (end)}}$ (mL)	2.00	3.40	1.80	3.10	1.80	2.90	
W (mL)	0.50	1.30	0.40	1.30	0.50	1.10	
$V_{R\text{(avg)}}$ (mL)	1.75	2.75	1.60	2.45	1.55	2.35	
L (cm)	1.25						
r (cm)	0.50						
V_M (mL)	0.49						
k'	2.57	4.61	2.27	4.00	2.16	3.80	
α	1.79		1.76		1.75		1.76
N	109		91		111		103.8
R	1.11		1.00		1.00		1.04

Analysis Questions

1. What does your value of R indicate?

The resolution is close to 1.0 which means the two dyes will come immediately after each other; a larger number would indicate better separation.

2. Propose an approach to improve the resolution.

Increasing the polarity of the solvents or changing the stationary phase improves resolution.

3. What conclusion can you draw about the polarity of the dye molecules relative to each other, based on the fact that the red dye came off first and the blue second with the 18% isopropanol solution?

The red dye is more polar than the blue as the blue was "retained" more on the non-polar C18 surface.

4. Would the solution process change if you used water (a more polar solvent than the 18% isopropanol solution) and if so, how?

Yes, it would change. The more polar molecules of the red dye probably would come off sooner and the less polar molecules of the blue dye would be retained longer on the surface of the stationary phase.

5. Would the solution process change if we used benzene (a non-polar solvent) and if so, how?

The separation of the two types of molecules would be poorer since both the stationary and mobile phases would be non-polar.

Synthesis Questions

Use available resources to help you answer the following questions.

1. What physical parameter of the column would you change to optimize separation?

Increasing the length should improve separation.

2. How would the elution process have been different if you used a column with a polar matrix?

A polar matrix would have retained the blue dye longer as it is more polar. Also, a non-polar solvent would have been necessary.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. The resolution is a measure of:

- **A.** The polarity of the molecules.
- **B.** The polarity of the eluent.
- **C. The effectiveness of the separation of the two types of molecules.**
- **D.** The polarity of the column.

2. The parameter of *k'* is a measure of:

- **A.** The resolution.
- **B. The retention for each of the dyes**.
- **C.** The selectivity, which is the ratio of the *k* values for the two dyes.
- **D.** The plate number.

3. You can tell the red dye is more polar than the blue dye because:

- **A.** It eluted last with 18% isopropanol, which means the red dye bound to the matrix more.
- **B.** It eluted last with 18% isopropanol, which means the blue dye bound to the matrix less.
- **C. It eluted first with 18% isopropanol, which means the blue dye bound to the matrix more.**
- **D.** It eluted first with 18% isopropanol which means the blue dye bound to the matrix less.

4. Decreasing the polarity of the eluent will*:*

- **A. Decrease the selectivity since the dye molecules will be equally attracted to the non-polar matrix and the non-polar eluent.**
- **B.** Increase the selectivity since the dye molecules will be attracted to the non-polar matrix more than the non-polar eluent.
- **C.** Decrease the selectivity since the dye molecules will be less attracted to the non-polar matrix than to the non-polar eluent.
- **D.** Increase the selectivity since the dye molecules will more attracted to the non-polar matrix and the non-polar eluent.

Extended Inquiry Suggestions

Since the resolution determined for this experiment may not be better than one, it would be a great challenge for students to devise a method to improve selectivity. Tackle the possible parameters to be changed with your students. The ideas should include attaching multiple columns together (effectively increasing the column length) and optimizing the solvent composition for separation.

Also, if an Amadeus spectrometer system is available, 0.5 mL aliquots of the eluent can be collected and analyzed using the spectrometer. The absorbance of both components would have to be recorded at the wavelength of maximum absorbance. The plot of absorbance as a function of aliquot number would be a simple representation of a "chromatogram". This technique would demonstrate how High Performance Liquid chromatography (HPLC) works with an absorbance detector.

18. Conductometric Titration

Objectives

Students determine the titration equivalence point with a conductometric titration method.

Procedural Overview

Students gain experience conducting the following procedures:

- Using a conductivity sensor and drop counter to perform titration measurements
- Determining equivalence points and solution concentrations

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Conductivity sensor
- Drop counter with micro stir bar
- Magnetic stirrer
- Buret, 50-mL
- Beaker (2), 100-mL
- Beaker, 50-mL
- Buret or volumetric pipet, 50-mL
- Ring stand
- Clamp, right-angle
- Clamp, buret
- 0.0200 M H_2SO_4 solution, 50-mL[1]
- Barium hydroxide [$Ba(OH)_2$], unknown concentration , 50-mL[1]
- Deionized water, 50 mL
- Wash bottle with deionized water
- Cotton swab or tissue

[1] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Acids and bases
- Electrolytes
- Molarity
- Titration

Related Labs in This Guide

Labs conceptually related to this one include:

- Standardizing a Solution of Sodium Hydroxide
- Acid–Base Titration
- Oxidation–Reduction Titration
- Mole Relationships in a Chemical Reaction
- Determination of a Solubility Product
- Determining K_a by Half-Titration of a Weak Acid

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system �(2.1)
- Connecting multiple sensors to your data collection system �(2.2)
- Calibrating the drop counter �(3.4)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Adjusting the scale of a graph �(7.1.2)

- Changing the variable on the x-axis and y-axis of a graph �(7.1.9)
- Finding coordinates of a point on a graph �(9.1)
- Saving your experiment �(11.1)
- Printing the graph �(11.2)

Background

As you may recall from titrations done in earlier labs, a titration determines the amount, or concentration, of a reactant in a chemical reaction. You might have used different methods to detect the equivalence point, which is the point at which stoichiometric quantities of reactants combine.

During this experiment, you will determine the equivalence point with a conductometric method, making use of the fact that solutions conduct electricity when ions are present. Higher ion concentration, in general, yields higher conductivity.

Consider a strong electrolyte of unknown concentration. The solution conducts electricity due to the presence of ions. Adding another strong electrolyte that reacts with those ions produces a precipitate or a very poorly conducting molecule (such as H_2O) or a gas which leaves the solution. Because of this, the ion concentration and conductivity decreases.

Continued addition of the second electrolyte continues to lower the ion concentration and the conductivity until the equivalence point is reached. At the equivalence point, the two electrolytes are combined in their stoichiometric ratio. That is, all ions are removed and conductivity is at its minimum.

Conductivity increases if more of the second electrolyte is added after the equilibrium point. Although no chemical reaction occurs at this point, ions are being added to the solution from that second electrolyte.

Pre-Lab Experiment

Setting the stage for the experiment

During this experiment, you will determine the concentration of a $Ba(OH)_2$ solution. You will titrate the $Ba(OH)_2$ solution with a H_2SO_4 solution, which react according to the following equation:

$$\mathrm{Ba(OH)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2H_2O}$$

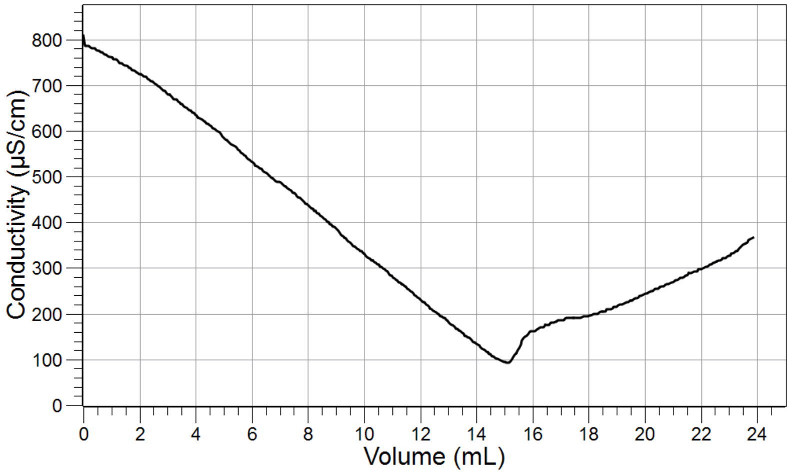
The net ionic equation of the reaction is:

$$\mathrm{Ba^{2+}(aq) + 2OH^{-}(aq) + 2H^{+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(aq) + 2H_2O}$$

Before the equivalence point, the Ba^{2+} and OH^{-} ions are responsible for the conductivity. After the equivalence point, the excess H^{+} and SO_4^{2-} ions are responsible for the conductivity. At the equivalence point, none of these ions are present in any significant concentration.

Example calculation to try

A sample of 50.00 mL $Ba(OH)_2$ solution with a concentration of about 5.00×10^{-3} M is pipetted into a 100-mL beaker. A conductivity sensor is placed into the solution and a drop counter is installed over the solution. The unknown solution is titrated with 0.0200 M H_2SO_4. The titration curve obtained is shown below:



The equivalence point (the point with the lowest conductivity) was reached after adding 15.12 mL of 0.0200 M H_2SO_4. The molarity of the barium hydroxide solution can be obtained knowing the volume and concentration of the sulfuric acid solution:

$$15.12 \text{ mL}\left(\frac{0.0200 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL H}_2\text{SO}_4}\right)\left(\frac{1 \text{ mol Ba(OH)}_2}{1 \text{ mol H}_2\text{SO}_4}\right)\left(\frac{1}{0.0500 \text{ L Ba(OH)}_2}\right)$$

$$= 6.05 \times 10^{-3} \text{ M Ba(OH)}_2$$

The concentration of the unknown $Ba(OH)_2$ solution was 6.05×10^{-3} M.

1. **Why is the conductivity curve not symmetrical around the equivalence point?**

The ions present before and after the equivalence point have different abilities to conduct electricity.

2. **What will happen in the titrated solution as the titrant solution is being added?**

Increasing amounts of white precipitate will appear.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***4.0×10^{-3} M $Ba(OH)_2$:*** Dissolve 1.262 g of $Ba(OH)_2 \cdot 8H_2O$ with water in a 1-L volumetric flask and fill it to the mark.
2. ***0.0200 M H_2SO_4:*** Combine 1.10 mL of 98% H_2SO_4 solution to about 300 mL of deionized water in a 1-L volumetric flask and fill it to the mark.

Note: Standardize the solution and report the actual concentration to the students.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

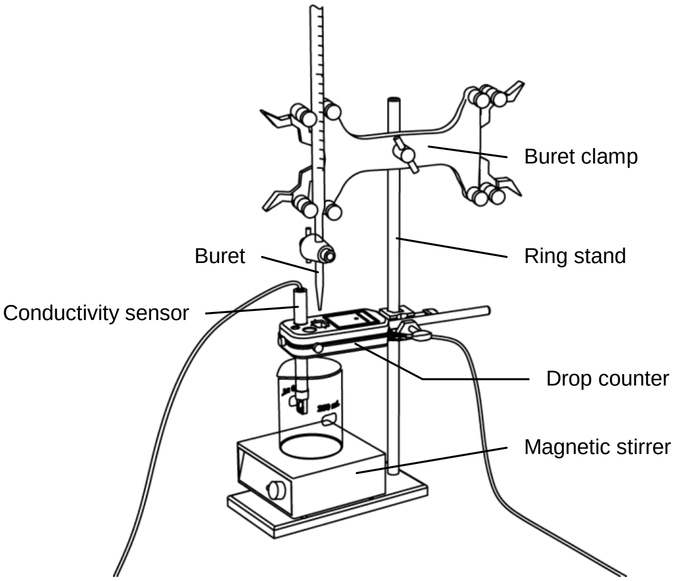
Set Up

1. Start a new experiment on the data collection system. �$^{(1.2)}$

2. Connect the conductivity sensor to the data collection system. �$^{(2.1)}$

3. Assemble the titration apparatus, using the steps below and the illustration as a guide.

- **a.** Position the magnetic stirrer on the base of the ring stand.
- **b.** Place a waste container (100-mL beaker) on the magnetic stirrer.
- **c.** Use the buret clamp to attach the buret to the ring stand.
- **d.** Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.
- **e.** Place the conductivity sensor through one of the slots in the drop counter.



Note: Do not connect the drop counter to the data collection system yet.

4. Rinse the buret with several milliliters of the standardized 0.0200 H_2SO_4 solution:

- **a.** Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized H_2SO_4 solution.
- **b.** Open the stopcock on the buret and drain the rinse H_2SO_4 solution into the waste container.
- **c.** Repeat this process two more times.

5. Why is it necessary to rinse the buret with the H_2SO_4 solution?

If there is any residual water or contaminant in the buret, it will dilute the H_2SO_4 solution and change its concentration. Rinsing eliminates any such contamination.

6. Make sure the stopcock on the buret is in the "off" position and then use a funnel to fill the buret with about 50 mL of the H_2SO_4 solution (titrant).

7. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

8. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of H_2SO_4. If this happens, the amount of titrant used will be inaccurate.

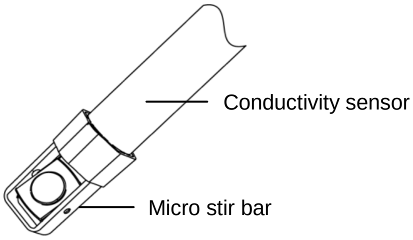
9. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

Note: Good control of the stopcock is important. Each drop should result in a blink of the LED on the drop counter. If the LED is continuously lit, you have opened the stopcock too far and you will have to start over.

10. Why will it be necessary to start your titration over again if you accidentally allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

11. Add the micro stir bar to the end of the conductivity sensor.



12. Why is it necessary to stir the solution during a titration?

Stirring thoroughly mixes the ions in the solution so that the recorded pH reflects the pH of the entire solution.

13. Add additional 0.0200 M H_2SO_4 to the buret so the solution is above the zero mark. Allow some of the H_2SO_4 solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 1.

14. Remove the waste container.

15. Use the volumetric pipet to transfer 50.00 mL of the $Ba(OH)_2$ solution with the unknown concentration into a 100-mL beaker.

16. Add enough deionized water to the beaker so the tip of the conductivity sensor is covered with solution.

17. Tap the sensor a few times to make sure any trapped air is expelled from the sensor.

18. Turn on the magnetic stirrer at a slow and steady rate.

19. Connect the drop counter to the data collection system. �(2.2)

20. Display the Conductivity on the y-axis of a graph and Drop Count on the x-axis. �(7.1.1)

Collect Data

21. Clean the lens of the drop counter inside the opening the drops go through with water and a cotton swab or tissue.

22. Start recording data. �(6.2)

23. Adjust the scale of the graph. �(7.1.2)

24. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

25. What do you expect to happen in the beaker during the titration?

There will be precipitation since $BaSO_4$ is not water soluble.

26. Continue data collection until the curve passes its minimum point by about 3 mL.

27. How can you recognize the equivalence point?

The conductivity should be at its minimum as all the ions from the reactants are removed at that point.

28. At the minimum, is the conductivity at 0? Explain your answer.

The conductivity will not be zero, since not all the ions are removed from the solution

29. Stop recording data. �(6.2)

30. In Table 1, record the final drop count and the final reading of the titrant in the buret to a precision of 0.01 mL.

31. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 1.

Table 1: Titration data for drop counter calibration

Titration Information	Trial 1	Trial 2
Initial reading of H_2SO_4 solution on the buret (mL)	0.00	0.00
Final reading of H_2SO_4 solution on the buret (mL)	21.10	22.80
Volume of titrant (mL)	21.10	22.80
Final drop count	441	482

32. Calibrate the drop counter. �(3.4)

33. On the graph, set the horizontal axis to the calculated volume. �(7.1.9)

34. Find the volume of H_2SO_4 solution (to a precision of 0.01 mL) used to reach the equivalence point. �(9.1) In Table 2, record the volume.

Note: The lowest point of the curve represents the volume of the H_2SO_4 solution that was required to reach the equivalence point.

35. Refill the buret above the zero mark with the H_2SO_4 solution.

a. Fill the buret above the zero mark and allow some of the H_2SO_4 solution to drip into a waste container until the top of the meniscus is lined up with the zero mark or just below.

b. Record the starting point in Table 1.

36. Rinse the conductivity sensor tip with deionized water.

37. Remove the beaker and dispose of its contents according to the instructor's instructions.

38. Rinse the beaker with distilled water.

39. Begin the second titration of $Ba(OH)_2$ as follows:

a. Use the volumetric pipet to transfer 50.00 mL of the $Ba(OH)_2$ solution with the unknown concentration into a 100-mL beaker.

b. Add enough deionized water to the beaker so the tip of the conductivity sensor is covered with solution.

c. Tap the sensor a few times to make sure any trapped air is expelled from the sensor.

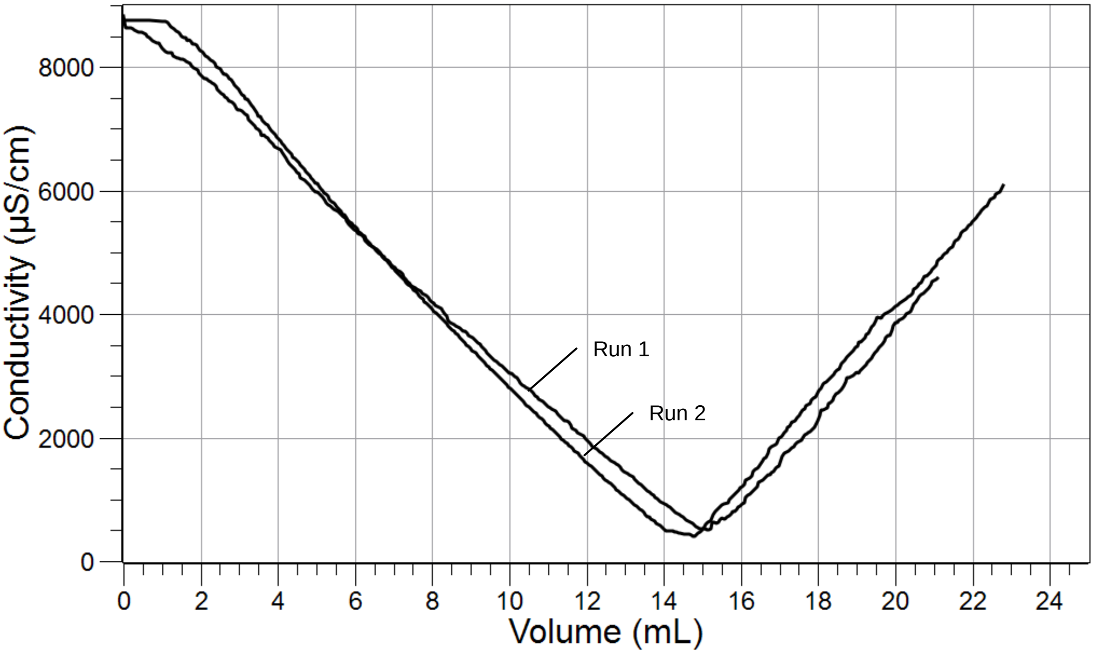
d. Turn on the magnetic stirrer at a slow and steady rate.

e. Display the Conductivity on the y-axis of a graph and Drop Count on the x-axis. �(7.1.1)

f. Repeat the steps following the Collect Data subheading to complete the titration.

40. Save your experiment �(11.1) and clean up according to your instructor's instructions.

41. For each titration curve, sketch the graphs or print the graphs �(11.2) and paste them below.



Data Analysis

1. Obtain the concentration of the H_2SO_4 solution from your instructor and record it in Table 2.

2. Calculate the number of moles of H_2SO_4 that was necessary to reach the equivalence point (the stoichiometrically necessary amount to react with the $Ba(OH)_2$).

For Trial 1:

$$15.08\text{ mL}\left(\frac{0.0200\text{ mol H}_2\text{SO}_4}{1000\text{ mL}}\right) = 3.02 \times 10^{-4}\text{ mol H}_2\text{SO}_4$$

3. Calculate the number of moles of $Ba(OH)_2$ that was in the beaker.

Since H_2SO_4 reacts in a 1:1 stoichiometric ratio with $Ba(OH)_2$, the number of moles of $Ba(OH)_2$ is the same as the number of moles of added H_2SO_4 up to the equivalence point: 3.02×10^{-4} mol.

4. Calculate the concentration of the original $Ba(OH)_2$ from the number of moles of $Ba(OH)_2$ that was present in the beaker and the volume of the $Ba(OH)_2$ solution. Record the results in Table 2.

For Trial 1:

$$\left(\frac{3.02 \times 10^{-4}\ \text{mol Ba(OH)}_2}{0.05000\ \text{L}}\right) = 6.04 \times 10^{-3}\ \text{M Ba(OH)}_2$$

Table 2: Determination of the concentration of the $Ba(OH)_2$ solution

Parameter	Trial 1	Trial 2
Concentration of standardized H_2SO_4 solution (M)	0.0200	
Volume of $Ba(OH)_2$ solution (mL)	50.00	50.00
Volume of H_2SO_4 to the equivalence point (mL)	15.08	14.76
Concentration of the $Ba(OH)_2$ solution (M)	6.04×10^{-3}	5.90×10^{-3}

Analysis Questions

1. Is the resulting titration curve what you expected?

Students may mention that, at the equivalence point, the conductivity was not zero.

2. Why would the titration curve be different than you expected?

Even at the equivalence point, there are ions present from the auto-dissociation of water.

Synthesis Questions

Use available resources to help you answer the following questions.

1. How would the titration curve be different if Na_2SO_4 were used instead of H_2SO_4? (Hint: Check which ions would be removed and which ones would not.)

The Na^+ and OH^- ions would remain in the solution. Therefore, the conductivity would have been significantly higher, even at the equivalence point.

2. What solution would allow you to measure the concentration of an unknown $AgNO_3$ solution?

Any strong electrolyte with Cl^- ions would suffice: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. At the equivalence point in this lab, what are the major species in the titrated solution?

A. Water and $BaSO_4$

B. Ba^{2+} and OH^{-} ions

C. H^{+} and SO_4^{2-} ions

D. Ba^{2+}, OH^{-}, H^{+}, and SO_4^{2-} ions

2. Which statement is *not* true?

A. The conductivity of solutions depends on the concentration of ions.

B. The conductivity of solutions depends on the nature of the ions that are present.

C. The conductivity of solutions depends on the concentration of undissociated molecules present in the solution.

D. The conductivity is lowest at the equivalence point.

3. What does doubling the volume of a solution by adding water do?

A. It doubles the ion concentration and therefore increases the conductivity.

B. It increases the conductivity since the ion concentration is lowered.

C. It decreases the conductivity since the ion concentration is increased

D. It lowers the conductivity since the ion concentration is lowered.

Extended Inquiry Suggestions

Consider filtering, drying, and measuring the mass of the resulting $BaSO_4$ to see how well the actual amount matches the proposed amount. The proposed amount can be calculated from the actual concentration of the $Ba(OH)_2$ solution.

19. Separation and Analysis of Cations

Objectives

Students use chemical properties to qualitatively classify and identify the cations present in a solution.

Procedural Overview

Students gain experience conducting the following procedures:

- Organizing and tracking the results of multiple reactions
- Performing basic laboratory separation processes

Time Requirement

♦ Preparation time	50 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	90 minutes

Materials and Equipment

For each student or group:

- Test tube (10), 10-mL
- Test tube rack
- Pipet, graduated, 10-mL
- Rubber bulb
- Pipet, plastic (7), 1-mL
- Centrifuge
- Beaker, 250-mL
- Evaporating dish
- Stirring rod
- Hot plate
- Litmus paper (10)
- pH paper (1 roll)
- 6 M Sodium hydroxide ($NaOH$), 20 mL[1]
- 6 M Ammonia (NH_3), 20 mL [2]
- 0.1 M Potassium chromate (K_2CrO_4), 20 mL[3]
- 1% Aluminon dye, 2 mL[4]
- 6 M Hydrochloric acid (HCl), 20 mL[5]
- Dimethylglyoxime (DMG) reagent, 5 drops[6]
- 0.2 M Potassium ferrocyanide ($K_4[Fe(CN)_6]$), 2 mL[7]
- 3 M Sulfuric acid (H_2SO_4), 3mL[8]
- 3% Hydrogen peroxide (H_2O_2), 2 mL[9]
- Unknown cation solution, 20 mL[10]
- Deionized water, 5 mL
- Marking pen

[1-8] To prepare the solutions, refer to the Lab Preparation section.

[6] This reagent is available premade from chemical suppliers.

[9] 3% hydrogen peroxide is readily available in pharmacies.

[10] The "unknown" cation solution can contain 2 to 4 of the cations. The unknown solutions can be prepared by combining any 2 to 4 of the cation solutions used in this lab. Refer to the Lab Preparation section for the list of cation solutions.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Balancing chemical equations
- Acid-base reactions
- Stoichiometry of chemical reactions

Related Labs in This Guide

Labs conceptually related to this one include:

- Analysis of Anions
- Analysis of a Coordination Compound

Using Your Data Collection System

Note: As this lab experiment does not use a data collection system, no Tech Tips (indicated by the symbol "�" and a superscripted number following a step) are needed.

Background

The primary goal of a qualitative analysis is to identify the substances present in a mixture. In the qualitative analysis procedure, chemical properties of an unknown substance are determined by systematically reacting the unknown with a number of different reagents. By knowing what a particular reaction will produce if a specific ion is present, the ions in the solution can be identified.

In some cases the products of a reaction cannot definitively confirm the presence of a specific ion. In these cases it is necessary to perform tests for a particular ion as well as to separate the components of the mixture.

Pre-Lab Experiment

Setting the stage for the experiment

In this exercise you will be given a solution containing 2 to 4 unknown cations. The analysis of cations uses a flowchart of reactions in the procedure. The flowchart is given at the end of the Procedure section.

It is important to perform the reactions in the procedure with great care so that complete precipitation and separation occur. Otherwise, unreacted ions may interfere with subsequent steps in the procedure and cause false positive results.

Example calculation to try

The analysis of a sample gave the following results. For procedural details refer to the Collect Data section.

Table 1: Identifying cations in a solution

Step	Action	Observation	Possible Explanation
1	Add NaOH solution (Procedure 1)	No ammonia production	NH_4^+ is ruled out.
2	Add 6 M HCl (Procedure 2)	White precipitate	Potential presence of Ag^+ or Pb^{2+} or both
3	Separate the precipitate from the supernatant. Add deionized water to the precipitate and heated it. (Procedure 3)	No change	The precipitate is AgCl, which confirms the presence of Ag^+.
4	Add NaOH solution (in excess) to the supernatant from Step 3. Separate the precipitate from the supernatant. (Procedure 6)	Green precipitate	The presence of Ni^{2+} is likely because of the color; Mn^{2+}, Fe^{3+}, Al^{3+} are possible.
5	Add H_2SO_4 in excess to the supernatant from Step 4. (Procedure 11)	No change	Al^{3+} can be ruled out.
6	Add NH_3 solution to the precipitate from Step 4. (Procedure 7)	Blue solution forms. All precipitate dissolves.	The presence of Ni^{2+} is confirmed, Mn^{2+} and Fe^{3+} are ruled out.

The analysis confirmed the presence of Ag^+ and Ni^{2+} ions.

1. **How would the result be different if, in Step 3, the precipitate did dissolve?**

The dissolving precipitate in Step 3 would indicate the presence of Pb^{2+}.

2. **Why was there no need to check for Mn^{2+} and Fe^{3+} after Step 6?**

If either Mn^{2+} or Fe^{3+} were present, the precipitate would not have dissolved completely in the NH_3 solution.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

Test solutions

1. ***6 M NaOH:*** Dissolve 240 g of NaOH in water in a 1-L volumetric flask and fill it to the mark.
2. ***6 M NH_3:*** Dissolve 340 mL of a 30% NH_3 solution in water in a 1-L volumetric flask and fill it to the mark.

3. ***0.1 M K_2CrO_4:*** Dissolve 19.4 g of K_2CrO_4 in water in a 1-L volumetric flask and fill it to the mark.

4. ***Aluminon dye:*** Dissolve 4.734 g of Aluminon dye (aurin tricarboxylic acid) in water in a 100-mL volumetric flask and fill it to the mark to make a 1% solution.

5. ***6 M HCl:*** Under a hood, slowly add 500 mL of 36% HCl solution to about 400 mL of water in a 1-L volumetric flask and fill it to the mark.

6. ***Dimethylglyoxime reagent:*** Dissolve 1 g of dimethylglyoxime in ethanol in a 100-mL volumetric flask and fill it to the mark.

7. ***0.2 M $K_4[Fe(CN)_6]$:*** Dissolve 84.5 g of $K_4[Fe(CN)_6]$ in water in a 1-L volumetric flask and fill it to the mark.

8. ***3 M H_2SO_4:*** Combine 167 mL of 98% H_2SO_4 solution *slowly* with at least 500 mL of water in a 1-L volumetric flask and fill it to the mark.

9. ***3% H_2O_2:*** Commercially available 3% hydrogen peroxide can be used directly.

For the unknown cation solution

10. ***0.1 M $AlCl_3$:*** Dissolve 24.1 g of $AlCl_3 .6H_2O$ in water in a 1-L volumetric flask and fill it to the mark.

11. ***0.1 M $NiCl_2$:*** Dissolve 23.8 g of $NiCl_2 .6H_2O$ in water in a 1-L volumetric flask and fill it to the mark.

12. ***0.1 M $Pb(NO_3)_2$:*** Dissolve 33.1 g of $Pb(NO_3)_2$ in water in a 1-L volumetric flask and fill it to the mark.

13. ***0.1 M $AgNO_3$:*** Dissolve 17.0 g of $AgNO_3$ in water in a 1-L volumetric flask and fill it to the mark.

14. ***0.1 M $MnSO_4$:*** Dissolve 22.3 g of $MnSO_4 \cdot 4H_2O$ in water in a 1-L volumetric flask and fill it to the mark.

15. ***0.1 M $(NH_4)_2Fe(SO_4)_2$:*** Dissolve 39.2 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in water in a 1-L volumetric flask and fill it to the mark.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: This experiment does not use a data collection system, so there are no Tech Tips (indicated by the symbol "�" and a superscripted number following a step).

You should have a solution containing 2 to 4 unknown cations. It is important to perform the reactions in the procedure so complete precipitation and separation occur. Otherwise, unreacted ions may interfere with subsequent steps in the procedure and cause false positive results.

Set Up

1. Make sure you have at least 10 clean test tubes in a test tube rack.

2. Read the various procedures in Table 2 and devise a method to organize and label the test tubes and other test materials.

Note: Label the disposable pipets before they are used, to avoid contamination.

3. Record the number of your unknown solution: ______________.

4. Prepare a hot water bath (approximately 80 °C).

Collect Data

5. Perform the reactions with your unknown solution according to Table 2. You can also refer to the Cation Flowchart at the end of this section.

6. After each procedure, record your observations of each test performed in Table 3 in the Data Analysis section.

Note: Use a fresh pipet for each procedure

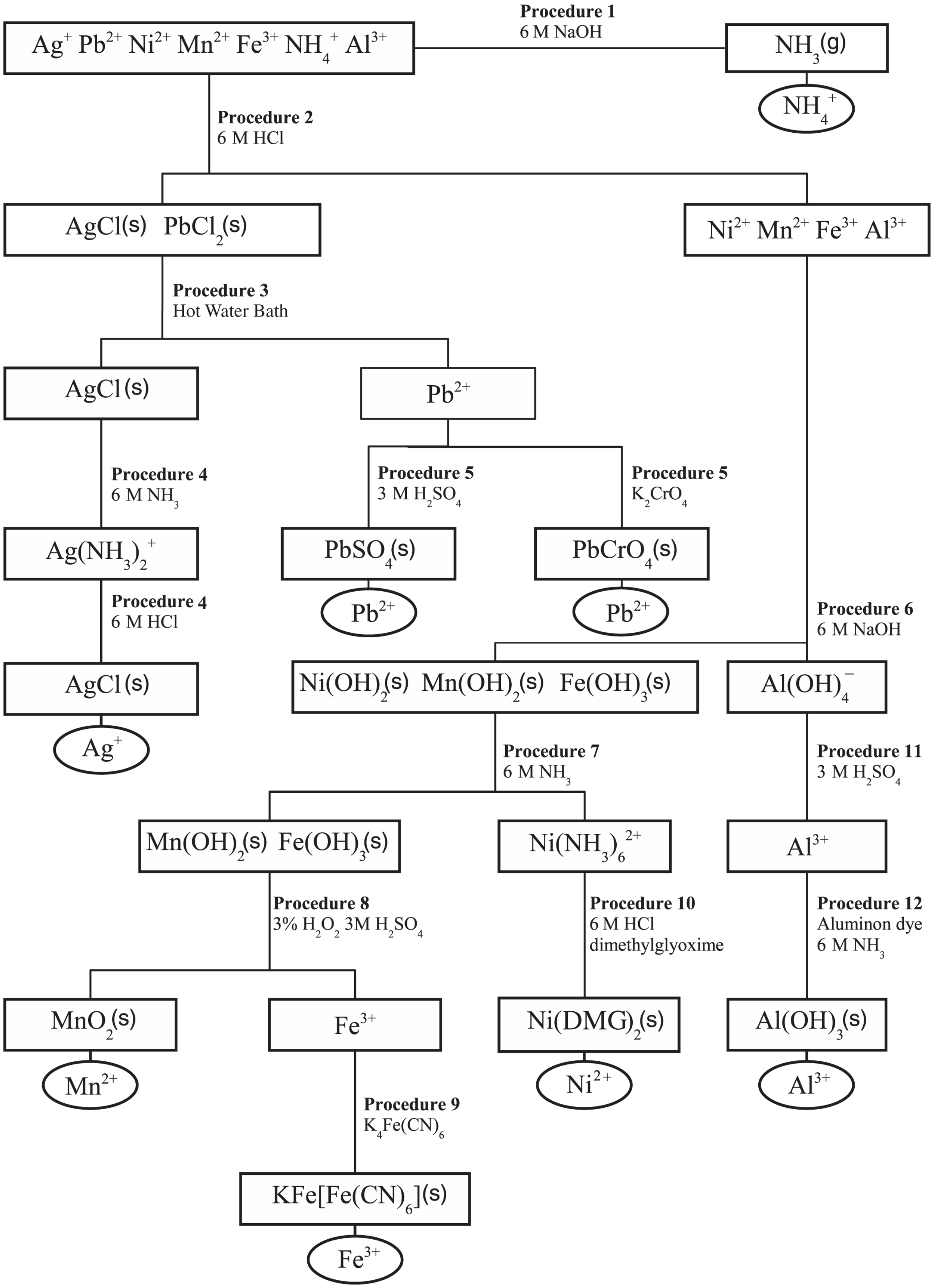
Table 2: Procedural steps to analyze cations

Procedure 1: Detection of ammonium ion	Measure 1 mL of the unknown solution into an evaporating dish. Add approximately 2 mL of 6 M NaOH with a plastic pipet and cover with a watch glass with a piece of moist red litmus paper attached. Observe the litmus paper for a color change from red to blue, indicating the presence of ammonia.
Procedure 2: Separation of silver and lead as chlorides	With a clean pipet transfer 2 mL of the unknown solution to a test tube. Add 2 to 3 drops of 6 M HCl. If a precipitate forms, continue adding 6 M HCl solution drop by drop while stirring until no more precipitate forms. If no precipitate forms, save the solution for *Procedure 6.* Centrifuge the mixture in the test tube and then add one drop of 6 M HCl. If no additional precipitate appears, pour the supernatant into another test tube. If more precipitate forms, repeat the last two steps until no new precipitate forms.

	Label the samples and save the supernatant for *Procedure 6*. Use the precipitate for *Procedure 3*.
Procedure 3: Separation of lead ion from silver ion	*Continue from Procedure 2.* With a clean pipet add 3 to 4 mL of deionized water to the precipitate from *Procedure 2*. Heat the test tube, swirling it while in a hot water bath for several minutes while stirring. Centrifuge the test tube to separate the supernatant from any remaining solid. Save the supernatant for use in *Procedure 5*. Use the precipitate for *Procedure 4*.
Procedure 4: Confirmation of silver ion	*Continue from Procedure 3.* Add 10 drops of 6 M ammonia solution to the precipitate from *Procedure 3* and stir. Add 6 M HCl drop by drop until the precipitate reappears or litmus paper indicates the solution is acidic.
Procedure 5: Confirmation of lead ion	*Continue from Procedure 3.* If the solution from *Procedure 3* contains any precipitation, reheat it in the water bath until the precipitate is completely dissolved. Divide the sample into two test tubes. Add several drops of 3 M H_2SO_4 to one of the test tubes. Add several drops of potassium chromate to the second test tube and stir.
Procedure 6: Precipitation of nickel, manganese and iron ions as hydroxides	*Continue from Procedure 2.* Add 6 M NaOH to the supernatant from *Procedure 2* until precipitation is complete. Add 0.5 mL more of the NaOH and stir. Separate the supernatant from any precipitate. Save the supernatant for *Procedure 11*. Use the precipitate for *Procedure 7*.
Procedure 7:	*Continue from Procedure 6.*

Separation of nickel ion from manganese and iron ion	Add 3 mL of 6 M ammonia and stir well. Separate the supernatant from any precipitate. Save the supernatant for *Procedure 10*. Use the precipitate for *Procedure 8*.
Procedure 8: Confirmation of manganese ion	*Continue from Procedure 7.* Add 1 mL of 3% hydrogen peroxide solution to the precipitate from *Procedure 7*. Stir, then heat the sample in the water bath until no more gas is generated. Add 3 M H_2SO_4 by drops until the mixture is acidic. Separate the supernatant from any precipitate and use it for *Procedure 9*
Procedure 9: Confirmation of iron ion	*Continue from Procedure 8.* Add two drops of 0.2 M $K_4[Fe(CN)_6]$ to the solution from *Procedure 8*.
Procedure 10: Confirmation of nickel ion	*Continue from Procedure 7.* Add 1 drop of 6 M HCl. Then add 5 drops of dimethylglyoxime reagent to the solution from *Procedure 7*.
Procedure 11: Detection of aluminum ion	*Continue from Procedure 6.* Neutralize the solution from *Procedure 6* by adding 3 M H_2SO_4. Use the pH paper to test the pH after adding each drop. Add 2 more drops of 3M H_2SO_4 after obtaining a neutral pH. Use the supernatant for *Procedure 12*.
Procedure 12: Confirmation of aluminum ion	*Continue from Procedure 11.* Add 2 drops of aluminon dye to the solution from *Procedure 11*. Add the 6 M ammonia by drops while stirring. Use litmus paper to detect when the solution is basic and then stop adding the ammonia.

Cation Flowchart



Data Analysis

1. Enter the equations and identified cations in Table 3 that conform to your observations.

Table 3: Complete the table

Procedure	Observation	Proposed Equations	Identified Cations
1	No change in color of litmus paper.	$2Ag^{+}(aq) + 2OH^{-}(aq) \rightarrow Ag_2O(s) + H_2O$ $Ni^{2+}(aq) + 2OH^{-}(aq) \rightarrow Ni(OH)_2(s)$ $Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_2(s)$ $Mn^{2+}(aq) + 2OH^{-}(aq) \rightarrow Mn(OH)_2(s)$ $Pb^{2+}(aq) + 2OH^{-}(aq) \rightarrow Pb(OH)_2(s)$ $Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s)$ $Al^{3+}(aq) + 3OH^{-}(aq) \rightarrow Al(OH)_3(s)$	Ag^{+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}
	Change in color	$NH_4^{+}(aq) + OH^{-}(aq) \rightarrow NH_3(g) + H_2O$	NH_4^{+}
2	White precipitate	$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$ $Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$	Ag^{+}, Pb^{2+}
	No precipitate		Ni^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}
3	Solid did not return into solution		Ag^{+}
	Solid returned into solution	$PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2Cl^{-}(aq)$	Pb^{2+}
4	Precipitate disappears	$AgCl(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^{+}(aq) + Cl^{-}(aq)$	Ag^{+}
	Precipitate reappears	$Ag(NH_3)_2^{+}(aq) + 2H^{+}(aq) + Cl^{-}(aq) \rightarrow$ $AgCl(s) + 2NH_4^{+}$	
5	Precipitate forms	$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$	Pb^{2+}
	Precipitate forms	$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$	

Procedure	Observation	Proposed Equations	Identified Cations
6	Precipitate forms	$2Ag^{+}(aq)+2OH^{-}(aq)\rightarrow Ag_2O(s)+H_2O$ $Ni^{2+}(aq)+2OH^{-}(aq)\rightarrow Ni(OH)_2(s)$ $Cu^{2+}(aq)+2OH^{-}(aq)\rightarrow Cu(OH)_2(s)$ $Mn^{2+}(aq)+2OH^{-}(aq)\rightarrow Mn(OH)_2(s)$ $Pb^{2+}(aq)+2OH^{-}(aq)\rightarrow Pb(OH)_2(s)$ $Fe^{3+}(aq)+3OH^{-}(aq)\rightarrow Fe(OH)_3(s)$ $Al^{3+}(aq)+3OH^{-}(aq)\rightarrow Al(OH)_3(s)$	Ni^{2+}, Mn^{2+}, Fe^{3+}
	Precipitate dissolves	$Ag^{+}(aq)+2OH^{-}(aq)\rightarrow Ag_2O(s)+H_2O$ $Ni^{2+}(aq)+2OH^{-}(aq)\rightarrow Ni(OH)_2(s)$ $Cu^{2+}(aq)+2OH^{-}(aq)\rightarrow Cu(OH)_2(s)$ $Mn^{2+}(aq)+2OH^{-}(aq)\rightarrow Mn(OH)_2(s)$ $Pb^{2+}(aq)+2OH^{-}(aq)\rightarrow Pb(OH)_2(s)$ $Fe^{3+}(aq)+3OH^{-}(aq)\rightarrow Fe(OH)_3(s)$ $Al^{3+}(aq)+3OH^{-}(aq)\rightarrow Al(OH)_3(s)$	Al^{3+}
7	Precipitate remains		Mn^{2+}, Fe^{3+}
	Precipitate disappears	$Ni^{2+}(aq)+6NH_3\rightarrow Ni(NH_3)_6^{2+}(aq)$	Ni^{2+}
8	Precipitate remains	$Mn(OH)_2(s)+H_2O_2\rightarrow MnO_2(s)+2H_2O$	Mn^{2+}
	Precipitate disappears	$Fe(OH)_3(s)+3H^{+}(aq)\rightarrow Fe^{3+}(aq)+3H_2O$	Fe^{3+}
9	Precipitate forms	$4Fe^{3+}(aq)+3\left[Fe(CN)_6\right]^{4-}(aq)\rightarrow$ $Fe_4\left[Fe(CN)_6\right]_3(s)$	Fe^{3+}
10	Precipitate forms	$Ni(NH_3)_6^{2+}(aq)+2DMG\rightarrow$ $Ni(DMG)_2(s)+6NH_3(aq)$	Ni^{2+}
11	No precipitate	$Al(OH)_4^{-}(aq)+4H^{+}(aq)\rightarrow$ $Al^{3+}(aq)+4H_2O$	Al^{3+}
12	Precipitate forms		Al^{3+}

Analysis Questions

1. If you had Mn^{2+} ions in your unknown solution, the reaction mixture with NaOH would eventually turn brown. Propose an explanation for that phenomenon (Hint: see Procedure 8).

The O_2 in the air can oxidize Mn^{2+} to manganese ions with a higher oxidation number, which are mostly brown.

2. NaOH reacts with Ag^+ to form Ag_2O. The reaction is based on the fact that one of the products of the expected exchange reaction is not stable and loses water. Propose an equation for the exchange reaction and an equation for one of the products losing water.

$Ag^+(aq) + OH^-(aq) \rightarrow AgOH(s)$

$2AgOH(s) \rightarrow Ag_2O(s) + H_2O$

3. The reaction mixture described above has a brown precipitate. What do you think it is?

Ag_2O

Synthesis Questions

Use available resources to help you answer the following questions.

1. How would you use the reactions described in Questions 2 and 3 above to identify Ag^+ and distinguish it from Pb^{2+}?

The color of the precipitate of Ag^+ with NaOH is unique. Using NaOH in Procedure 2 would reveal the presence of Ag^+.

2. The reaction of a sample solution with NaOH forms a white precipitate. Which ions could be present? (Hint: one possible ion could have been present in Procedure 6, the other could not have.) You may have to perform a reaction to answer this question.

Al^{3+} ion and Pb^{2+} ion.

3. Propose a reaction to distinguish between the ions named in the above question.

Excess NaOH would dissolve the $Al(OH)_3$ precipitate (Procedure 6) but not the $Pb(OH)_2$. Also, Pb^{2+} forms a precipitate when reacted with H_2SO_4 (Procedure 5) and Al^{3+} does not.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. A white precipitate with NaOH could indicate the presence of:

- **A.** **Al^{3+}**
- **B.** Fe^{3+}
- **C.** Mn^{2+}
- **D.** None of these

2. A yellow precipitate can be:

- **A.** AgCl
- **B.** $Ni(OH)_2$
- **C.** **$PbCrO_4$**
- **D.** $PbCl_2$

3. A green solution forms a precipitate when mixed with NaOH. The solution must:

- **A.** React with excess NaOH.
- **B.** Not react with NH_3 solution.
- **C.** Give precipitate with H_2SO_4.
- **D.** **Give a red precipitate with dimethylglyoxime**.

Extended Inquiry Suggestions

You can challenge your students by giving them a number of unknown solutions in test tubes (TT) and have them perform reactions among only those solutions, without using any other reagents. Allow them to identify the content of the test tubes using a reaction matrix and what they have learned in this experiment. An example of a reaction matrix is shown below.

The following solutions are used: $AgNO_3$, Na_2SO_4, HCl, $Pb(NO_3)_2$, $Al(NO_3)_3$, NaOH and put in test tubes numbered “1” through “6.” (The dash indicates there was no change when the solutions were combined.)

Reaction Matrix

TT	1	2	3	4	5	6
1		White precipitate, does not dissolve with heat.	Brown precipitate	—	—	—
2			—	—	White precipitate that dissolves with heat.	—
3				White precipitate	White precipitate	—
4					—	—
5						White precipitate
6						

The following strategy can be followed:

1. A brown precipitate forms when solution from test tubes #1 and #3 are mixed, resulting in Ag_2O (this has a characteristic precipitate). Therefore, #1 and #3 are $AgNO_3$ and NaOH.

2. The precipitate that dissolves when heated is $PbCl_2$. Therefore, #2 and #5 are HCl and $Pb(NO_3)_2$.

3. To identify the specific test tube, first assume #3 is $AgNO_3$. If #3 is $AgNO_3$ and #2 is HCl, then mixing #3 and #2 would yield AgCl, a white precipitate. This did not happen.

4. If #3 is $AgNO_3$ then #1 has to be NaOH.

5. If #3 is $AgNO_3$ then #2 has to be $Pb(NO_3)_2$ (no reaction) and #5 has to be HCl (white precipitate).

6. The results of steps 3 to 5 cannot be possible since they resulted in #1 being NaOH and #2 being HCl. These mixed would not yield a visible reaction. This is inconsistent with our observations (there was a white precipitate between #1 and #2). Therefore, our assumption that #3 is $AgNO_3$ is wrong.

7. If #1 is $AgNO_3$, then #3 has to be NaOH.

8. If #1 is $AgNO_3$ then #5 has to be $Pb(NO_3)_2$ (no reaction) and #2 has to be HCl (#5 mixed with #2 formed a white precipitate).

9. #5 ($Pb(NO_3)_2$) reacts with #6 but not with #4. Therefore, #6 has to be Na_2SO_4 ($PbSO_4$ precipitate) and #4 has to be $Al(NO_3)_3$.

10. #4 ($Al(NO_3)_3$) reacts with #3 (NaOH) yielding white $Al(OH)_3$ precipitate. This is consistent with our results (and can be further confirmed by adding an excess of NaOH, which would dissolve the $Al(OH)_3$).

Therefore the solutions are as follows:

Test Tube	**Solution**
1	$AgNO_3$
2	HCl
3	NaOH
4	$Al(NO_3)_3$
5	$Pb(NO_3)_2$
6	Na_2SO_4

20. Analysis of Anions

Objectives

Students analyze solutions of known anions and apply the knowledge gained to identify the anions in an unknown solution.

Procedural Overview

Students gain experience conducting the following procedures:

- Comparing the results of test tube reactions of known anions with the results of the solution containing unknown anions.
- Performing basic laboratory separation processes.

Time Requirement

♦ Preparation time	60 minutes
♦ Pre-lab discussion and experiment	50 minutes
♦ Lab experiment	60 minutes

Materials and Equipment

For each student or group:

- Test tube (13), 10-mL
- Test tube rack
- Pipets (13), 1-mL, disposable
- Stirring rods (several)
- Litmus paper (15)
- 0.2 M Sodium sulfate (Na_2SO_4), 10 mL[1]
- 0.2 M Monopotassium phosphate (KH_2PO_4), 5 mL[2]
- 0.2 M Sodium nitrate ($NaNO_3$), 5 mL[3]
- 0.2 M Sodium chloride (NaCl), 5 mL[4]
- Unknown anion solution, 20 mL[5]
- 0.2 M Barium nitrate ($Ba(NO_3)_2$), 5 mL[6]
- Saturated iron(II) sulfate ($FeSO_4$), 2 mL[7]
- 0.1 M Silver nitrate ($AgNO_3$), 5 mL[8]
- 6 M Nitric acid (HNO_3), 5 mL[9]
- 5 M Ammonia (NH_3), 5 mL[10]
- 3 M Sulfuric acid (H_2SO_4), 5 mL[11]
- Concentrated H_2SO_4, 2 mL
- Distilled water
- Centrifuge
- Marking pen

[1–11] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Balancing chemical equations
- Acid–base reactions
- Stoichiometry of chemical reactions

Related Labs in This Guide

Labs conceptually related to this one include:

- Separation and Analysis of Cations
- Analysis of a Coordination Compound

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Note: As this lab experiment does not use a data collection system, no Tech Tips (indicated by the symbol "�" and a superscripted number following a step) are needed.

Background

Anion analysis is somewhat simpler than cation analysis because separations are not usually required. In this exercise, known solutions of four common anions are analyzed. The anions are:

- PO_4^{3-} (phosphate)
- Cl^- (chloride)
- SO_4^{2-} (sulfate)
- NO_3^- (nitrate)

After the reactions used to identify the individual anions have been completed, you will identify the anions present in an unknown solution.

Pre-Lab Experiment

Setting the stage for the experiment

In this exercise you will be given a solution containing 2 to 4 unknown anions. The analysis of anions does not need a flowchart of reactions because it is much simpler than that of cations.

You must perform the reactions in the procedure with great care so that complete precipitation and separation occur. Otherwise, unreacted ions might interfere with subsequent steps in the procedure and cause false positive results.

Example calculation to try

The table below summarizes results obtained from the analysis of a sea water sample. For procedural details refer to the Procedure section of this experiment.

Table 1: Steps of anion identification of a sea water sample

Step	Action	Observation	Possible Explanation
1	Added $Ba(NO_3)_2$ solution by drops until precipitation occurs.	White precipitate formed.	Possibly SO_4^{2-} and PO_4^{3-} are present.
2	Separated the precipitate from the supernatant. Added HNO_3 solution to the precipitate.	Some precipitate dissolved.	The remaining precipitate is $BaSO_4$, indicating the presence of SO_4^{2-}.
3	Separated the precipitate from the supernatant. Added $AgNO_3$ to the supernatant.	Yellow precipitate formed.	The precipitate is Ag_3PO_4, which confirms the presence of PO_4^{3-}.
4	Added $AgNO_3$ solution to the supernatant from Step 2, and then added NH_3 solution.	White precipitate formed. Adding NH_3 solution dissolved the precipitate.	The precipitate that dissolves in NH_3 is AgCl, indicating the presence of Cl^-.
5	Tested for NO_3^-.	No change.	NO_3^- can be excluded.

The analysis confirmed the presence of Cl^-, SO_4^{2-}, and PO_4^{3-} ions.

1. What would be another method to identify the Cl^- ions? (Hint: Remember the experiment dealing with the reactions of cations.)

Cl^- ions result in a $PbCl_2$ precipitate when reacted with Pb^{2+}. The $PbCl_2$ can be dissolved by heating.

2. Why is Ba^{2+} used in Step 1 in the above table instead of Pb^{2+}?

While Pb^{2+} would precipitate with both, SO_4^{2-} and PO_4^{3-} anions, the latter substance would not dissolve in HNO_3. This means you would not be able to detect PO_4^{3-}.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

Anion solutions

1. ***0.2 M Na_2SO_4:*** Dissolve 28 g of Na_2SO_4 in some distilled water in a 1-L volumetric flask and fill it to the mark.
2. ***0.2 M KH_2PO_4:*** Dissolve 27 g of KH_2PO_4 in some distilled water in a 1-L volumetric flask and fill it to the mark.
3. ***0.2 M $NaNO_3$:*** Dissolve 17 g of $NaNO_3$ in some distilled water in a 1-L volumetric flask and fill it to the mark.
4. ***0.2 M NaCl:*** Dissolve 12 g of NaCl in some distilled water in a 1-L volumetric flask and fill it to the mark.
5. ***Unknown solution:*** Mix equal volumes of $NaNO_3$, KH_2PO_4, NaCl, and Na_2SO_4 solution.

Test solutions

6. ***0.2 M $Ba(NO_3)_2$:*** Dissolve 52 g of $Ba(NO_3)_2$ in some distilled water in a 1-L volumetric flask and fill it to the mark.
7. ***Saturated $FeSO_4$***: Add solid $FeSO_4 \cdot 7H_2O$ to distilled water until no more will dissolve.
8. ***0.1 M $AgNO_3$:*** Dissolve 16 g of $AgNO_3$ in some distilled water in a 1-L volumetric flask and fill it to the mark.
9. ***3 M HNO_3:*** Combine 190 mL of 60% HNO_3 solution *slowly* with some distilled water in a 1-L volumetric flask and fill it to the mark.
10. ***5 M NH_3:*** Combine 340 mL of 30% NH_3 solution with some distilled water in a 1-L volumetric flask and fill it to the mark.
11. ***3 M H_2SO_4:*** Combine 167 mL of 98% H_2SO_4 solution *slowly* with some distilled water in a 1-L volumetric flask and fill it to the mark.

    Note: Add the 98% H_2SO_4 solution slowly to some distilled water while mixing and not the other way around.

Safety

Add these important safety precautions to your normal laboratory procedures:

- Wear safety goggles throughout this experiment.
- Concentrated acids are extremely dangerous. Pay extra attention to avoid contact with skin and eyes.
- Wash acids off with plenty of water in case of skin contact.
- Add concentrated acids to water or solutions *very slowly*.

Procedure with Inquiry

Note: The procedure section of this set of labs typically comes with Tech Tips (indicated by the symbol "�" and a superscripted number following a step). No Tech Tips apply to this particular lab.

Set Up

1. To prepare a fresh set of test tubes: Procedures 1 and 2 should be performed with a set of test tubes in which each test tube contains a known anion. To set up your test tubes:

a. Label 4 clean test tubes "1" through "4" and place them in the test tube rack.

b. Label the disposable pipets to prevent contamination of the solutions.

c. Add 4 to 5 drops of KH_2PO_4, Na_2SO_4, NaCl, and $NaNO_3$ to the test tubes in the order shown in Table 2.

Table 2: Solutions for Step 1.

Test Tube	Known Anion
1	PO_4^{3-}, phosphate
2	SO_4^{2-}, sulfate
3	Cl^-, chloride
4	NO_3^-, nitrate
5	Unknown solution

d. Add 5 M ammonia to each solution by drop until it is basic when tested with litmus paper: After thoroughly mixing, touch the solution in the test tube with a clean stirring rod and then touch a piece of litmus paper with the stirring rod for testing.

Note: Use different stirring rods for each solution or, if using a single stirring rod, thoroughly rinse and dry the stirring rod before mixing the next solution.

2. In a fifth test tube, prepare the unknown solution as follows:

a. Add 10 to 15 drops of the unknown solution. The unknown solution has some of the anions you are testing.

b. Add 5 M ammonia to the unknown solution by drops until it is basic when tested with litmus paper: After thoroughly mixing, touch the solution in the test tube with a clean stirring rod and then touch a piece of litmus paper with the stirring rod for testing.

Collect Data

Procedure 1: $Ba(NO_3)_2$ test

3. Prepare a fresh set of test tubes as described in the Set Up section.

4. Add 2 to 3 drops of $Ba(NO_3)_2$ to test tubes 1 through 4 to form precipitates between Ba^{2+} and some of the anions.

5. Which anions precipitate with Ba^{2+} ions?

Precipitation occurs with SO_4^{2-} and PO_4^{3-} ions.

6. Record your observations in Table 3 in the Data Analysis section.

7. ***Unknown***: Add $Ba(NO_3)_2$ solution drop by drop to your unknown until precipitation occurs.

Note: Precipitation should occur after adding 1-2 drops of $Ba(NO_3)_2$. If there is no precipitate after adding 1-2 drops, stop adding $Ba(NO_3)_2$.

8. ***Unknown***: Centrifuge the mixture in the test tube. Using a clean test tube, separate the supernatant (label it Supernatant 1) from the precipitate (label it Precipitate 1) and save them both.

9. ***Unknown***: Record your observations in Table 4.

10. To each test tube (from 1 through 4), that contains a precipitate formed with $Ba(NO_3)_2$, add 6 M HNO_3 drop by drop until the solution is acidic when tested with litmus paper after stirring.

11. Which precipitate dissolved in HNO_3?

The precipitate formed with PO_4^{3-} ions dissolves.

12. Record your observations in Table 3.

13. ***Unknown***: Add 6 M HNO_3 drop by drop to the precipitate obtained (if any) from your unknown (Precipitate 1).

14. ***Unknown***: Observe if there is any partial or complete dissolution. Record your observations in Table 4.

15. ***Unknown***: Using a clean test tube, separate the supernatant from the precipitate, if there is any, and label them as Precipitate 2 and Supernatant 2.

16. ***Unknown***: Was there any dissolution? If so, which anion was present? If not or if there was precipitate left, that would prove the presence of which ion?

Partial dissolution is evidence of the presence of PO_4^{3-} ions. Any remaining precipitate is $BaSO_4$, which indicates the presence of SO_4^{2-} ions in the original solution.

17. ***Unknown***: Record your observations in Table 4.

Procedure 2: $AgNO_3$ test

18. Prepare a fresh set of test tubes labeled 1 through 4 as described in the Set Up section.

19. Using the graduated cylinder, dilute each solution with 1 mL of distilled water.

20. Add 2 drops of $AgNO_3$ to each of the four test tubes. Some of the anions should combine with the silver ion to form insoluble precipitates.

21. Add NH_3 solution by drops to the solution that contained the Cl^- ions until the precipitate dissolves.

22. Record your observations in Table 3 in the Data Analysis section.

23. ***Unknown***: Which anions have been removed with $Ba(NO_3)_2$ and which might be present in Supernatant 1?

SO_4^{2-} and PO_4^{3-} ions have been removed and Cl^- and NO_3^- ions could be present.

24. ***Unknown***: Add 2 drops of $AgNO_3$ solution to Supernatant 1.

25. ***Unknown***: If there is a precipitate, what anion had to be present?

Since there only Cl^- and NO_3^- ions could be present, precipitation indicates the presence of Cl^-.

26. ***Unknown***: Record your observations in Table 4.

27. ***Unknown***: Which anions might be present in Supernatant 2?

SO_4^{2-} ions were removed and remain removed. PO_4^{3-} ions have been removed but dissolved again with HNO_3. Therefore PO_4^{3-} ions could be present.

28. ***Unknown***: Add 2 drops of $AgNO_3$ solution to Supernatant 2. Add NH_3 solution until the precipitate dissolves.

29. ***Unknown***: If there is precipitation, what anion has to be present?

Since only PO_4^{3-} and NO_3^- ions could be present, precipitation indicates the presence of Cl^-.

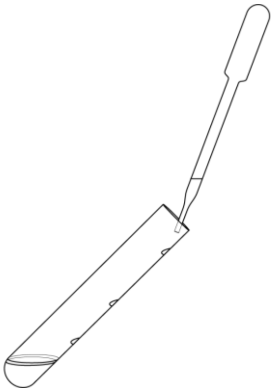
30. ***Unknown***: Record your observations in Table 4.

Procedure 3: The brown ring test for nitrate ion

31. Add 10 drops of 0.2 M $NaNO_3$ solution into a clean test tube.

32. Add 3 M H_2SO_4 drop by drop while stirring until the solution is acidic when tested with litmus paper.

33. Add 5 drops of freshly prepared saturated iron(II) sulfate ($FeSO_4$) solution.



34. Gently tilt the test tube to a 45° angle and very carefully add 5 drops of concentrated H_2SO_4 so the drops flow down the side of the test tube and float on top of the solution.

Note: Do not mix the solutions.

35. Observe the indication of the presence of NO_3^-. Record your observations in Table 3.

Note: A very faint brown ring will appear at the interface between the liquid layers in the test tube.

36. ***Unknown***: Add a few drops of fresh unknown in a clean test tube and perform the analysis for nitrate ions.

37. ***Unknown***: Record your observations in Table 4.

Data Analysis

1. Enter the equations and identified cations in Table 3 that conform to your observations.

Table 3: Test observations and results with known anions

Procedure	Anion	Actions	Observations	Proposed Equations
1: $Ba(NO_3)_2$ test for PO_4^{3-} and SO_4^{2-} ions	PO_4^{3-}	$Ba(NO_3)_2$ added	white precipitate formed	$2PO_4^{3-}(aq) + 3Ba^{2+}(aq) \rightarrow Ba_3(PO_4)_2(s)$
		HNO_3 added	precipitate disappears	$Ba_3(PO_4)_2(s) + 3H^+(aq) \rightarrow$ $3Ba^{2+}(aq) + H_3PO_4(aq)$
	SO_4^{2-}	$Ba(NO_3)_2$ added	white precipitate formed	$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
		HNO_3 added	precipitate remains	
	Cl^-	$Ba(NO_3)_2$ added	no precipitate formed	
	NO_3^-	$Ba(NO_3)_2$ added	no precipitate formed	

2: AgNO$_3$ test for Cl$^-$ ions and PO$_4^{3-}$ ions	PO$_4^{3-}$	AgNO$_3$ added	yellow precipitate formed	$3\,Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3(PO_4)(s)$
		NH$_3$ added	no change—precipitate didn't dissolve	
	SO$_4^{2-}$	AgNO$_3$ added	no precipitate formed	
	Cl$^-$	AgNO$_3$ added	white precipitate formed	$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
		NH$_3$ added	precipitate dissolves	
	NO$_3^-$	AgNO$_3$ added	no precipitate formed	
3: Brown ring test for NO$_3^-$	NO$_3^-$	NaNO$_3$, H$_2$SO$_4$, FeSO$_4$, and H$_2$SO$_4$ added	Very faint brown ring	

Table 4: Analysis of unknown solution

Step	Action	Observations	Anion Present
1	Add Ba(NO$_3$)$_2$ solution by drops until precipitation occurs.	White precipitate	Possibly SO$_4^{2-}$ and PO$_4^{3-}$ are present.
2	Separate the precipitate (Precipitate 1) from the supernatant (Supernatant 1). Add HNO$_3$ solution to the precipitate. Separate supernatant (Supernatant 2) from precipitate (Precipitate 2)	Some precipitate dissolved	The remaining precipitate is BaSO$_4$, indicating the presence of SO$_4^{2-}$.
3	Add AgNO$_3$ to Supernatant 2.	Yellow precipitate is observed.	The precipitate is Ag$_3$PO$_4$, which confirms the presence of PO$_4^{3-}$.
4	Add AgNO$_3$ solution Supernatant 1and then added NH$_3$ solution.	White precipitate. Adding NH$_3$ solution dissolves the precipitate.	The precipitate that dissolves in NH$_3$ is AgCl, indicating the presence of Cl$^-$.
5	Test for NO$_3^-$.	Ring should be observed.	Presence of NO$_3^-$ can be confirmed.

2. List the anions present in your unknown.

In this example, PO_4^{3-}, SO_4^{2-}, Cl^-, and NO_3^- were present.

Analysis Questions

1. Ag^+ ions in a solution with PO_4^{3-} ions resulted in a precipitate. HNO_3 was then added. Provide an equation for the reaction between the precipitate and HNO_3.

$Ag_3PO_4(s) + 3H^+(aq) \rightarrow 3Ag^+(aq) + H_3PO_4(aq)$

2. Consider the result of the $Ba(NO_3)_2$ test with SO_4^{2-} ions. What happened when you added HCl to the reaction mixture? Also consider that adding HNO_3 would not change the precipitate. What conclusion can you draw about the product of $BaCl_2$ and SO_4^{2-}?

The product, $BaSO_4$, is rather stable because it is insoluble in HCl and HNO_3.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Ag^+ reacts with all three types of phosphate ions. Show the equation for each type.

$3Ag^+(aq) + H_2PO_4^-(aq) \rightarrow Ag_3PO_4(s) + 2H^+(aq)$

$3Ag^+(aq) + HPO_4^{2-}(aq) \rightarrow Ag_3PO_4(s) + H^+(aq)$

$3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)$

2. Propose a method to distinguish between the PO_4^{3-} and $H_2PO_4^-$ ions.

After the reaction is completed, the reaction mixture with the $H_2PO_4^-$ ion is acidic because of the released H^+ ions that can be detected with an acid-base indicator such as litmus paper.

3. CO_3^{2-} ions behave very much like SO_4^{2-} ions with Ag^+ and Ba^{2+}. However, they react with HCl differently. Propose a possible equation for the reaction between CO_3^{2-} and HCl. (Hint: One of the products is unstable and decomposes to form a gas.)

$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2CO_3$

$H_2CO_3 \rightarrow CO_2(g) + H_2O$

CO_2 leaves the test tube as gas and fizzing can be observed.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. $AgNO_3$ added to a solution formed a white precipitate. This could indicate the presence of:

A. Cl^-

B. NO_3^-
C. SO_4^{2-}
D. None of these

2. A yellow precipitate can be:

A. **Ag_3PO_4**
B. $AgCl$
C. $BaSO_4$
D. $Ba_3(PO_4)$

3. A PO_4^{3-} ion yields a white precipitate when mixed with an unknown cation. The resulting precipitate can then be dissolved in HCl. The cation could be:

A. Ag^+
B. Pb^{2+}
C. **Ba^{2+}**
D. Ni^{2+}

Extended Inquiry Suggestions

Challenge your students by giving them a number of unknown solutions in test tubes and have them perform the reactions among only those solutions without using any other reagents. Allow your students to identify the contents of the test tubes using a reaction matrix and what they have learned in this experiment. An example of a reaction matrix is shown below.

Analysis of Anions

The following solutions are included: $BaCl_2$, $AgNO_3$, HCl, Na_3PO_4, Na_2SO_4, and $Pb(NO_3)_2$ and are put in test tubes (TT) numbered "1" through "6." (The dash indicates there was no change when the solutions were combined.)

Reaction Matrix

TT	1	2	3	4	5	6
1		—	White precipitate that does not dissolve with heat or by adding HCl	—	—	Yellow precipitate
2			—	White precipitate that does not dissolve with heat or by adding HCl	White precipitate that does not dissolve with heat or by adding HCl	—
3				White precipitate that dissolves with heat	—	—
4					White precipitate that dissolves with heat	White precipitate that does not dissolve with heat or by adding HCl
5						White precipitate that does not dissolve with heat. It does dissolve by adding HCl
6						

Your students can apply the following strategy:

1. The white precipitate that dissolves by heat has to be $PbCl_2$. Therefore #3 and #4 are Pb^{2+} and HCl. Since 3 has fewer reactions, let's assume it is HCl, and then 4 has to be Pb^{2+}. Indeed, among the solutions, Pb^{2+} reacts with four of the solutions, which is the case with solution #4. Therefore solution #3 is HCl and solution #4 is $Pb(NO_3)_2$.

2. The white precipitate which dissolves in HCl has to be $Ba_3(PO_4)_2$. Therefore, either #5 is $BaCl_2$ and #6 is Na_3PO_4 or the other way around.

3. As Ag^+ and PO_4^{3-} are among the cations and anions, there should be a yellow precipitate, Ag_3PO_4. The only yellow precipitate is from the reaction between #1 and #6. In the light of the previous point, #6 must be Na_3PO_4 then and #1 should be $AgNO_3$. Also in the light of the previous point, #5 must be $BaCl_2$.

4. $AgNO_3$ forms a white precipitate with HCl. The only white precipitate that #1 gives is with #3, therefore #3 is confirmed as HCl and #1 is $AgNO_3$.

5. #2 must then be Na_2SO_4 which can be confirmed with the reaction with #4 (white precipitate forms: $PbSO_4$) and #5 (white precipitate forms: $BaSO_4$).

Therefore, the solutions are as shown in the following table.

Answers for the Reaction Matrix

Test Tube	**Solution**
1	$AgNO_3$
2	Na_2SO_4
3	HCl
4	$Pb(NO_3)_2$
5	$BaCl_2$
6	Na_3PO_4

Acid–Base Chemistry

21. Standardizing a Solution of Sodium Hydroxide

Objectives

Students determine the concentration of a sodium hydroxide solution by titrating it with a standard solution of known concentration.

Procedural Overview

Students gain experience conducting the following procedures:

- Calibrating a pH sensor and a drop counter
- Preparing a titrant solution
- Preparing a standard solution
- Performing a titration and using the results to calculate the concentration of the titrant

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	60 minutes

Materials and Equipment

For each student or group:

- Data collection system
- pH sensor
- Drop counter with micro stir bar
- Magnetic stirrer
- Ring stand
- Beaker (1), 250-mL
- Beaker (1), 100-mL
- Beaker (2), 10-mL
- Volumetric flask, 250-mL
- Buret, 50-mL
- Buret clamp
- Clamp, right-angle
- Funnel
- Potassium hydrogen phthalate (KHP), 0.6 g
- Sodium hydroxide (NaOH), 1.0 g
- Buffers, pH 4 and pH 10, 10 mL
- Water, deionized, 500 mL
- Wash bottle with deionized water
- Parafilm® or aluminum foil
- Cotton swab or tissue

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Acid–base reactions
- Balancing chemical equations
- Basic stoichiometric calculations
- Concentration calculations
- Formula weight

Related Labs in This Guide

Labs conceptually related to this one include:

- Acid–Base Titration
- Oxidation–Reduction Titration
- Using Different Indicators for pH Determination
- Properties of Buffer Solutions
- Determination of a Solubility Product
- Determining K_a by Half-Titration of a Weak Acid

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system. �(2.1)
- Connecting multiple sensors to the data collection system �(2.2)
- Calibrating a drop counter �(3.4)
- Calibrating a pH sensor �(3.6)
- Starting and stopping data recording �(6.2)

- Displaying data in a graph �(7.1.1)
- Adjusting the scale of the graph �(7.1.2)
- Displaying multiple runs in a graph �(7.1.3)
- Changing the variable on the x-axis and y-axis of a graph �(7.1.9)
- Finding the slope at a point on the data plot �(9.3)
- Saving your experiment �(11.1)
- Printing the graph. �(11.2)

Background

Chemicals react in strict stoichiometric ratios based on the coefficients of the balanced chemical reaction. This fact allows one to predict the amount of one reactant or product when another is known. When reactions occur in solution, the amount of one reactant is determined by the relationship between concentration, volume, and amount of the substance:

$$c = \frac{n}{V}$$

where

c = concentration of the substance (mol/L)

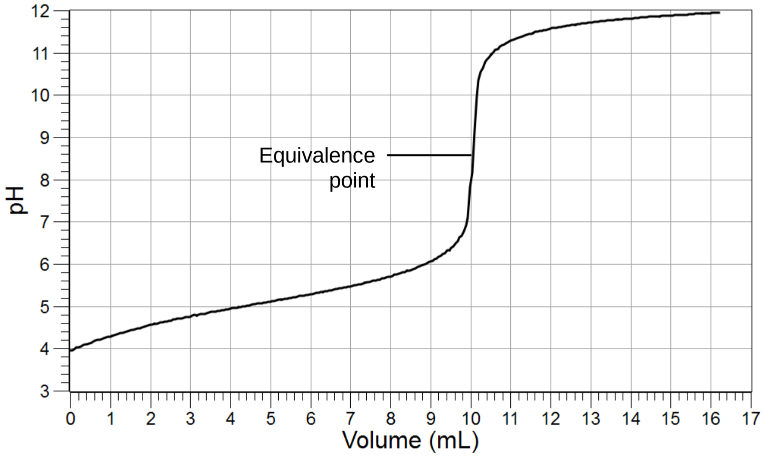
V = volume of the solution (L)

n = amount of substance (mol)

Titration is a common technique used to determine the quantity of one reactant when another is known. In a titration, an indicator gives a visual signal to the experimenter when one reactant has been completely used up. At this point, called the equivalence point, the experimenter will know the volume and molarity, and, therefore, the number of moles of one reactant. By using the stoichiometric ratios, the experimenter can determine the number of moles of the other reactant.

In this lab, a titration is used to standardize a solution of sodium hydroxide. In other words, this experiment uses the laboratory procedure known as “titration” to accurately determine the molarity of a sodium hydroxide solution.

Determination of the equivalence point can be done using indicators, but there is always a level of subjectivity when looking for specific colors. This can lead to large uncertainties in the equivalence point. To avoid subjectivity, a pH sensor is used to detect the equivalence point. A pH sensor monitors the pH as the titrant solution is added. The steepest point of the titration curve represents the equivalence point.



Pre-Lab Experiment

Setting the stage for the experiment

Sodium hydroxide solution is often used as the base in acid–base titrations. Unfortunately, solid NaOH is hygroscopic, which means that it readily absorbs moisture from the air. Therefore, its mass does not provide precise information about the amount of NaOH present in a sample.

NaOH also absorbs CO_2 from the air, forming sodium carbonate. This further reduces the amount of NaOH in the pellets. For these reasons, NaOH is not a suitable primary standard and a solution cannot be prepared with precisely known molarity using mass. Additionally, once prepared, a solution of NaOH will continue to react with CO_2 from the air and can even react slowly with glass if stored in a glass container for too long.

To overcome these obstacles, we will standardize our NaOH solution using an acid as the primary standard. Potassium hydrogen phthalate ($KHC_8H_4O_4$) is often referred to as KHP. KHP is available as a pure, stable, crystalline solid with an accurately measurable mass.

The solid $KHC_8H_4O_4$ dissociates in aqueous solutions:

$$KHC_8H_4O_4 \rightarrow K^+ + HC_8H_4O_4^-$$

The hydrogen phthalate is a weak acid and the dissociation process is:

$$HC_8H_4O_4^- + H_2O \rightleftharpoons C_8H_4O_4^{2-} + H_3O^+$$

The H_3O^+ represents the acid in the solution. The amount of that acid can be measured using NaOH.

NaOH also dissociates in aqueous solutions:

$$NaOH \rightarrow Na^+ + OH^-$$

This means that 1 mol of NaOH will yield 1 mol of OH^- ions. The net ionic equation for the acid–base reaction between solutions of NaOH and KHP is:

$$HC_8H_4O_4^- + OH^- \rightleftharpoons C_8H_4O_4^{2-} + H_2O$$

The stoichiometric ratio between NaOH and KHP is 1:1:

$$n_1 = n_2$$

where

n_x = number of moles and the subscript "1" represents NaOH and subscript "2" represents KHP.

Measuring the mass of KHP, we can easily calculate its number of moles:

$$n_2 = \frac{m_2}{\mathrm{FW_{KHP}}} \tag{1}$$

where

n_2 = amount of KHP (mol)

m_2 = mass of KHP (g)

$\mathrm{FW_{KHP}}$ = formula weight of KHP (g/mol)

The number of moles of KHP will react with the same number of moles of NaOH (using $n_1 = c_1V_1$) because there is a stoichiometric ratio of 1:1 between KHP and NaOH:

$$n_2 = c_1 V_1$$

$$c_1 = \frac{n_2}{V_1} = \frac{m_2}{\mathrm{FW_{KHP}}\, V_1} \tag{2}$$

where

n_2 = amount of NaOH (mol)

c_1 = concentration of KHP (mol/L)

V_1 = volume of KHP (L)

In this way, the concentration of the NaOH solution can be calculated.

A question remains. How do we know what volumes of solutions will contain the stoichiometric ratio? The pH sensor answers this question. Immerse the tip of the pH sensor in one of the solutions and gradually add the other solution. When the amount of solution added is the stoichiometrically required amount of reactant, there will be a huge jump in the pH. This indicates that the reaction is over and that the equivalence point has been reached.

In the past, color change from using organic dyes indicated the endpoint of the reaction. However, the color change from an acidic to an alkaline medium was not distinct. It relied on the subjective impression of human eyes. The pH sensor more accurately and objectively detects the equivalence point.

The experiment starts by placing a KHP solution with a known amount of KHP on a stirring plate and adding, drop by drop, a NaOH solution with unknown concentration. While adding the NaOH, monitor the pH of the KHP solution with a pH sensor and record the pH readings as a function of the added amount of NaOH solution.

After each additional drop of NaOH solution is added to the KHP solution, the pH is recorded. The pH signals how much NaOH solution was necessary to react with KHP to reach the equivalence point.

Example calculation to try

In this example, 0.41 g of solid NaOH was dissolved in a beaker with water. The solution was transferred into a 100-mL volumetric flask and filled to the 100 mL mark. 0.2400 g of KHP was dissolved in water in another beaker. By titrating the KHP solution while monitoring the pH and the volume of NaOH solution added, the equivalence point was reached after 10.50 mL of a NaOH solution was added to the KHP.

Necessary conversion:

$$V_1 = 10.50 \text{ mL} = 1.050 \times 10^{-2} \text{ L}$$

Using Equation 1, the number of moles of KHP is calculated:

$$n_2 = \frac{(0.2400 \text{ g})}{(204.22 \frac{\text{g}}{\text{mol}})}$$

$$n_2 = 1.175 \times 10^{-3} \text{ mol KHP}$$

Recall that the stoichiometry between KHP and NaOH suggests a 1:1 ratio. Using Equation 2, calculate the concentration of the NaOH solution as follows:

$$c_1 = \frac{(1.175 \times 10^{-3} \text{ mol NaOH})}{(1.050 \times 10^{-2} \text{ L})}$$

$$c_1 = 1.119 \times 10^{-1} \frac{\text{mol}}{\text{L}} = 1.119 \times 10^{-1} \text{ M}$$

The concentration of the NaOH solution was 1.119×10^{-1} M.

1. Does it matter how much water you use to make the KHP solution?

No, it does not. The required volume of NaOH solution would depend only on the number of moles of KHP and that does not depend on how much water was used to make the solution.

2. If you accidentally overfill the volumetric flask with the NaOH solution above the mark would that introduce an error?

No, the titration determines the concentration of the solution, regardless of its preparation.

3. If you accidentally spilled a few crystals of KHP when you make the KHP solution, would that introduce an error?

Yes, the titration method relies on the fact that you know exactly how many moles of KHP are in the solution. Spilling some of it makes it impossible to know how much KHP was actually used to make the solution.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. Before the experiment, place the KHP in a desiccator, if available, to eliminate any moisture that the KHP might have absorbed.
2. An improperly closed jar can result in significant absorption of moisture and CO_2 in the NaOH. Make sure that the surface of the NaOH pellets are not covered with moisture.

Safety

Add these important safety precautions to your normal laboratory procedures:

- NaOH is caustic. If NaOH gets on your skin, rinse the exposed surface thoroughly with running water.

Procedure with Inquiry

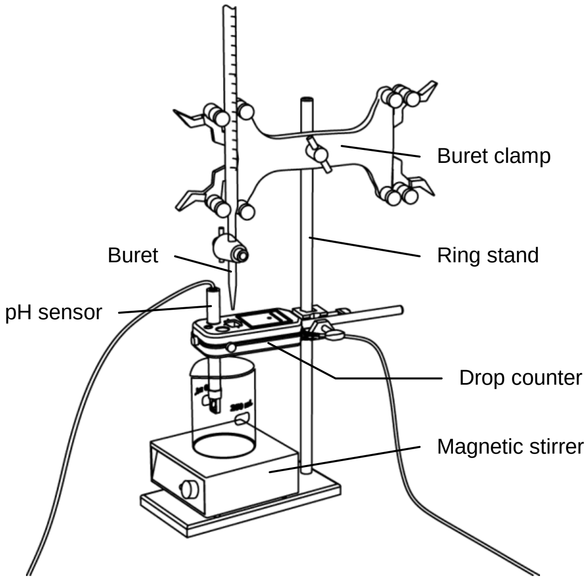
Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �$^{(1.2)}$
2. Connect a pH sensor to the data collection system. �$^{(2.1)}$
3. Connect the drop counter to the data collection system. �$^{(2.2)}$
4. Display the pH on the y-axis of a graph and Drop Count on the x-axis. �$^{(7.1.1)}$
5. Calibrate the pH sensor. �$^{(3.6)}$

6. Assemble the titration apparatus, using the steps below and the illustration as a guide.

- **a.** Position the magnetic stirrer on the base of the ring stand.
- **b.** Place a waste container (100-mL beaker) on the magnetic stirrer.
- **c.** Use the buret clamp to attach the buret to the ring stand.
- **d.** Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.
- **e.** Place the pH sensor through one of the slots in the drop counter.



7. Measure about 1.00 g of NaOH into a 250-mL beaker with 100 mL of deionized water to make a solution. Record the mass of the NaOH:

Mass of NaOH (g): 1.02

8. Carefully transfer the solution into a 250-mL volumetric flask and fill the flask to the 250 mL mark with deionized water.

9. Seal the flask with its stopper, invert the flask, and shake it gently. Then vent the flask.

10. What happens if you do not mix the solution well?

The solution will not be homogeneous and every time you draw solution from the flask it will have a different concentration.

11. What is the expected concentration of the NaOH solution?

The expected concentration is 0.1 M, determined as follows:

$$c_1 = \frac{n_1}{V_1} = \frac{m_1}{\mathrm{FW_{NaOH}}\,V_1}$$

$$c_1 = \frac{(1.00\text{ g})}{(40\,\frac{\text{g}}{\text{mol}})(0.25\text{ L})} = 0.1\text{ M}$$

12. Rinse the buret with several milliliters of the NaOH solution:

- **a.** Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the NaOH solution.
- **b.** Open the stopcock on the buret and drain the rinse NaOH into the waste container.
- **c.** Repeat this process two more times.

13. Why is it necessary to rinse the buret with the NaOH solution?

If there is any residual water or contaminant in the buret, it will dilute the NaOH and change its concentration. Rinsing eliminates any such contamination.

14. Make sure the stopcock on the buret is in the "off" position and then use a funnel to fill the buret with about 50 mL of the NaOH solution (titrant).

15. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

16. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of NaOH. If this happens, the amount of titrant used will be inaccurate.

17. Cover the beaker containing the remaining titrant solution with a piece of Parafilm® or aluminum foil.

18. What happens if you do not cover the solution?

The solution will absorb CO_2 from the air and the NaOH concentration will change.

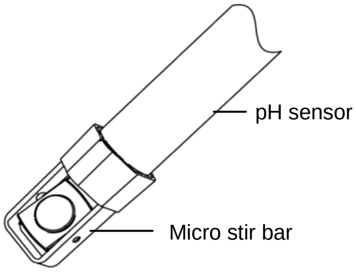
19. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

Note: Good control of the stopcock is important. Each drop should result in a blink of the LED on the drop counter. If the LED is continuously lit, you have opened the stopcock too far and you will have to start over.

20. Why will it be necessary to start your titration over again if you accidently allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

21. Add the micro stir bar to the end of the pH sensor.



22. Why is it necessary to stir the solution during a titration?

Stirring thoroughly mixes the ions in the solution so that the recorded pH reflects the pH of the entire solution.

23. Add additional NaOH to the buret so the solution is above the zero mark. Allow some of the NaOH solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 1.

24. Remove the waste container.

25. Measure about 0.200 g of KHP to the nearest milligram and record this value in Table 2. Then place the KHP, with about 50 mL of water, into a 100-mL beaker.

26. Place the beaker containing the KHP solution on the magnetic stirrer.

27. Add enough deionized water to the solution so that the tip of the pH sensor is covered with solution.

28. Turn on the magnetic stirrer at a slow and steady rate.

29. What will happen if the solution is stirred too fast? What will happen if it is too slow?

If the solution is stirred too fast, the solution will spatter or spill, introducing error. If it is to slow, the titrated solution will not be homogeneous and the pH sensor will report a false reading.

Collect Data

30. Clean the lens of the drop counter inside the opening through which the drops are going with water and a cotton swab or tissue.

31. Start recording data. �(6.2)

32. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

33. Continue the titration past the equivalence point until the pH curve flattens.

34. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

35. Stop recording data. �(6.2)

36. In Table 1, record the final drop count and the final volume of the titrant in the buret to a precision of 0.01 mL.

37. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 1.

Table 1: Titration data

Titration Information	Trial 1	Trial 2	Trial 3
Initial reading of NaOH in the buret (to 0.01 mL)	0.00	0.00	0.00
Final reading of NaOH in the buret (to 0.01 mL)	17.20	16.90	16.20
Volume of titrant (to 0.01 mL)	17.20	16.90	16.20
Final drop count	192	201	202

38. Calibrate the drop counter. �(3.4)

39. Set the horizontal axis to the calculated volume. �(7.1.9)

40. In Table 2, record the volume of titrant used to reach the equivalence point. The equivalence point will be where the slope of the titration curve is the steepest. Find the steepest slope of the data plot to determine this point. �(9.3)

41. Refill the buret above the zero mark with the NaOH solutions.

- **a.** Fill the buret above the zero mark and allow some of the NaOH solution to drip into a waste container until the bottom of the meniscus is lined up with the zero mark or just below.
- **b.** Record the starting point in Table 1.

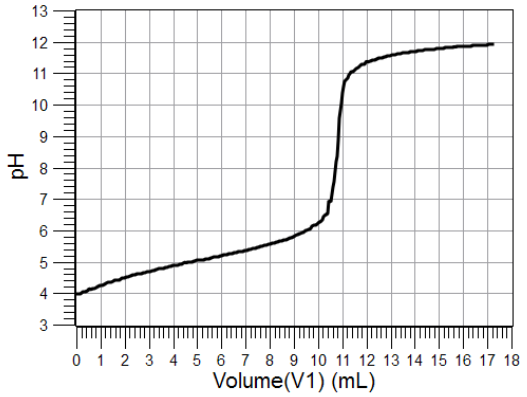
42. Clean the lens of the drop counter between runs with water and a cotton swab or tissue.

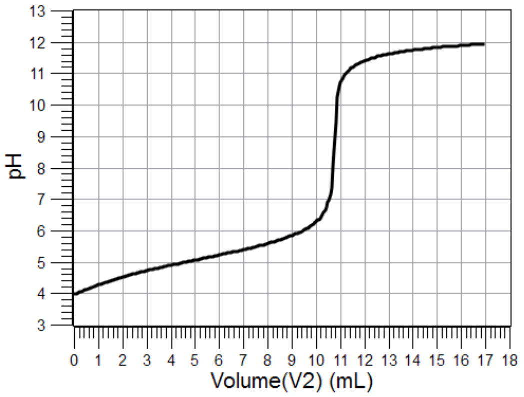
43. Repeat the titration procedure with two more KHP samples. Record the mass of the samples in Table 2.

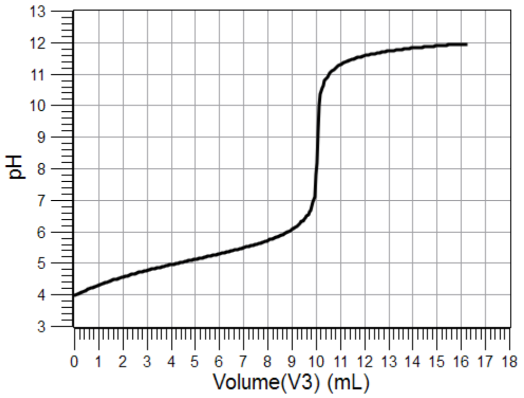
44. Once you determine the concentration of the NaOH solution, label the solution and place it in a safe place for use in the “Acid–Base Titration” experiment.

45. Save your experiment �(11.1) and clean up according to your instructor's instructions.

46. For each titration curve, sketch the graphs or print the graphs �(11.2) and paste them below.







Data Analysis

1. What is the expected concentration of the NaOH titrant?

0.1 M

2. Determine the number of moles of KHP and NaOH used in the titration.

For Trial 1: $n_2 = \dfrac{(0.2160\text{ g})}{(204.22\ \frac{\text{g}}{\text{mol}})} = 1.058 \times 10^{-3}\text{ mol KHP}$

The number of moles of KHP reacts with the same number of moles of NaOH, so there is 1.058×10^{-3} mol of NaOH.

3. What is the concentration of the NaOH solution for each trial? What is the average concentration?

For Trial 1: $c_1 = \dfrac{(1.058 \times 10^{-3}\text{ mol})}{(1.080 \times 10^{-2}\text{ L})} = 0.09790\text{ mol/L}$

The average concentration is (0.09790 mol/L + 0.1000 mol/L + 0.1000 mol/L)/3 = 0.09932 mol/L

Table 2: Determination of the NaOH solution concentration

Parameter	Trial 1	Trial 2	Trial 3
Mass of KHP (g)	0.2160	0.2210	0.2070
Number of moles of KHP (mol)	1.058×10^{-3}	1.082×10^{-3}	1.014×10^{-3}
Number of moles of NaOH that can react the KHP (mol)	1.058×10^{-3}	1.082×10^{-3}	1.014×10^{-3}
Volume of titrant to reach the equivalence point (mL)	10.80	10.80	10.10
Concentration of NaOH solution (mol/L)	0.09790	0.1000	0.1000
Average concentration of NaOH solution (mol/L)	0.09932		

Analysis Questions

1. If you measure 0.001 mol of KHP and you know the approximate concentration of NaOH is 0.1 M, what do you expect the volume of NaOH must be to reach the equivalence point?

$$V = \frac{n}{c}$$

$$V = \frac{(0.001\ \text{mol})}{0.1\ \frac{\text{mol}}{\text{L}}} = 0.01\ \text{L} = 10\ \text{mL}$$

2. If you measure the NaOH and notice there is moisture on the pellets, how does the moisture affect the concentration of the NaOH solution?

It will lower the actual concentration since only part of the measured mass is NaOH.

3. Do you have to worry about experimental error if there is moisture on the NaOH pellets?

No, the solution will be standardized anyway.

Synthesis Questions

Use available resources to help you answer the following questions.

1. If no NaOH is available, would KOH work in place of NaOH?

Yes, it would. KOH, however, is more sensitive to both moisture and CO_2. You would need to be more careful.

2. Why did we not use diluted HCl solution to standardize the NaOH solution? (Hint: HCl solutions are dilutions of concentrated HCl, which is *about* a 12 M concentration).

The exact concentration of the concentrated HCl solution is not known. Therefore, we cannot measure an exact amount of it to standardize the NaOH solution.

3. What method will allow you to use diluted HCl solution as a standardizing solution?

If you standardized your NaOH solution, you can use that to standardize a diluted HCl solution that you prepared.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Which of the following statements is incorrect?

- **A. An error in measuring the mass of KHP will not cause experimental error.**
- **B.** An error in the final volume reading from the buret will result in experimental error.
- **C.** KOH could be a viable option for replacing NaOH.
- **D.** Overfilling the volumetric flask with the NaOH solution does not introduce experimental error.

2. If you had to add 65 mL more of water to make sure that the tip of the pH sensor is covered with KHP solution (more than the 50 mL of water you initially put in the beaker), do you have to consider this additional 65 mL in your calculations?

- **A.** Yes. You have to recalculate the concentration of KHP accordingly.
- **B.** You do if you measured the precise amount of water that you added.
- **C. No, regardless of how much water is in the beaker, the amount of KHP is the same. Therefore, it will use the same amount of NaOH solution.**
- **D.** Yes, regardless of how much KHP is in the beaker, the amount of water will determine how much NaOH solution is necessary.

3. Does moisture in the KHP introduce error?

- **A.** No, only contaminations will. The solution of KHP is aqueous, in any case.
- **B.** Yes, moisture may cause some crystals to stick to the tools you use to measure the KHP.
- **C. Yes, for KHP, the measurement of mass will include an unknown amount of water. You will not know how much of that mass is KHP.**
- **D.** It depends on how carefully you do the experiment.

Extended Inquiry Suggestions

Extend the standardization process to include diluted HCl solutions. To solve problems requiring an HCl solution with known concentration, an HCl solution must be standardized. For instance, the $CaCO_3$ content of a stomach-acid neutralizing pill can be determined using an HCl solution with known concentration.

If $KHCO_3$ is available, consider showing that there are other standardizing materials besides KHP.

If the class has a sufficiently solid math background, consider introducing the first derivative of the pH versus the volume curve to determine the equivalence point more accurately. As the equivalence point occurs where the slope of the pH versus the volume curve is the highest, the first derivative of that function will have a sharp maximum.

22. Acid–Base Titration

Objectives

Students determine the molar concentration of a strong acid solution by titrating measured volumes with a strong base of known concentration.

Note: Use the sodium hydroxide solution students determined the concentration of in the “Standardizing a Solution of Sodium Hydroxide” experiment.

Procedural Overview

Students gain experience conducting the following procedures:

- Performing a titration and using the equivalence point volume of the titrant to calculate the concentration of the analyte
- Calibrating a pH sensor and drop counter

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- pH sensor
- Drop counter and micro stir bar
- Magnetic stirrer
- Buret, 50-mL
- Graduated pipet with rubber bulb, 25-mL
- Beaker, 100-mL (2)
- Beaker, 25-mL (2)
- Clamp, right-angle
- Clamp, buret
- Ring stand
- Parafilm® or aluminum foil
- Funnel
- Hydrochloric acid, unknown concentration, 70 mL[1]
- Sodium hydroxide (NaOH), standardized by student in previous experiment, 100 mL[2, 3]
- Buffers, pH 4 and pH 10, 10 mL
- Deionized water, 100 mL
- Wash bottle with deionized water
- Cotton swab or tissue

---

[1] To prepare the solution, refer to the Lab Preparation section.

[2] The NaOH solution should have been determined to at least three decimal places in the range of 0.1 M concentration.

[3] The sodium hydroxide was prepared during the “Standardizing a Solution of Sodium Hydroxide” experiment.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Acid-base reactions
- Balancing chemical equations
- Basic stoichiometric calculations
- Concentration calculations (mol/L)
- Formula weight
- Preparing standard solutions

Related Labs in This Guide

Pre-requisites:

- Standardizing a Solution of Sodium Hydroxide

Labs conceptually related to this one include:

- Oxidation–Reduction Titration
- Using Different Indicators for pH Determination
- Properties of Buffer Solutions
- Determining K_a by Half-Titration of a Weak Acid
- Conductometric Titration
- Determination of the K_a values of Two Isomer Multi-Protic Acids

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system. �(2.1)
- Connecting multiple sensors to the data collection system �(2.2)
- Calibrating a drop counter �(3.4)

- Calibrating a pH sensor �(3.6)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Adjusting the scale of the graph �(7.1.2)
- Displaying multiple data runs in a graph �(7.1.3)
- Changing the variable on the x-axis and y-axis of a graph �(7.1.9)
- Finding the slope at a point on the data plot �(9.3)
- Saving your experiment �(11.1)
- Printing the graph. �(11.2)

Background

Titration, a common quantitative laboratory method, determines the concentration of a reactant. A reagent of known concentration, called the titrant, is used to react with a measured volume of the reactant, called the analyte. Because volume measurements of the analyte and titrant are key factors in this type of analysis, titration is also known as a “volumetric analysis.”

In this experiment the titration is between an acid and a base, using an acid-base reaction:

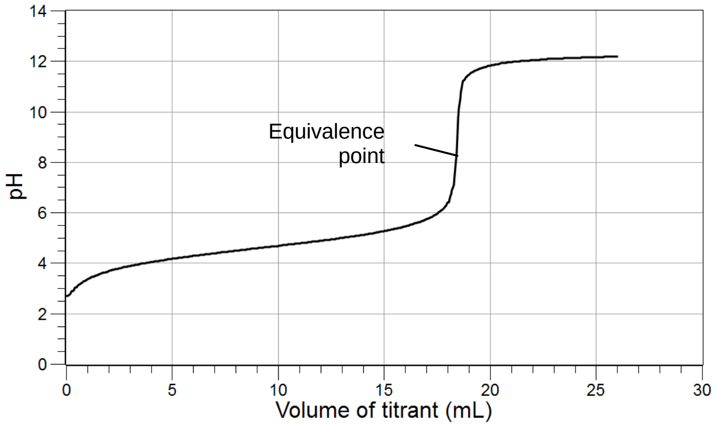
$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$

Acids contain hydronium (H_3O^+) ions and bases contain hydroxide (OH^-) ions. The product of an acid-base reaction is always water. This type of reaction is also known as a neutralization reaction; that is, this is a type of reaction where one reactant neutralizes the other.

Pre-Lab Experiment

Setting the stage for the experiment

When a basic solution is added to an acidic solution of unknown concentration, hydroxide ions from the basic solution react with hydronium ions from the acidic solution. This reaction forms neutral water. Since pH is a measure of the molarity of hydronium ions, the pH changes as hydronium ions react with the added hydroxide ions. The point at which the number of moles of hydroxide ions added is equal to the number of moles of hydronium ions is called the equivalence point. The detection of the equivalence point usually is easy since the pH tends to jump very sharply at that point, as shown in the graph:



The net ionic equation shown below is an example of the reaction of a strong acid (HCl) with a strong base (NaOH).

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$

The titration in this experiment is performed using the same configuration as in the "Standardizing a Solution of Sodium Hydroxide" experiment.

Example calculation to try

In an experiment, 20.00 mL of an HCl solution with an unknown concentration was titrated with a 0.0980 M NaOH solution:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$$

The equivalence point appeared when 22.45 mL of the NaOH solution was added to the HCl solution, which works out to the following number of moles of NaOH:

$$n_1 = c_1 V_1$$

$$n_1 = \left(0.0980\ \tfrac{\text{mol}}{\text{L}}\right)\left(0.02245\ \text{L}\right)$$

$$n_1 = 2.20 \times 10^{-3}\ \text{mol NaOH}$$

where

n_1 = number of moles of NaOH added to reach the equivalence point (mol)

V_1 = volume of NaOH added to reach the equivalence point (L)

c_1 = concentration of the NaOH standard (mol/L)

Since HCl and NaOH react in a 1:1 stoichiometric ratio, the number of moles of HCl in the sample with unknown concentration must be the same. Knowing the number of moles, the concentration of the hydrochloric acid solution can be calculated:

$$n_1 = n_2$$

$$n_2 = c_2 V_2$$

$$c_2 = \frac{n_2}{V_2}$$

$$c_2 = \frac{\left(2.20 \times 10^{-3} \text{ mol HCl}\right)}{\left(0.02000 \text{ L}\right)}$$

$$c_2 = 0.110 \text{ M}$$

where

n_1 = number of moles of NaOH added to reach the equivalence point (mol)

n_2 = number of moles of HCl in the sample solution (mol)

V_2 = volume of the HCl sample (L)

c_2 = concentration of the HCl solution (mol/L)

Therefore, the concentration of the unknown HCl solution is 0.1100 M.

1. Does it matter what the volume is of the unknown solution you choose to titrate?

No, if more solution was chosen, then the reaction would require proportionally more NaOH solution.

2. Assuming an experiment is performed using a 50-mL buret filled to the zero mark with a standardized 0.10 M NaOH solution, and the approximate concentration of the HCl solution being titrated is 0.05 M, what is the logical amount of the unknown that you would titrate? Explain.

With a 50-mL buret, using about 25 mL of the standard is common. Knowing the concentration of HCl to be about half the concentration of NaOH, twice the volume of the HCl solution, 50 mL, will have the same number of moles as 25 mL of NaOH solution.

3. How would you measure precisely 20.00 mL of the solution?

For the most precise measurement, use a 20-mL volumetric pipet. A 20-mL or 25-mL graduated pipet can provide sufficient accuracy as well.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.100 M HCl:*** Carefully add 16.7 mL of 36% (12 M concentrated) HCl to some distilled water in a 2-L volumetric flask. Fill the flask to the mark with distilled water. Label the solution “HCl—Unknown Concentration.”

Safety

Add these important safety precautions to your normal laboratory procedures:

- If the NaOH or HCl comes in contact with skin or eyes, rinse the exposed surface thoroughly with running water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect a pH sensor to the data collection system. �(2.1)

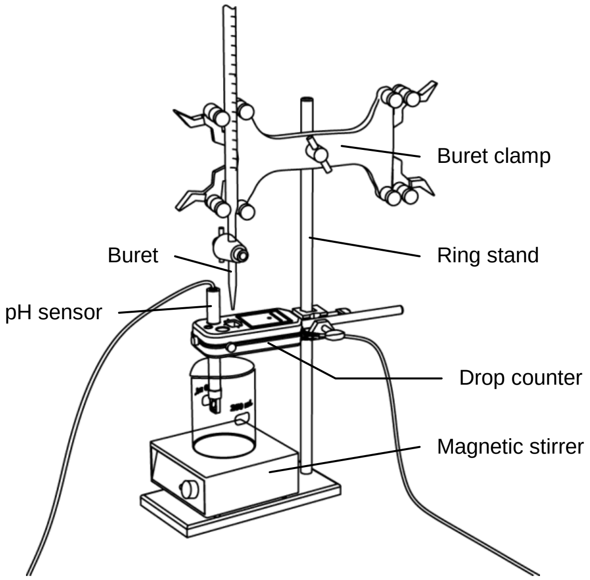
3. Connect the drop counter to the data collection system. �(2.2)

4. Display the pH on the y-axis of a graph and Drop Count on the x-axis. �(7.1.1)

5. Calibrate the pH sensor. �$^{(3.6)}$

6. Assemble the titration apparatus, using the steps below and the illustration as a guide.

- **a.** Position the magnetic stirrer on the base of the ring stand.
- **b.** Place a waste container (100-mL beaker) on the magnetic stirrer.
- **c.** Use the buret clamp to attach the buret to the ring stand.
- **d.** Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.
- **e.** Place the pH sensor through one of the slots in the drop counter.



7. Rinse the buret with several milliliters of the standardized NaOH solution:

- **a.** Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the NaOH solution.
- **b.** Open the stopcock on the buret and drain the rinse NaOH into the waste container.
- **c.** Repeat this process two more times.

8. Why is it necessary to rinse the buret with the NaOH solution?

If there is any residual water or contaminant in the buret, it will dilute the NaOH and change its concentration. Rinsing eliminates any such contamination.

9. Make sure the stopcock on the buret is in the "off" position and then use a funnel to fill the buret with about 50 mL of the NaOH solution (titrant).

10. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

11. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of NaOH. If this happens, the amount of titrant used will be inaccurate.

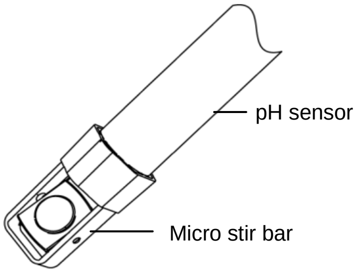
12. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

Note: Good control of the stopcock is important. Each drop should result in a blink of the LED on the drop counter. If the LED is continuously lit, you have opened the stopcock too far and you will have to start over**.**

13. Why will it be necessary to start your titration over again if you accidently allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

14. Add the micro stir bar to the end of the pH sensor.



15. Why is it necessary to stir the solution during a titration?

Stirring thoroughly mixes the ions in the solution so that the recorded pH reflects the pH of the entire solution.

16. Add additional standardized NaOH solution to the buret so the solution is above the zero mark. Allow some of the NaOH solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 1.

17. Cover the beaker containing the remaining titrant solution with a piece of Parafilm® or aluminum foil.

18. Why is it necessary to cover the beaker? (Hint: What is in the air that can potentially react with the solution?)

The CO_2 content of air can react with NaOH. This can change the concentration of the standardized solution, resulting in error.

19. Remove the waste container.

Perform the titration of the HCl solution three times, following the steps below.

20. Use the graduated pipet to transfer 20.00 mL of the HCl solution into a 100-mL beaker and set the beaker on the magnetic stirrer.

21. Add enough deionized water to the solution so the tip of the pH sensor is covered with solution.

22. Turn on the magnetic stirrer at a slow and steady rate.

Collect Data

23. Clean the lens of the drop counter inside the opening through which the drops are going with water and a cotton swab or tissue.

24. Start recording data. �(6.2)

25. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

26. Continue the titration past the equivalence point until the pH curve flattens.

27. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

28. Stop recording data. �(6.2)

29. In Table 1, record the final drop count and the final reading of the titrant in the buret to a precision of 0.01 mL.

30. Which part of the meniscus do you read?

Almost always, you read the bottom of the meniscus. If a solution is dark or cloudy, reading from the top of the meniscus may be necessary. Initial and final measurements always should be read from the same part of the meniscus.

31. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 1.

Table 1: Titration data

Titration Information	Trial 1	Trial 2	Trial 3
Initial reading of NaOH on the buret (mL)	00.00	00.00	00.00
Final reading of NaOH on the buret (mL)	28.00	26.00	34.50
Volume of titrant (mL)	28.00	26.00	34.50
Final drop count	515	486	655

32. Calibrate the drop counter. �(3.4)

33. Set the horizontal axis to the calculated volume. �(7.1.9)

34. In Table 2, record the volume of titrant, to 2 decimal places, used to reach the equivalence point. The equivalence point will be where the slope of the titration curve is the steepest. Find the steepest slope of the data plot to determine this point. �(9.3)

35. Refill the buret above the zero mark with the NaOH solution:

- **a.** Fill the buret above the zero mark and allow some of the NaOH solution to drip into a waste container until the bottom of the meniscus is lined up with the zero mark or just below.
- **b.** Record the initial reading in Table 1.

36. Clean the lens of the drop counter between runs with water and a cotton swab or tissue.

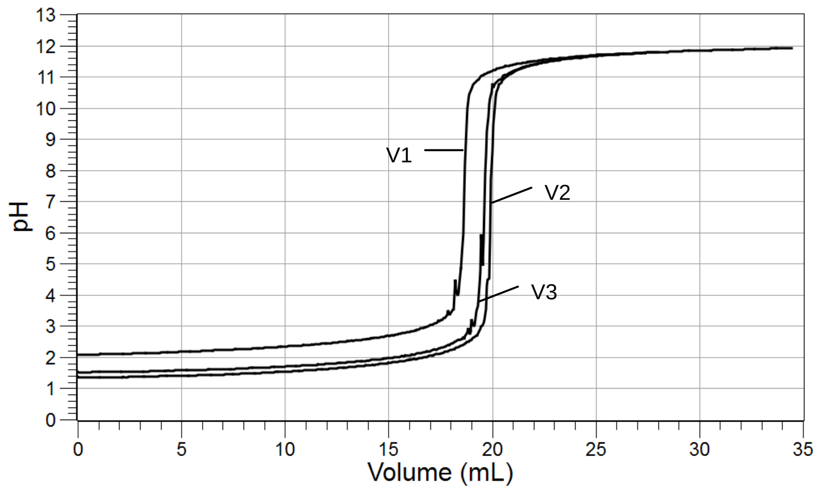
37. Remove the beaker and dispose of its contents according to the instructor’s instructions.

38. Rinse the beaker with distilled water.

39. Repeat the titration procedure with two more samples of the HCl solution.

40. Save your experiment �(11.1) and clean up according to your instructor's instructions.

41. For each titration, sketch or print the graphs�(11.2) and paste them below. Label the axes and each of the 3 curves.



Data Analysis

1. Calculate the number of moles of NaOH needed to reach the equivalence point for each trial. Record the values in Table 2.

For Trial 1:

$$n_1 = c_1 V_1$$

$$n_1 = \left(0.100\ \tfrac{\text{mol}}{\text{L}}\right)\left(0.01865\ \text{L}\right) = 1.86 \times 10^{-3}\ \text{mol}$$

2. What is the number of moles of HCl that reacted to reach the equivalence point for each trial? Record the values in Table 2.

Since HCl and NaOH react in a 1:1 stoichiometric ratio, the number of moles of HCl in the unknown sample must be the same.

For Trial 1: 1.86×10^{-3} mol HCl

3. Calculate the concentration of the HCl solution for each trial. Record the values in Table 2.

For Trial 1:

$$c_2 = \frac{n_2}{V_2}$$

$$c_2 = \frac{\left(1.86 \times 10^{-3}\ \text{mol}\right)}{\left(0.02000\ \text{L}\right)} = 0.0930\ \text{M}$$

Table 2: Determine the concentration of the HCl solution

Parameter	**Trial 1**	**Trial 2**	**Trial 3**
Initial volume of acid (mL)	20.00	20.00	20.00
Concentration of NaOH solution (M)	0.100	0.100	0.100
Volume of NaOH solution to reach the equivalence point (mL)	18.65	19.90	19.59
Amount of NaOH to reach the equivalence point (mol)	1.86×10^{-3}	1.99×10^{-3}	1.96×10^{-3}
Amount of HCl in the solution (mol)	1.86×10^{-3}	1.99×10^{-3}	1.96×10^{-3}
Concentration of the HCl solution (M)	0.0930	0.0995	0.0980
Average concentration of the HCl solution (M)	0.0968		

Analysis Questions

1. How would your results be different if you used a graduated cylinder to measure the unknown HCl solution instead of a pipet?

Expect less precise results using a graduated cylinder. This means a less accurate determination of the concentration of the unknown and a greater standard deviation from the average.

2. Why perform the experiment three times?

Each step results in random error. In order to minimize the human error, the experiment has to be performed at least three times.

3. What is the pH of the mixture of NaOH and HCl at the equivalence point? Explain.

The pH is about 7. At this point the NaOH neutralized the HCl in the sample, and the pH of a neutral solution is 7.

Synthesis Questions

Use available resources to help you answer the following questions.

1. If you analyze (using titration) a sulfuric acid (H_2SO_4) solution with approximately the same concentration and volume as the HCl solution, how would the volume of NaOH consumed be different? (Hint: H_2SO_4 yields two H^+ ions when it dissociates.)

About twice the volume of the NaOH solution is needed to reach the equivalence point.

2. How would your results be different if you pipet some of the NaOH standard solution into a beaker and titrate with the unknown HCl solution?

The results would be the same. It makes no difference which solution is the titrant and which the analyte.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. On which of the following does the accuracy of the measurement *not* depend?

A. The accuracy of the buret you are using.
B. The accuracy of the pipet you are using.
C. Concentration of the standard NaOH solution.
D. How long the NaOH solution is left uncovered, exposed to air.

2. If you substitute the same concentration of a $Ca(OH)_2$ solution for the NaOH solution, which of the following statements is correct? (Hint: $Ca(OH)_2$ yields two OH^- ions when it dissociates.) To reach the equivalence point,

A. It would require the same volume of $Ca(OH)_2$ as of the NaOH solution.
B. It would require half the volume of $Ca(OH)_2$ as of the NaOH solution.
C. It would require twice the volume of $Ca(OH)_2$ as of the NaOH solution.
D. $Ca(OH)_2$ would not work for this experiment.

Extended Inquiry Suggestions

The acid content of waste water is a real environmental concern. If you can secure waste water samples from a chrome/nickel plating plant or a food processing plant, for example, students can analyze the samples.

Consider the additional challenge that no approximate acid concentration is available. Have students discuss how to address this problem.

23. Using Different Indicators for pH Determination

Objectives

Students determine the CO_2 content of a beverage.

Procedural Overview

Students gain experience conducting the following procedures:

- Performing titrations with multiple acid-base indicators
- Comparing the use of pH indicators with electronic sensors for detecting the equivalence point of a titration

Time Requirement

♦ Preparation time	30 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	90 minutes plus overnight sample preparation

Materials and Equipment

For each student or group:

- Data collection system
- Drop counter and micro stir bar
- pH sensor
- Clamp, right-angle
- Clamp, buret
- Buret, 50-mL
- Beaker (2), 25-mL
- Beaker (2), 250-mL
- Erlenmeyer flask, 250-mL
- Graduated cylinder, 100-mL
- Phenolphthalein, 5 drops
- Methyl orange, 5 drops
- Magnetic stirrer and stir bar
- Ring stand
- Commercial soda drink, 1 can
- Kimwipes®[1]
- 4.00 M HCl solution, 100 mL[1]
- 1 M NaOH solution, 100 mL[2]
- Wash bottle with deionized water
- Funnel
- Balloon (fits on Erlenmeyer flask; holds 100 mL)
- Buffers, pH 4 and pH 10, 10 mL
- Cotton swab or tissue

[1-2] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Titration
- Acid-base reactions
- Stoichiometry of chemical reactions
- Chemical equilibrium

Related Labs in This Guide

Labs conceptually related to this one include:

- Standardizing a Solution of Sodium Hydroxide
- Acid–Base Titration
- Oxidation–Reduction Titration
- Properties of Buffer Solutions
- Determination of a Solubility Product
- Determining K_a by Half-Titration of a Weak Acid

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system. �(2.1)
- Connecting multiple sensors to the data collection system �(2.2)
- Calibrating a drop counter �(3.4)
- Calibrating a pH sensor �(3.6)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Changing the variable on the x-axis and y-axis of a graph �(7.1.9)
- Identifying data points on a graph �(9.1)

- Finding the slope at a point on the data plot �(9.3)
- Saving your experiment �(11.1)
- Printing the graph. �(11.2)

Background

Certain organic substances have a property which allows them to change color in dilute solutions when the hydrogen ion concentration of the solution attains a specific value. Substances such as phenolphthalein, which is colorless in an acid solution but becomes pink or purple in a basic solution, are called acid-base indicators. (The pH of the color change depends on the dissociation constant of the indicator, which may not be 7.) They are often used for determining the pH of solutions or to determine the equivalence point of a titration.

The most common indicators, in addition to phenolphthalein, are litmus, methyl orange, and methyl red. Litmus is a naturally occurring organic dye which turns red in an acid and blue in a base. Methyl red and methyl orange solutions turn yellow in basic solutions and red in acidic solutions.

These indicators should be used in colorless solutions, otherwise the color of the solution may mask the color changes of the indicator.

The indicator (In) comes to equilibrium in aqueous solutions:

$$\underset{\text{(Color 1)}}{HIn} + H_2O \rightleftharpoons \underset{\text{(Color 2)}}{In^- + H_3O^+}$$

Therefore, indicators behave like weak acids with a specific pK_a value. The equilibrium is shifted as the pH of the solution changes. Knowing the pH at which an indicator will change color is useful for determining the equivalence point of an acid-base titration. However, the pH of the equivalence point depends on the pK_a value of the acid, which is different for each acid. Therefore, the indicator has to be chosen to match the pK_a value of the acid. The most common indicators are listed in Table 1 with the pH range in which they change color and the color change.

Table 1: pH indicators

Indicator	pH range	Colors
Crystal violet	0.0 – 1.6	yellow → blue
Thymol blue	1.2 – 2.8	red → yellow
Orange IV	1.4 – 2.8	red → yellow
Methyl orange	3.2 – 4.4	red → yellow
Bromocresol green	3.8 – 5.4	yellow → blue
Methyl red	4.8 – 6.2	red → yellow
Chlorophenol red	5.2 – 6.8	yellow → red
Bromothymol blue	6.0 – 7.6	yellow → blue
Phenol red	6.6 – 8.0	yellow → red
Neutral red	6.8 – 8.0	red → amber
Thymol blue	8.0 – 9.6	yellow → blue
Phenolphthalein	8.2 – 10.0	colorless → pink
Thymolphthalein	9.4 – 10.6	colorless → blue
Alizarin yellow	10.1 – 12.0	yellow → blue
Indigo carmine	11.4 – 13.0	blue → yellow

You will be using phenolphthalein and methyl orange indicators in this experiment to continuously monitor the pH of a titrated solution.

In this experiment, indicators will be used to show the end point of titrations to determine the CO_2 content of a commercial beverage.

Pre-Lab Experiment

Setting the stage for the experiment

Many commercial products contain dissolved carbon dioxide (CO_2) or some type of carbonate. In this experimental procedure, CO_2 gas produced by a chemical reaction is transferred into a balloon containing excess sodium hydroxide (NaOH) solution. The CO_2 is absorbed and converted into an equivalent amount of sodium carbonate (Na_2CO_3):

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The resulting mixture, consisting of sodium carbonate and excess sodium hydroxide, will be titrated with a standardized hydrochloric acid solution using phenolphthalein and methyl orange as indicators. Titration to the first end point, when phenolphthalein becomes colorless, neutralizes the excess sodium hydroxide and converts all the sodium carbonate to sodium bicarbonate ($NaHCO_3$):

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

Continued titration to the methyl orange end point converts the sodium bicarbonate to sodium chloride (NaCl), CO_2 and water:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

Therefore, the number of moles of the titrant necessary for the second step will be equivalent to the number of moles of CO_2 absorbed.

Example calculation to try

The content of a can of commercial soda was transferred into a 500-mL Erlenmeyer flask with a magnetic stirring bar already inside. A balloon containing 100 mL of 1.0 M NaOH solution was secured onto the neck of the flask. The flask was then placed on a magnetic stirrer and stirred overnight. Initially the balloon expanded but eventually collapsed, indicating that the CO_2 had been removed from the beverage and absorbed by the NaOH solution.

The solution from the balloon was then transferred into a 250-mL beaker. A few drops of phenolphthalein indicator were added to the solution which was then titrated with a 4.00 M HCl solution. It took 16.5 mL of the 4.00 M solution to change the color of the indicator from purple to colorless. From there, a few drops of methyl orange indicator was added and titrated further with 4.00 M HCl. Once the solution changed from orange to red, indicating the equivalence point, it was found that the total HCl consumption was 25.00 mL .

The amount of HCl consumed in the second step was

$$(25.00\text{ mL} - 16.48\text{ mL})\left(\frac{1\text{ L}}{1000\text{ mL}}\right)\left(\frac{4.00\text{ mol}}{1\text{ L}}\right) = 3.41 \times 10^{-2}\text{ mol HCl}$$

This is equivalent to the number of moles of CO_2 in the sample, which were:

$$\left(3.41 \times 10^{-2}\text{ mol } CO_2\right)\left(\frac{44.01\text{ g}}{1\text{ mol}}\right) = 1.50\text{ g } CO_2$$

The beverage sample had 1.50 g of CO_2.

1. Why is the number of moles of HCl consumed in the second step equivalent to the number of moles of CO_2 in the sample?

The second step involves converting $NaHCO_3$ to NaCl with HCl. In this reaction the HCl and $NaHCO_3$ react in a 1:1 ratio. Also the number of moles of $NaHCO_3$ is the same as the number of moles of CO_2, since each CO_2 molecule is converted to one $NaHCO_3$ molecule.

2. How many moles of HCl were necessary to remove the excess amount of NaOH in the first step? (Hint: In the first step, the same number of moles of HCl was used to convert Na_2CO_3 to $NaHCO_3$ as in the second step to convert $NaHCO_3$ to CO_2 and water.)

The amount of HCl necessary to convert $NaHCO_3$ to CO_2 is 3.41×10^{-2} mol. It took the same number of moles of HCl to convert Na_2CO_3 to $NaHCO_3$. This latter number of moles has to be subtracted from the number of moles of HCl added up to the first equivalence point to get the number of moles of HCl that reacted with the excess amount of NaOH.

$$(16.48\text{ mL HCl})\left(\frac{4.00\text{ mol HCl}}{1000\text{ mL}}\right) - \left(3.41 \times 10^{-2}\text{ mol HCl}\right) = 3.18 \times 10^{-2}\text{ mol HCl}$$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***4.00 M HCl:*** Under a hood, slowly add 650 mL of 36% HCl solution to about 1000 mL of water in a 2-L volumetric flask and fill it to the mark.
2. ***1 M NaOH:*** Dissolve 80 g of NaOH in approximately 500 mL of water in a 2-L volumetric flask. Cool the solution under running tap water and fill it to the mark.

Safety

Add these important safety precautions to your normal laboratory procedures:

- If the NaOH or HCl solutions come in contact with your skin or eyes, rinse immediately with a large amount of running water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

Sample preparation

1. Chill a can of soda.

2. When the soda is cold, open the can and use the 100-mL graduated cylinder to slowly transfer 100 mL into a 250-mL Erlenmeyer flask.

3. Place a stirring bar in the flask.

4. Why do you think it is important to chill the soda before opening it? (Hint: how does temperature change the solubility of gases in liquids and how does that affect the loss of CO_2 when the can is opened.)

The solubility of CO_2 increases as the soda is cooled so the loss of CO_2 upon opening the can is reduced.

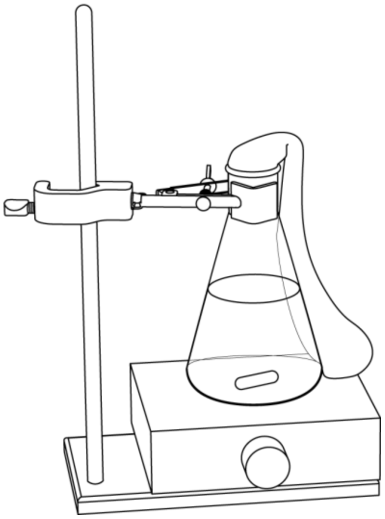
5. Place 100.00 mL of 1 M NaOH in a balloon and secure the balloon on the mouth of the Erlenmeyer flask.

6. Set the Erlenmeyer flask on the magnetic stirrer and leave it stirring overnight.

Note: Set the balloon next to the Erlenmeyer flask securely.

7. What do you think will happen overnight?

The CO_2 escapes from the soda and dissolves in the NaOH solution.



Titration preparation

8. Remove the Erlenmeyer flask and the attached balloon from the magnetic stirrer.

9. Carefully transfer the NaOH solution from the balloon into a 250-mL beaker and add 3 to 5 drops of phenolphthalein indicator solution.

10. Start a new experiment on the data collection system. �(1.2)

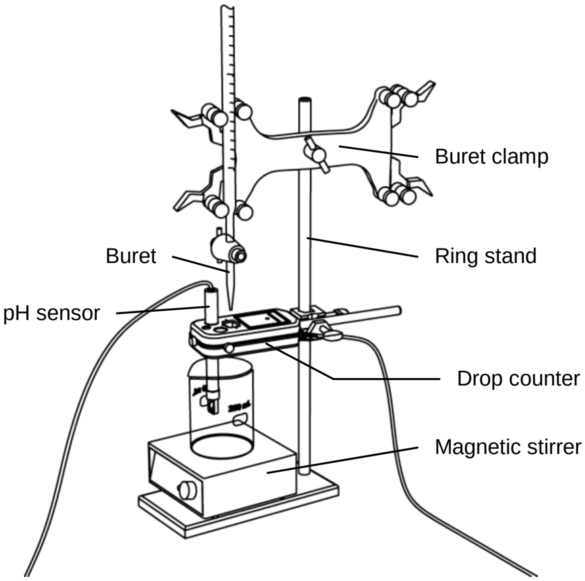
11. Connect a pH sensor to the data collection system. �(2.1)

12. Connect the drop counter to the data collection system. �(2.2)

13. Display the pH on the y-axis of a graph and Drop Count on the x-axis. �(7.1.1)

14. Calibrate the pH sensor. �(3.6)

15. Assemble the titration apparatus, using the steps below and the illustration as a guide.



- **a.** Position the magnetic stirrer on the base of the ring stand.
- **b.** Place a waste container (250-mL beaker) on the magnetic stirrer.
- **c.** Use the buret clamp to attach the buret to the ring stand.
- **d.** Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.
- **e.** Place the pH sensor through one of the slots in the drop counter.

16. Rinse the buret with several milliliters of the 4.00 M HCl solution:

- **a.** Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized HCl solution.
- **b.** Open the stopcock on the buret and drain the rinse HCl into the waste container.
- **c.** Repeat this process two more times.

17. Why is it necessary to rinse the buret with the HCl solution?

If there is any residual water or contaminant in the buret, it will dilute the HCl and change its concentration. Rinsing eliminates any such contamination.

18. Make sure the stopcock on the buret is in the “off” position and then use a funnel to fill the buret with about 50 mL of the 4.00 M HCl solution (titrant).

19. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

20. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of HCl . If this happens, the amount of titrant used will be inaccurate.

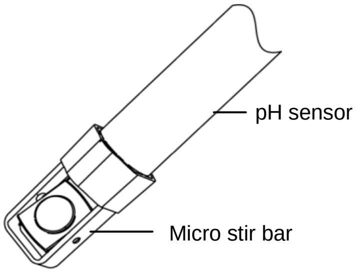
21. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

Note: Good control of the stopcock is important. Each drop should result in a blink of the LED on the drop counter. If the LED is continuously lit, you have opened the stopcock too far and you will have to start over**.**

22. Why will it be necessary to start your titration over again if you accidentally allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

23. Add the micro stir bar to the end of the pH sensor.



24. Why is it necessary to stir the solution during a titration?

Stirring thoroughly mixes the ions in the solution so that the recorded pH reflects the pH of the entire solution.

25. Add additional 4.00 M HCl to the buret so the solution is above the zero mark. Allow some of the HCl solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the starting volume in Table 2.

26. Remove the waste container.

27. Set the beaker with the NaOH solution on the magnetic stirrer.

28. Turn on the magnetic stirrer at a slow and steady rate.

Collect Data

29. Clean the lens of the drop counter inside the opening through which the drops are going with deionized water and a cotton swab or tissue.

30. Start recording data. �(6.2)

31. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

32. When the solution turns colorless, add 3 to 5 drops of methyl orange indicator solution and continue the titration

33. How did the pH change at the equivalence point?

The pH suddenly dropped at the equivalence point.

34. What species are in the solution at this time?

All Na_2CO_3 has been converted to $NaHCO_3$ and all excess NaOH has been converted to NaCl.

35. When the solution turns red, continue the titration past the equivalence point until the pH curve flattens.

36. How did the pH change at the equivalence point?

The pH suddenly dropped at the second equivalence point as well.

37. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

38. Stop recording data. �(6.2)

39. In Table 2, record the final drop count and the final reading of the titrant in the buret to a precision of 0.01 mL.

40. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 2.

Table 2: Titration data

Parameter	**Measurement or Calculation**
Starting volume of HCl in the buret (to 0.01 mL)	0.00
Final volume of HCl in the buret (to 0.01 mL)	29.00
Volume of titrant (to 0.01 mL)	29.00
Final drop count	562

41. Calibrate the drop counter. �(3.4)

42. Set the horizontal axis to the calculated volume. �(7.1.9)

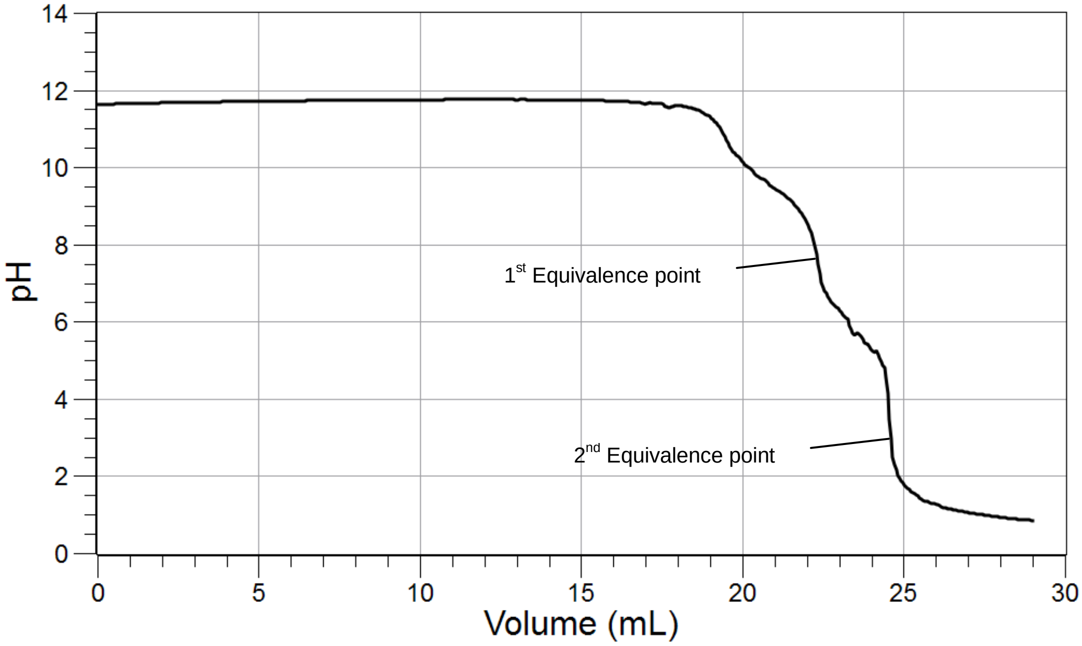
43. From the graph, locate the phenolphthalein end point and record the volume in Table 3. �$^{(9.1)}$

Note: The equivalence point will be where the slope of the titration curve is the steepest. Find the steepest slope of the data plot to determine this point. �$^{(9.3)}$

44. From the graph, locate the methyl orange end point and record the volume in Table 3. �$^{(9.1)}$

45. Save your experiment. �$^{(3.4)}$and clean up according to your instructor's directions.

46. Sketch the graph or print the graph. �$^{(11.2)}$ of the titration curve of pH versus Volume and attach it below.



Data Analysis

1. Calculate the volume of HCl consumed to convert $NaHCO_3$ to NaCl and CO_2.

$$(24.56\text{ mL}) - (22.32\text{ mL}) = 2.24\text{ mL HCl}$$

2. Calculate the number of moles of HCl consumed to convert $NaHCO_3$ to NaCl and CO_2.

$$(2.24\text{ mL})\left(\frac{4.00\text{ mol}}{1000\text{ mL}}\right) = 8.96 \times 10^{-3}\text{ mol HCl}$$

3. Calculate the number of moles of $NaHCO_3$ converted to CO_2 from the number of moles of HCl consumed.

The number of moles of $NaHCO_3$ is the same as the number of moles of HCl consumed: 8.96×10^{-3} mol, because of the 1:1 stoichiometry.

4. Calculate the number of moles of CO_2 that was needed to produce the number of moles of $NaHCO_3$.

It is the same as the number of moles of $NaHCO_3$, since 1 mol of CO_2 yields 1 mol of $NaHCO_3$. Therefore the number of moles of CO_2 is 8.96×10^{-3} mol.

5. Calculate the mass of CO_2 in the sample.

$$(8.96 \times 10^{-3}\ \text{mol})\left(\frac{44.0\ \text{g}}{1\ \text{mol}}\right) = 0.394\ \text{g CO}_2$$

Table 3: Determination of the amount of CO_2 in 100 mL of soda

Parameters	Values
Molarity of HCl of titrant (M)	4.0
Volume of titrant at phenolphthalein end point (mL)	22.32
Volume of titrant at methyl orange end point (mL)	24.56
Volume of titrant, 1st end point to 2nd end point (mL)	2.24
Amount of titrant, 1st end point to 2nd end point (mol)	8.96×10^{-3}
Amount of CO_2 in the sample (mol)	8.96×10^{-3}
Mass of CO_2 in sample (g)	0.394

Analysis Questions

1. Usually the CO_2 content obtained this way is lower than the actual value listed on the container of the drink. List a few possible reasons.

Not all the CO_2 leaves the drink, some escapes when the can is opened, and CO_2 that didn't dissolve in the NaOH escapes when the balloon is removed from the Erlenmeyer flask.

2. How would you minimize the error introduced by losing CO_2 in the process?

Cooling down the drink as much as possible, minimizing the time it takes to transfer the drink into the Erlenmeyer flask.

3. Why can't we simply add the NaOH solution to the soda and titrate the excess NaOH?

We cannot just add the NaOH solution to the drink because most drinks have unknown amounts of various acids making it impossible to know how much NaOH actually reacts with the CO_2.

4. What aspect of this method is subjective and therefore prone to human error?

Detection of color changes makes this method subjective.

5. How would you minimize the error introduced by the detection of colors in the titration process?

Using a pH electrode instead of the results obtained with the indicator solutions minimize the error.

6. Many of the limitations in a titration using an indicator can be eliminated by using a drop counter and a pH sensor. What is a drop counter and why is it used in a titration? How does it overcome some of the limitations of indicator-based titrations?

A drop counter is exactly what its name implies; it counts the number of drops that pass through it. The volume of each drop can be determined by dividing the volume of titrant used by the total number of drops used to dispense that volume. A calculation can then be used to convert the number of drops at the equivalence point of a titration curve to the volume of titrant used.

This procedure eliminates the need for stopping the titration exactly at the equivalence point, which can be tricky when using an indicator. The procedure can also be completed for titrations that cannot use indicators.

Synthesis Questions

Use available resources to help you answer the following questions.

1. How would you adapt this method to determine the $CaCO_3$ content of a stomach acid pill (Hint: $CaCO_3$ reacts with HCl to form CO_2) ?

The acid could be reacted with excess amount of HCl to form CO_2.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

The rest of the method would be the same as in the original experiment.

2. Why do you think we don't usually use this method to determine the $CaCO_3$ content of a stomach acid pill but rather, react three pills with known amounts of HCl and then titrate the excess amount of NaOH? (Hint: what was the major source of error in the process?)

The method applied in this experiment is prone to significant error due to the potential loss of CO_2. The back titration method is more accurate.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. The number of moles of CO_2 is equal to:

- **A.** The number of moles of NaOH in the solution.
- **B.** The number of moles of HCl added up to the 1st equivalence point.
- **C.** The number of moles of HCl added up to the 2st equivalence point.
- **D. The number of moles of HCl added between the 1st and 2nd equivalence points.**

2. The number of moles of excess NaOH is:

- **A.** The number of moles of NaOH in the solution.
- **B.** The number of moles of HCl added up to the 1st equivalence point.
- **C**. The number of moles of HCl added up to the 2st equivalence point.
- **D. The number of moles of HCl added up to the 1st equivalence point minus the number of moles of HCl added between the 1st and 2nd equivalence points.**

3. Up to the first equivalence point:

- **A.** All NaOH was converted to NaCl.
- **B. All CO_2 was converted to $NaHCO_3$ and all excess NaOH was converted to NaCl**.
- **C.** All CO_2 was converted to NaCl.
- **D.** All NaOH was converted to $NaHCO_3$.

4. Between the 1st and 2nd equivalence points:

- **A.** All NaOH was converted to NaCl.
- **B. All $NaHCO_3$ was converted to NaCl and CO_2**.
- **C.** All CO_2 was converted to NaCl.
- **D.** All NaOH was converted to $NaHCO_3$.

Extended Inquiry Suggestions

Have students use the back-titration method to determine the $CaCO_3$ content of a stomach acid pill. Assuming the pills have 500 mg $CaCO_3$, two pills can be ground and reacted with 25.00 mL of 1.0 M HCl. The excess amount of HCl can be back-titrated with a 1.0 M NaOH solution. For this titration, methyl orange indicator can be used.

Then 25.00 mL of the HCl solution would be titrated with 1.0 M NaOH solution. The difference between the two titrations is due to the $CaCO_3$ present in the pill. The number of moles of NaOH that is the difference between the two titrations is the same as the number of moles of HCl that reacted with the $CaCO_3$ in the sample.

In a sample experiment, two pills were ground and transferred into a 100-mL beaker. The mass of the sample was 0.995 g. Then 25.00 mL of 1.00 M HCl was added and the solution was gently heated to eliminate the CO_2 generated. The solution was titrated with 1.0 M NaOH in the presence of methyl orange indicator and it took 16.50 mL titrant solution to reach the equivalence point. Then, 25.00 mL of 1.0 M HCl solution was titrated with 1.0 M NaOH in a separate experiment. It took 23.95 mL titrant solution to reach the equivalence point. The $CaCO_3$ that was present in the sample used up:

$$(23.95\text{ mL} - 16.50\text{ mL})\left(\frac{1.00\text{ mol HCl}}{1000\text{ mL}}\right) = 7.45 \times 10^{-3}\text{ mol HCl}$$

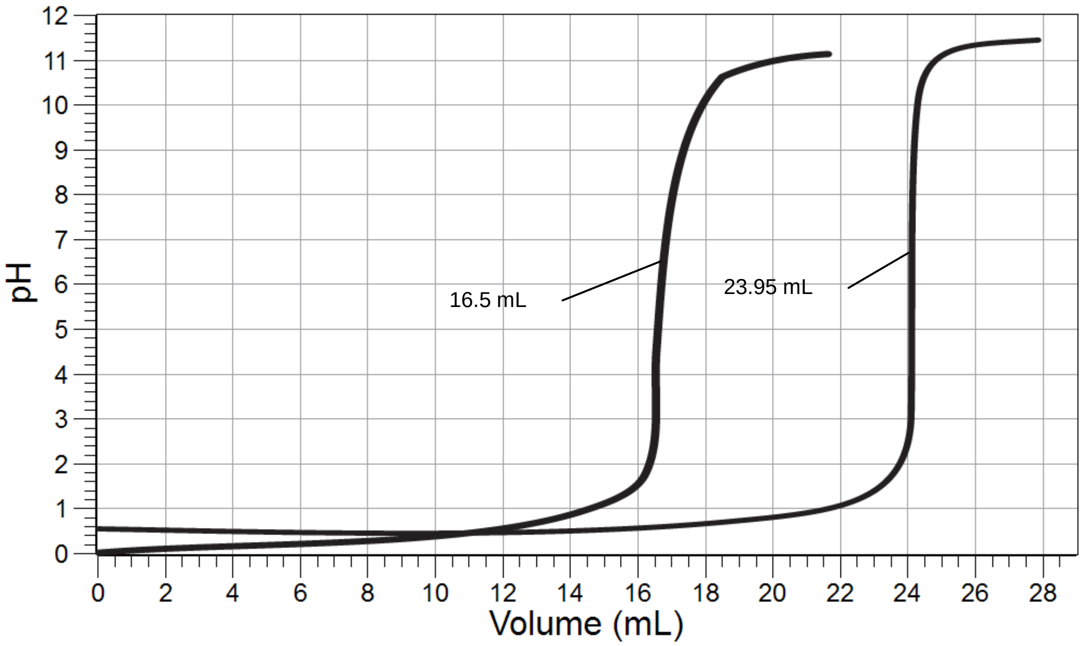
This much HCl is equivalent to

$$\left(7.45 \times 10^{-3}\text{ mol HCl}\right)\left(\frac{1\text{ mol CaCO}_3}{2\text{ mol HCl}}\right)\left(\frac{100.1\text{ g CaCO}_3}{1\text{ mol CaCO}_3}\right) = 3.72 \times 10^{-1}\text{ g CaCO}_3$$

The percentage of the stomach acid pills that is $CaCO_3$ is

$$\text{Percent CaCO}_3\text{ content} = \left(\frac{0.372\text{ g}}{0.995\text{ g}}\right) \times 100 = 37.2\%\text{ CaCO}_3$$

The titration curve obtained using a pH electrode appears as follows:



24. Properties of Buffer Solutions

Objectives

Students learn the properties of buffer solutions and buffer capacity.

Procedural Overview

Students gain experience conducting the following procedures:

- Preparing three buffer solutions using different concentrations of acetic acid
- Testing the buffering capacity of the three buffers by adding HCl
- Calculating the predicted and actual buffer capacity of the three buffer solutions
- Comparing the buffer capacity and buffering effect of the three buffer solutions and water

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- pH sensor
- Beaker, 400-mL
- Buret, 50-mL
- Pipet, 5-mL and rubber bulb
- Beaker, 100-mL
- Beaker (2), 25-mL
- Graduated cylinder, 250-mL
- Magnetic stirrer and stirring bar
- Ring stand
- Clamp, buret
- Clamp, utility
- Funnel
- 2.000 M Sodium hydroxide (NaOH), 250 mL[1]
- 0.1 M Acetic acid (HOAc), 250 mL[2]
- 0.3 M HOAc, 250 mL[3]
- 0.5 M HOAc, 250 mL[4]
- 6.00 M Hydrochloric acid (HCl), 5 mL[5]
- Buffers, pH 4 and pH 10, 10 mL
- Wash bottle with deionized water

[1–5] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Acids and bases
- Electrolytes
- Le Chatelier's Principle
- Molarity

Related Labs in This Guide

Labs conceptually related to this one include:

- Determining K_a by Half-Titration of a Weak Acid
- Determination of the K_a Values of Two Isomeric Multi-Protic Acids

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system � (1.2)
- Connecting a sensor to the data collection system � (2.1)
- Calibrating the pH sensor �(3.6)
- Monitoring live data without recording �(6.1)

Background

Adding small amounts of acid or base to water dramatically changes the hydrogen ion concentration, which changes the pH. If species are present in the water that can neutralize the added acid or base, then the pH change will be much smaller. Solutions that resist pH change in this fashion are called buffers.

A buffer is made by adding a weak acid and a conjugate base of the same weak acid to water. If acid is then added to the buffer system, the conjugate base “consumes” the added acid. The opposite is true for the addition of a base. In either case, the resulting hydrogen ion concentration changes little.

Pre-Lab Experiment

Setting the stage for the experiment

Weak acids (HA) partially dissociate, as shown below:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The corresponding acid dissociation constant is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If the solution contains the salt of the acid (that is, the conjugate base of the acid, A^-) the equilibrium shifts to the left in accordance with the Le Chatelier Principle. This also means that the auto-dissociation of the acid is suppressed, so that:

$$[HA] \approx c_{HA}$$

$$[A^-] \approx c_{A^-}$$

$$K_a = \frac{[H_3O^+]c_{A^-}}{c_{HA}}$$

where c_{HA} and c_{A}^- are the concentrations of the weak acid and the salt, respectively. Solving for $[H_3O^+]$ yields

$$[H_3O^+] = K_a \frac{c_{HA}}{c_{A^-}}$$

$$\log[H_3O^+] = \log K_a + \log\frac{c_{HA}}{c_{A^-}}$$

$$-\log[H_3O^+] = -\log K_a + \log\frac{c_{A^-}}{c_{HA}}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{c_{A^-}}{c_{HA}}$$

The final equation is known as the Henderson-Hasselbach equation.

It is worth mentioning that the pH of buffers does not depend on the actual concentration of the acid or salt; it only depends on the ratio of the two.

How well buffers maintain their pH when acids and bases are added is measured by their buffer capacity. Buffer capacity is the amount of acid or base, in mol/L, that changes the pH by one unit. Adding x mol/L of acid increases the amount of acid by x amount and removes the same amount of salt. Notice that the larger the value of x is, the more acid or base it takes to change the pH one unit, hence the larger the buffer capacity. The Henderson-Hasselbach equation can be modified to incorporate the pH change of one unit:

$$\mathrm{pH} - 1 = \mathrm{p}K_a + \log\frac{c_{A^-} - x}{c_{HA} + x}$$

Solving for x, the buffer capacity, from this last equation yields:

$$x = \frac{c_{A^-} - c_{HA}10^{pH - 1 - pKa}}{1 + 10^{pH - 1 - pKa}}$$

A buffer can be made by adding, for example, some NaOH solution to the solution of a weak acid, HA, producing the solution of the conjugate base, A^-. You must ensure that the acid is in excess. The necessary concentrations can be calculated using the ICE box. (Keep in mind that concentrations change not only because of the reaction but also because the volume of the solution changes by adding the NaOH solution.)

The ICE box (an acronym made from the first letter of the words Initial, Change, and End or, in this case, Equilibrium) is a representation of the chemical reaction, where the progress of the reaction is shown vertically (Initial/Change/Equilibrium) and horizontally, the components of the reaction are listed. The table is completed based on the stoichiometric relationship among the components:

Table 1: ICE box for calculating concentrations of the weak acid and conjugate base

Conditions	**[HA]**	**[A⁻]**
Initial	$c_{HA}{}^{0}\frac{V_{HA}}{V_{NaOH} + V_{HA}}$	0
Change	$-c_{NaOH}{}^{0}\frac{V_{NaOH}}{V_{NaOH} + V_{HA}}$	$c_{NaOH}{}^{0}\frac{V_{NaOH}}{V_{NaOH} + V_{HA}}$
Equilibrium	$\frac{c_{HA}{}^{0}V_{HA} - c_{NaOH}{}^{0}V_{NaOH}}{V_{NaOH} + V_{HA}}$	$c_{NaOH}{}^{0}\frac{V_{NaOH}}{V_{NaOH} + V_{HA}}$

Therefore from the table the equilibrium concentrations of the conjugate base and the acid are:

$$c_{A^-} = \frac{c_{NaOH}{}^{0}V_{NaOH}}{V_{NaOH} + V_{HA}}$$

$$c_{HA} = \frac{c_{HA}{}^{0}V_{HA} - c_{NaOH}{}^{0}V_{NaOH}}{V_{NaOH} + V_{HA}}$$

where

c_{A^-} = concentration of conjugate base (salt) in the buffer (M)

$c_{NaOH}{}^0$ = initial concentration of NaOH solution (M)

V_{NaOH} = added volume of NaOH solution (mL)

c_{HA} = concentration of HA in buffer (M)

$c_{HA}{}^0$ = initial concentration of HA (M)

V_{HA} = volume of acid (mL)

Example calculation to try

In an experiment, acetic acid was analyzed. The formula for acetic acid is CH_3COOH; however, we will be using an abbreviated version of the formula: "CH_3CO" is called an "acetyl group" and has the symbol of "Ac". Therefore the formula for acetic acid used in this experiment is "HOAc" and the formula for the acetate ion will be "OAc^-".

A sample of 100 mL of 0.5 M HOAc solution was titrated with 2.000 M NaOH solution to make a buffer with a pH of 5.5. To reach the desired pH, 21.20 mL of NaOH solution had to be added. The concentration of the conjugate base (salt) and acid can be calculated by using the ICE box.

Table 2: Example calculations using the ICE box

Conditions	**[HOAc]**	**[OAc⁻]**
Initial	$\frac{(0.500\ \text{M})(100.00\ \text{mL})}{(21.20\ \text{mL} + 100.00\ \text{mL})} = 4.12 \times 10^{-1}\ \text{M}$	0
Change	$-\frac{(2.000\ \text{M})(21.20\ \text{mL})}{(21.20\ \text{mL} + 100.00\ \text{mL})} = -0.350\ \text{M}$	$\frac{(2.000\ \text{M})(21.20\ \text{mL})}{(21.20\ \text{mL} + 100.00\ \text{mL})}$ $= 0.350\ \text{M}$
Equilibrium	$0.412\ \text{M} - 0.350\ \text{M} = 6.2 \times 10^{-2}\ \text{M}$	$\frac{(2.000\ \text{M})(21.20\ \text{mL})}{(21.20\ \text{mL} + 100.00\ \text{mL})}$ $= 0.350\ \text{M}$

Therefore from the table the equilibrium concentrations of the conjugate base and the acid are:

$$c_{Ac^-} = \frac{(2.000\ \text{M})(21.20\ \text{mL})}{(21.20\ \text{mL} + 100.00\ \text{mL})} = 0.350\ \text{M}$$

$$c_{HOAc} = \frac{(0.500\ \text{M})(100.00\ \text{mL}) - (2.000\ \text{M})(21.20\ \text{mL})}{(21.20\ \text{mL} + 100.00\ \text{mL})} = 6.2 \times 10^{-2}\ \text{M}$$

The buffer capacity of the prepared buffer is predicted to be

$$x = \frac{(0.350\ \text{M}) - (6.2 \times 10^{-2}\ \text{M})10^{5.5-1-4.75}}{1 + 10^{5.5-1-4.75}} = 0.20\ \text{M}$$

To test the buffer capacity of the buffer, 6.00 M HCl solution was added by drops until the pH of the buffer reached 4.5. This required 4.00 mL of the HCl solution. The concentration of HCl in the final solution is

$$c_{\text{HCl}} = \frac{(6.00\ \text{M})(4.00\ \text{mL})}{(21.20\ \text{mL} + 100.00\ \text{mL} + 4.00\ \text{mL})} = 0.192\ \text{M}$$

This is close to the predicted value of 0.20 M.

1. Would adding NaOH solution to acetic acid solution increase or decrease the pH of the solution?

The pH would increase.

2. When calculating the added acid concentration (c_{HCl}) why didn't we convert the volume to liters to be consistent with M?

The volume units cancel out. Therefore, the answer does not depend on the volume units as long as the same unit is used throughout the calculation.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***2.000 M NaOH:*** Dissolve 80 g of NaOH in some water in a 1-L volumetric flask, and fill it to the mark.

   Note: Standardize the solution and report the actual concentration to the students.

2. ***0.1 M HOAc:*** Combine 11.20 mL of glacial HOAc with some water in a 2-L volumetric flask and fill it to the mark.
3. ***0.3 M HOAc:*** Combine 33.60 mL of glacial HOAc with some water in a 2- L volumetric flask and fill it to the mark.
4. ***0.5 M HOAc:*** Combine 56 mL of glacial HOAc with some water in a 2-L volumetric flask and fill it to the mark.
5. ***6.00 M HCl:*** Combine 50 mL of a 36% HCl solution with some water in a 100-mL volumetric flask and fill it to the mark.

   Note: Standardize the solution and report the actual concentration to the students.

Safety

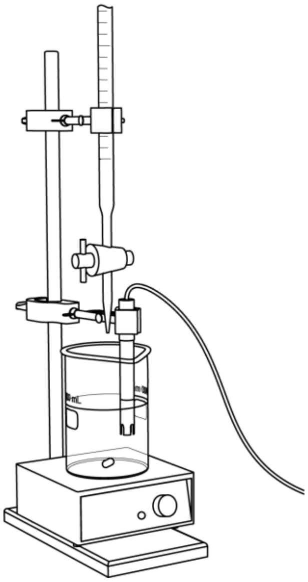
Add these important safety precautions to your normal laboratory procedures:

♦ Wash off any HCl solution that comes in contact with your skin with large amounts of water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up



1. Start a new experiment on the data collection system. �(1.2)

2. Connect a pH sensor to the data collection system. �(2.1)

3. Monitor live data without recording (you will not need to collect data). �(6.1)

4. Use pH 4 and pH 10 buffer solutions to calibrate the pH sensor. �(3.6)

Collect Data

5. Which solution do you expect to take the greatest amount of NaOH solution to set the pH to 5?

The solution with the highest concentration since that solution has the most HOAc.

6. Set up a buret over a waste beaker (100-mL beaker).

7. Rinse the buret with several milliliters of the 2.000 M NaOH solution:

- **a.** Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized NaOH solution.
- **b.** Open the stopcock on the buret and drain the rinse NaOH into the waste container.
- **c.** Repeat this process two more times.

8. Why is it necessary to rinse the buret with the NaOH solution?

If there is any residual water or contaminant in the buret, it will dilute the NaOH and change its concentration. Rinsing eliminates any such contamination.

9. Make sure the stopcock on the buret is in the “off” position and then use a funnel to fill the buret with about 50 mL of the 2.000 M NaOH solution (titrant).

10. Drain a small amount of the titrant through the drop counter into the waste beaker (100-mL beaker) to remove any air in the tip of the buret.

11. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of NaOH. If this happens, the recorded amount of NaOH added will be inaccurate.

12. Add additional 2.000 M NaOH to the buret so the solution is above the zero mark. Allow some of the NaOH solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 3.

Prepare the buffer and test the buffer capacity with each of the following solutions:

250 mL of 0.1 M HOAc
250 mL of 0.3 M HOAc
250 mL of 0.5 M HOAc

13. To prepare the buffer:

a. Transfer 250 mL of the acetic acid solution into a 400-mL beaker and set it on the magnetic stirrer (remove the waste beaker).

b. Place a stirring bar into the solution and set the stirring to a gentle rate.

c. Slowly add the NaOH solution by drops (1 to 2 per second) until the pH reaches 5.0.

d. Record the final reading of the NaOH solution in Table 3.

e. Calculate the volume of NaOH added (final reading minus initial reading) and record this value in Table 3 and Table 4.

Table 3: Amount of NaOH added to HOAc solutions to reach pH 5.0

Addition of NaOH	0.1 M HOAc	0.3 M HOAc	0.5 M HOAc
Initial reading of NaOH on the buret (mL)	0.0	0.0	0.0
Final reading of NaOH on the buret (mL)	9.20	25.20	42.00
Volume of NaOH added (mL)	9.20	25.20	42.00

14. To measure buffer capacity, use the pipet to add the 6 M HCl solution, by drops, until the pH reaches 4.0. Record the volume added in Table 4.

15. Which solution do you expect to need the greatest volume of the HCl solution to set the pH to 4; that is, which solution do you think will have the highest buffer capacity?

The solution with the highest concentration of acids and conjugate base will have the highest buffer capacity.

16. To prepare for the next HOAc solution:

- **a.** Refill the buret with 2.000 M NaOH so the solution is above the zero mark. Allow some of the NaOH solution to drip into the beaker until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 3.
- **b.** Rinse the pH probe tip with deionized water.
- **c.** Remove the beaker and dispose of its contents according to the instructor's instructions.

17. Repeat this process to prepare the buffer and test the buffer capacity for the next HOAc solution.

18. Clean up according to your instructor's instructions.

Data Analysis

1. Obtain the exact concentration of the NaOH solution from your instructor and record it in Table 2.

2. Calculate the concentration of the conjugate base after adding the necessary amount of NaOH solution. Record the results for all three HOAc solutions in Table 4.

For the 0.1 M HOAc solution:

$$c_{\text{A}^-} = \frac{(2.000\ \text{M})(9.20\ \text{mL})}{(9.20\ \text{mL} + 250.00\ \text{mL})} = 7.10 \times 10^{-2}\ \text{M}$$

3. Calculate the concentration of the acid after adding the necessary amount of NaOH solution. Record the results for all three HOAc solutions in Table 4.

For the 0.1 M HOAc solution:

$$c_{\text{HA}} = \frac{(0.100\ \text{M})(250.00\ \text{mL}) - (2.000\ \text{M})(9.20\ \text{mL})}{(9.20\ \text{mL} + 250.00\ \text{mL})} = 2.55 \times 10^{-2}\ \text{M}$$

4. Calculate the predicted buffer capacity of the solutions. Record the results for all three HOAc solutions in Table 4.

For the 0.1 M HOAc solution:

$$x = \frac{(7.10 \times 10^{-2}\ \text{M}) - (2.55 \times 10^{-2}\ \text{M})10^{5.00 - 1 - 4.75}}{1 + 10^{5.00 - 1 - 4.75}} = 5.64 \times 10^{-2}\ \text{M}$$

5. Calculate the actual buffer capacity, which is the final concentration of HCl in the solution, for all 3 HOAc solutions. Record the results for all three solutions in Table 4.

$$c_{HCl} = \frac{(6.00\text{ M})(1.80\text{ mL})}{(9.20\text{ mL} + 250.00\text{ mL} + 1.80\text{ mL})} = 4.14 \times 10^{-2}\text{ M}$$

Table 4: Buffer capacity measurements and calculation results

Parameters	0.1 M HOAc	0.3 M HOAc	0.5 M HOAc
Concentration of standardized NaOH solution (M)	2.000		
Concentration of standardized HCl solution (M)	6.00		
Volume of acetic acid solution (mL)	250.00	250.00	250.00
Volume of 2.0 M NaOH added to reach pH 5.00 (mL)	9.20	25.20	42.00
Volume of 6.0 M HCl solution added to reach pH 4.0 (mL)	1.80	5.50	8.90
Concentration of conjugate base (M)	7.10×10^{-2}	1.83×10^{-1}	2.88×10^{-1}
Concentration of remaining acid (M)	2.55×10^{-2}	8.94×10^{-2}	1.40×10^{-1}
Predicted buffer capacity (M)	5.64×10^{-2}	1.41×10^{-1}	2.23×10^{-1}
Actual buffer capacity (M)	4.14×10^{-2}	1.18×10^{-1}	1.77×10^{-1}

Analysis Questions

1. Does the pH of the buffer depend on the concentration of the conjugate base (salt) and the acid concentration? Explain your answer

The pH of a buffer does not depend on the actual value of either concentration. It depends only on the ratio of the concentration of the conjugate base (salt) and the acid.

2. How does the buffer capacity change as the weak acid concentration increases?

Increasing acid concentration results in increasing buffer capacity.

3. In the example, the volume of the buffer solution was 121.20 mL. By adding 4.0 mL of 6 M HCl solution the pH changed one unit. How much will the pH change if the same amount of 6 M HCl is added to 121.20 mL of water?

$$[H_3O^+] = \frac{(6.000\ \text{M})(4.00\ \text{mL})}{(121.20\ \text{mL} + 4.00\ \text{mL})} = 0.192\ \text{M}$$

$$\text{pH} = -\log[H_3O^+] = -\log(0.192) = 0.717$$

The pH would change from 7.00 to 0.717

4. Consider the buffer capacity of the solution that was made with the 0.5 M HOAc. How would the pH change if the same amount of acid was added to pure water instead?

The buffer capacity was 0.177 M. Adding 0.177 M acid to pure water will change the pH to

$$\text{pH} = -\log(0.177) = 0.75$$

Synthesis Questions

Use available resources to help you answer the following questions.

1. If you had to design a buffer from phosphoric acid (H_3PO_4), what conjugate bases could you use?

You can use any salt made from H_3PO_4, for example, Na_3PO_4, NaH_2PO_4, and Na_2HPO_4, and a strong base, such as KOH or NaOH.

2. One of the many buffer systems in the human body is one that maintains the pH of blood. How do you think the pH of blood would be affected if too much CO_2 is inhaled (in an environment where the air is stale)?

Excess CO_2 will cause the pH to shift towards more acidic values:

$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. **The pH of a buffer:**

    A. Depends on the concentration of the acid, the concentration of the conjugate base (salt), and the pK_a of the acid.

    B. Depends on the ratio between the concentration of the acid, the concentration of the conjugate base (salt), and the pK_a of the acid.

    C. Depends on the concentration of the acid, and the concentration of the conjugate base (salt) only.

    D. Depends only on the p*K*a of the acid.

2. **Buffer capacity for acids is:**

    A. The amount of acid, in M, that increases the pH of a buffer to a measurable extent.

    B. The amount of acid, in M, that decreases the pH of a buffer to a measurable extent.

    C. The amount of acid, in M, that increases the pH of a buffer by one pH unit.

    D. The amount of acid, in M, that decreases the pH of a buffer by one pH unit.

3. **A buffer can be made by mixing:**

    A. A weak acid and a strong acid.

    B. A weak acid and a strong base, allowing the weak acid to be in excess.

    C. A weak base and a salt of the weak base.

    D. Water and a salt (conjugate base).

4. **The pH of a buffer will:**

    A. Not change at all when adding any amount of an acid or base.

    B. Not change substantially if the amount of acid or base added is less than the buffer capacity.

    C. Slightly increase as acid is added and slightly decrease as base is added.

    D. Change 0.1 pH units if the amount of acid added is equal to the buffer capacity.

Extended Inquiry Suggestions

Buffers can be discussed in context by analyzing the so called *buffer zone* in a titration of a weak acid with strong base. Please refer to the experiment "Determining K_a by Half-Titration of a Weak Acid."

25. Determining K_a by Half-Titration of a Weak Acid

Objectives

Students determine the equilibrium constant for the ionization of a weak acid (K_a) to ascertain the identity of the acid.

Procedural Overview

Students gain experience conducting the following procedures:

- Determining the K_a of a weak acid by measuring the pH of a solution titrated halfway to the equivalence point
- Using a pH sensor
- Performing a titration

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- pH sensor
- Drop counter
- Ring stand
- Clamp, right-angle
- Clamp, buret
- Beaker (2), 100-mL
- Buret, 50-mL
- Graduated cylinder, 100-mL
- Funnel
- Magnetic stirrer and stir bar
- 0.20 M Sodium hydroxide (NaOH), 75 mL[1]
- Unknown weak acid solution, 50 mL[2]
- Buffer solutions, pH 4 and pH 10, 10 mL
- Cotton swab or tissue

[1] To prepare 0.20 M NaOH, refer to the Lab Preparation section.

[2] Use 0.1 M acetic acid as the unknown weak acid for this experiment. To prepare this solution, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Acids and bases
- Electrolytes
- Le Chatelier's Principle
- Molarity

Related Labs in This Guide

Labs conceptually related to this one include:

- Standardizing a Solution of Sodium Hydroxide
- Acid–Base Titration
- Determination of the K_a Values of Two Isomer Multi-Protic Acids

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system �(2.1)
- Connecting multiple sensors to the data collection system �(2.2)
- Calibrating a drop counter �(3.4)
- Calibrating a pH sensor �(3.6)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Changing the variable on the x-axis and y-axis of a graph �(7.1.9)
- Finding the slope at a point on a data plot �(9.3)

Background

K_a is the symbol for the equilibrium constant for the ionization of an acid. The following equation describes the ionization of an acid:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

An equilibrium exists, and an acid dissociation constant can be written:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{1}$$

The value of K_a is an indication of the extent to which an acid dissociates. Strong acids dissociate nearly completely. Weak acids reach equilibrium, where the fraction that has dissociated becomes a constant at a given temperature. The numerical value of the equilibrium constant is unique to the acid and can be used to identify an unknown acid.

Before the titration has begun, the initial pH of the solution is controlled by the auto-dissociation of the acid. At this point, the concentration of H_3O^+ and A^- are very small compared to the concentration of HA. When the basic titrant solution is added, it is assumed that the OH^- ions react completely with the weak acid, HA, to form water and the conjugate base, A^-:

$$HA + OH^- \rightarrow H_2O + A^-$$

The resulting solution now has a smaller amount of HA and a larger amount of A^-. Due to stoichiometry, the increase in A^- is the same magnitude as the decrease in HA. Solutions that contain a weak acid and also contain the corresponding conjugate base are called buffers.

When the number of moles of added base is equal to the original number of moles of HA, the equivalence point has been reached. A titration curve, in which pH is plotted versus volume of titrant added, can be used to quickly determine the K_a of the acid.

The acid dissociation constant equation (Equation 1) can be revised to form an expression used to calculate the pH of mixtures of weak acids and their salts:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Taking logarithms,

$$\log K_a = \log[H_3O^+] + \log\frac{[A^-]}{[HA]}$$

Multiplying by –1,

$$-\log K_a = -\log[H_3O^+] - \log\frac{[A^-]}{[HA]}$$

Substituting pK_a for $-\log K_a$ and pH for $-\log[H_3O^+]$,

$$pK_a = pH - \log\frac{[A^-]}{[HA]}$$

Reordering,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \qquad (2)$$

Equation 2 is known as the Henderson-Hasselback equation which gives the pH of buffer solutions. Notice that when enough base has been added to reach the point that is halfway between the starting point and the equivalence point, the molarity of A^- and HA will be equal. Their ratio will be 1 and since log 1 = 0, the pH will be equal to the $\mathrm{p}K_\mathrm{a}$. The resulting K_a can be used to determine the identity of the acid.

The acid dissociation constants for several weak acids are shown in Table 1.

Table 1: Acid dissociation constants for 5 weak acids

Name	**Formula**	K_a	$\mathrm{p}K_\mathrm{a}$
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}	4.7
Benzoic acid	$HC_7H_5O_2$	6.4×10^{-5}	4.2
Formic acid	$HCHO_2$	1.8×10^{-4}	3.7
Nitrous acid	HNO_2	4.6×10^{-4}	3.4
Hypochlorous acid	HOCl	3.5×10^{-8}	7.5

Pre-Lab Experiment

Setting the stage for the experiment

In this lab you will use a method of titration that will bring the analyte halfway to the equivalence point. Halfway to the equivalence point, half of the acid molecules are converted to A^-, therefore, for a monoprotic acid

$$[\mathrm{HA}] = [\mathrm{A}^-]$$

In the expression of K_a (Equation 2), $[A^-]$ and [HA] cancel out, giving

$$K_\mathrm{a} = [\mathrm{H_3O^+}]$$

$$-\log K_\mathrm{a} = -\log\,[\mathrm{H_3O^+}]$$

$$\mathrm{p}K_\mathrm{a} = \mathrm{pH}$$

The pH of the analyte at this point is equal to the $\mathrm{p}K_\mathrm{a}$. You will convert this value to K_a and compare this K_a value to a table of known K_a values in order to identify the unknown acid.

You will perform the titration and determine the equivalence point; that is, how much of the titrant is necessary to react with all of the acid in the solution. The pH of the half-titration point is the pH of the solution after adding half the amount of titrant needed to reach the equivalence point.

Example calculation for students to try

A sample of 10.00 mL of dilute HNO_2 solution was titrated with 0.1 M NaOH solution. The equivalence point was reached after 10.10 mL. The half-titration point, therefore, was at 5.05 mL. The pH that corresponded to that volume of titrant was 3.34, so the value of K_a is

$$\begin{aligned} \text{pH} &= 3.34 \\ \text{p}K_a &= 3.34 \\ -\log K_a &= 3.34 \\ K_a &= 4.6 \times 10^{-4} \end{aligned}$$

The published value for the K_a of nitrous acid is 4.6×10^{-4}.

1. Would adding NaOH solution to the HA solution increase or decrease the pH of the solution?

The pH would increase.

2. Use the Henderson-Hasselbach equation to show that the pH of the solution at the half-titration point is equivalent to the pK_a value of the weak acid.

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

At the half-titration point

$$[A^-] = [HA];\ \frac{[A^-]}{[HA]} = 1;\ \log\frac{[A^-]}{[HA]} = 0$$

Therefore, at the half-titration point

$$\text{pH} = \text{p}K_a$$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.20 M Sodium Hydroxide***: Dissolve 8.00 g of NaOH in some distilled water in a 1-L volumetric flask and fill it to the mark.

2. ***0.1 M Acetic Acid:*** Combine 11.2 mL of glacial acetic acid with some distilled water in a 2-L volumetric flask and fill it to the mark.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect a pH sensor to the data collection system. �(2.1)

3. Connect the drop counter to the data collection system. �(2.2)

4. Display pH versus Drop Count (drops) on a graph. �(7.1.1)

5. Calibrate the pH sensor. �(3.6)

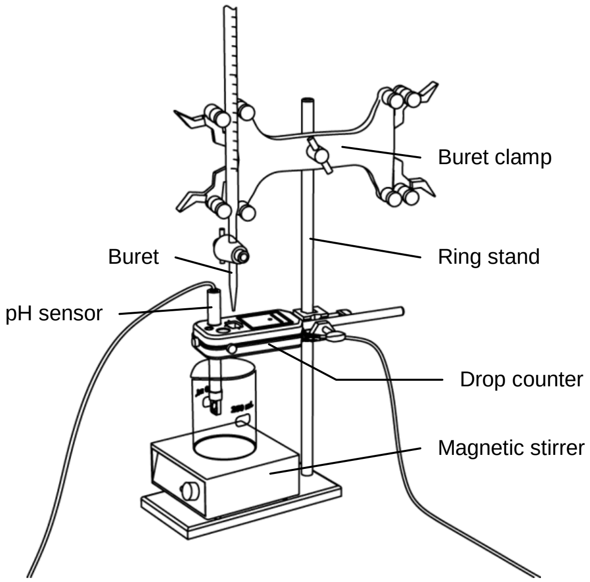
6. Assemble the titration apparatus, using the steps below and the illustration as a guide.

   a. Position the magnetic stirrer on the base of the ring stand.

   b. Place a waste container on the magnetic stirrer.

   c. Use the buret clamp to attach the buret to the ring stand.

   d. Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.



   e. Place the pH sensor through one of the slots in the drop counter.

7. Rinse the buret with several milliliters of the 0.20 M NaOH solution:

  a. Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized NaOH solution.

  b. Open the stopcock on the buret and drain the rinse NaOH into the waste container.

  c. Repeat this process two more times.

8. Why is it necessary to rinse the buret with the NaOH solution?

If there is any residual water or contaminant in the buret, it will dilute the NaOH and change its concentration. Rinsing eliminates any such contamination.

9. Make sure the stopcock on the buret is in the "off" position and then use a funnel to fill the buret with about 50 mL of the 0.20 M NaOH solution (titrant).

10. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

11. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of NaOH. If this happens, the amount of titrant used will be inaccurate.

12. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

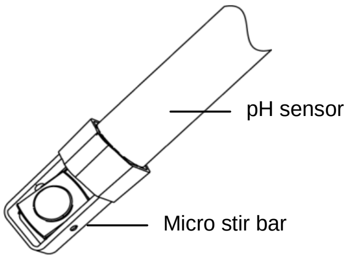
Note: Good control of the stopcock is important. If you accidentally open the stopcock too far and the NaOH streams out (as opposed to coming out in drops), you will have to start over.

13. Why will it be necessary to start your titration over again if you accidentally allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

14. Remove the waste container.

15. Add the micro stir bar to the end of the pH sensor.



16. Add additional 0.20 M NaOH to the buret so the solution is above the zero mark. Allow some of the NaOH solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 2.

17. Use the graduated cylinder to pour 50.0 mL of the unknown weak acid solution into a 100-mL beaker and set the beaker on the magnetic stirrer.

18. Turn on the magnetic stirrer at a gentle rate.

Collect Data

19. Clean the lens of the drop counter with water and a cotton swab or tissue.

20. Start recording data. �(6.2)

21. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

22. Continue the titration past the equivalence point until the pH curve flattens.

23. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

24. Do you expect a pH drop or a pH rise at the equivalence point? Explain your answer.

Since the pH is low in the initial acid solution and high after the equivalence point when the titrant base solution is in excess, the pH is expected to rise at the equivalence point.

25. Do you expect the pH to be alkaline, neutral, or acidic at the equivalence point? Explain!

At the equivalence point only the salt of the weak acid (its conjugate base) is present. Since the acid is weak, its conjugate base is strong and therefore it will remove some protons from water molecules resulting in OH^- ions. Therefore the solution will be slightly alkaline:

$A^- + H_2O \rightleftharpoons HA + OH^-$

26. Stop recording data. �(6.2)

27. Record the final drop count and the final reading of the titrant in the buret to a precision of 0.01 mL in Table 2.

28. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 2.

Table 2: Titration data

Titration Information	**Measurement or Calculation**
Initial reading of NaOH in the buret (to 0.01 mL)	0.89
Final reading of NaOH in the buret (to 0.01 mL)	24.69
Volume of titrant (to 0.01 mL)	23.80
Final drop count	714

29. Calibrate the drop counter. �(3.4)

30. Set the horizontal axis to the calculated volume. �(7.1.9)

31. In Table 3, record the volume of titrant used to reach the equivalence point. The equivalence point will be where the slope of the titration curve is the steepest. Find the steepest slope of the data plot to determine this point. �(9.3)

32. Record the pH at the half-titration point (half the volume of titrant used to reach the equivalence point) in Table 3.

33. Remove the beaker and dispose of its contents according to the instructor's instructions.

Data Analysis

Table 3: Measurements and determination of the pK_a of an unknown solution

Parameter	**Measured or Calculated Quantity**
Volume of 0.20 M NaOH to reach the equivalence point (mL)	23.80
Volume of NaOH to the half-equivalence (or half-titration) point (mL)	11.90
pH at the half-titration point	4.38
Experimental pK_a	4.38
Possible solution	Acetic acid
pK_a of the possible solution	4.75
Percent error (%)	7.7

1. What is the experimental pK_a of the unknown solution?

The pK_a is the same as the pH at the half-titration point, so in this example it is 4.38.

2. How can you identify the unknown solution based on the experimental pK_a?

The pK_a is unique to an acid and can be used to identify an unknown acid. You can use a table that lists acids and their corresponding pK_a values to identify the unknown solution.

3. What is the unknown solution?

Acetic acid.

4. What are sources of error from the titration? Calculate the percent error and record it in Table 3.

The sources of error include inaccuracy of the concentration of either solution, inaccuracy in measuring 50.00 mL of the unknown acid, air bubbles in the buret tip, and parallax error when reading buret volumes.

$$\text{Percent Error} = \frac{|\text{Theoretical Value} - \text{Experimental Value}|}{\text{Theoretical Value}} \times 100$$

$$\text{Percent Error} = \frac{4.75 - 4.38}{4.75} \times 100 = 7.7\%$$

Analysis Questions

1. Is the pH of the solution neutral, alkaline, or acidic at the equivalence point?

The pH at the equivalence point will be alkaline because the conjugate base of a weak acid is stronger than OH^-. Therefore it takes a proton away from a water molecule, producing OH^- ion: $A^- + H2O \rightleftharpoons HA + OH^-$

2. At the half-titration point, the solution is considered to be a buffer. Explain why.

The solution has a weak acid and the salt of a weak acid (the conjugate base of the weak acid) which makes the solution a buffer.

3. Would the half-titration volume (the volume of titrant used to reach the half-titration point) be different if propionic acid (which is also a monoprotic weak acid), with the same concentration, had been the unknown weak acid?

No, the half-titration point would be the same because it depends only on the stoichiometry, which is the same for both acids.

4. Would the pH of the half-titration point be different if propionic acid (which is also a monoprotic weak acid), with the same concentration, had been the unknown weak acid?

Yes, the pH of the half-titration point depends on the pK_a value of the acid and as such, it depends on the nature of the acid.

Synthesis Questions

Use available resources to help you answer the following questions.

1. The acidity constant of formic acid (HCOOH) is $K_a = 1.8 \times 10^{-4}$. Would you expect a higher or lower pH if formic acid were used instead of your unknown at the half-titration point? Explain your answer!

Since the K_a value is larger, formic acid is a stronger acid. Therefore the $[H^+]$ at the half-titration point will be greater, hence the pH will be lower.

2. If you had to determine the acidity constants of oxalic acid, which is a diprotic acid ($K_{a1} = 6.5 \times 10^{-2}$, $K_{a2} = 6.1 \times 10^{-5}$), what differences would you expect to find in the titration curve?

The titration curve would have two jumps, one for each of the deprotonation steps.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. At the equivalence point the solution contains:

- **A.** Only water
- **B.** Half of the untitrated acid and the same amount of salt
- **C. The product of the titration (salt) and water**
- **D.** Some acid left untitrated

2. At the half-titration point:

- **A. Half of the acid molecules are still untitrated**
- **B.** Half of the acid molecules are dissociated
- **C.** Half of the acid molecules are overtitrated
- **D.** There are no acid molecules left

3. The pH at the half-titration point:

- **A.** Can be calculated from the volume of the titrant necessary to reach the equivalence point
- **B.** Is the same as the pH at the equivalence point
- **C. Is the same as the pK_a of the weak acid**
- **D.** Is half of the pK_a of the weak acid

4. The solution is considered a buffer at:

- **A.** The equivalence point
- **B.** The beginning, before the titration
- **C. Any point after the titration starts and before the equivalence point**
- **D.** Only at the half-titration point

Extended Inquiry Suggestions

Provide the students with a sample of an unknown solid acid and have them identify the acid as monoprotic (potassium acid phthalate, potassium bitartrate, or benzoic acid), diprotic (oxalic acid or salicylic acid), or triporotic (citric acid). Have them further identify the acid by determining the molar mass of the acid and comparing it to a list of known acids.

26. Determination of the K_a Values of Two Isomeric Multi-Protic Acids

Adapted from the work of Dr. Frazier Nyasulu

Objectives

Students determine the acidity constants of two isomeric multi-protic acids, use these values to identify the acids, and provide an explanation for the difference in values based on molecular force considerations.

Procedural Overview

Students will gain experience conducting the following procedures:

- Determining the pK_a of the multiple equivalence points of two isomeric multi-protic acids (fumaric acid and maleic acid) through titration

- Using a pH sensor and drop counter to perform titration measurements and determine equivalence points and solution concentrations

Time Requirement

♦ Preparation time	50 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	120 minutes

Materials and Equipment

For each student or group:

- Data collection system
- pH sensor
- Drop counter with micro stir bar
- Ring stand
- Clamp, right-angle
- Clamp, buret
- Beaker (2), 250-mL
- Beaker (2), 25-mL
- Buret, 50-mL
- Graduated cylinder, 100-mL
- Magnetic stirrer
- Unidentified fumaric acid solution, 50 mL[1]
- Unidentified maleic acid solution, 50 mL[2]
- 0.500 M Sodium hydroxide (NaOH), 150 mL[3]
- Funnel
- Buffers, pH 4 and pH 10, 10 mL
- Wash bottle with deionized water
- Cotton swab or tissue

[1-3] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Titration
- Acid-base reactions
- Stoichiometry of chemical reactions
- Molarity
- Acidity constant: K_a and pK_a

Related Labs in This Guide

Labs conceptually related to this one include:

- Standardizing a Solution of Sodium Hydroxide
- Acid–base Titration
- Properties of Buffer Solutions
- Determination of a Solubility Product
- Determining *K*a by Half-Titration of a Weak Acid

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system �(2.1)
- Connecting multiple sensors to the data collection system �(2.2)
- Calibrating a drop counter �(3.4)
- Calibrating a pH sensor �(3.6)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)

♦ Changing the variable on the x-axis and y-axis of a graph �$^{(7.1.9)}$

♦ Finding the coordinates of a point on a graph �$^{(9.1)}$

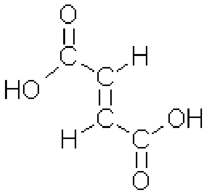
♦ Finding the slope at a point on the data plot �$^{(9.3)}$

♦ Saving your experiment �$^{(11.1)}$

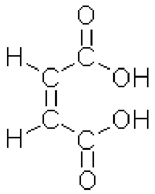
♦ Printing the graph �$^{(11.2)}$

Background

Multi-protic acids are those acids that have more than one acidic proton. Among the organic molecules, those considered to be multi-protic have more than one carboxylic group (COOH). Maleic and fumaric acids are both multi-protic:



Fumaric acid



Maleic acid

Furthermore, these two acids are structural isomers, which means they have the same formula, but the 3-dimensional orientations of the atoms in the molecule are different. These kinds of differences usually result in some significant differences in chemical and physical properties.

Looking at fumaric acid first, the two acidic hydrogen atoms are identical; therefore, they are bound with the same strength to the rest of the molecule. This means their acidity is the same. Once the first hydrogen is removed, however, the molecule is negatively charged. The second positively charged hydrogen then has to be removed by a negatively charged ion. The second acidity constant, therefore, is somewhat smaller than the first:

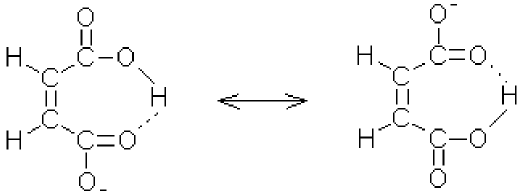
$$K_{a1} = 9.33 \times 10^{-4}, \quad pK_{a1} = 3.03$$

$$K_{a2} = 3.63 \times 10^{-5}, \quad pK_{a2} = 4.44$$

where 1 and 2 refer to the first and second acidic hydrogen ions.

When fumaric acid is titrated, both acidic protons detach at nearly the same time and the two equivalence points are not easily detected separately. Usually the equivalence points show up as a single equivalence point somewhere between the two values.

Maleic acid behaves differently. The first hydrogen detaches easily. However, there is a stabilizing effect that prevents the second hydrogen from detaching:



The now negatively-charged oxygen binds to the other acidic hydrogen atom through a hydrogen bond. The hydrogen is now firmly bonded in a six-member ring, which is usually a very stable geometrical arrangement among organic molecules. The result is that the second hydrogen has very little ability to dissociate, and has a very small acidity constant.

$$K_{a1} = 1.26 \times 10^{-2}, \quad pK_{a1} = 1.90$$

$$K_{a2} = 8.51 \times 10^{-7}, \quad pK_{a2} = 6.07$$

Pre-Lab Experiment

Setting the stage for the experiment

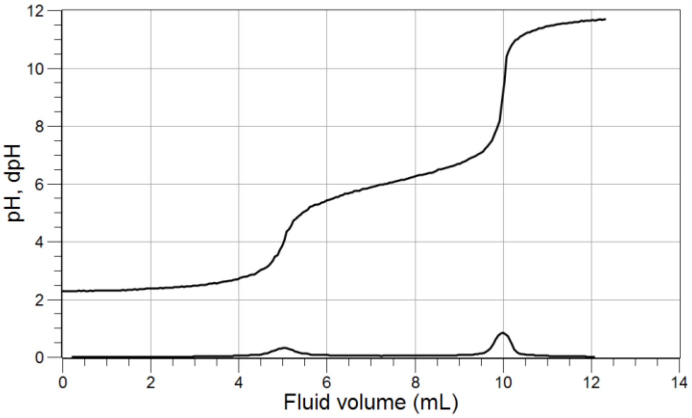
In this experiment, you will titrate a sample of both acids and determine their acidity constants. The equivalence point will be detected using a pH electrode and the pK_a values will be determined from the half-titration point.

Example calculation to try

Both fumaric acid and maleic acid are made from maleic anhydride through hydrolysis. We analyzed two samples in order to identify maleic acid as one of the samples and fumaric acid as the other sample.

Sample I

A solution made from Sample I was analyzed first: 50.00 mL of solution was titrated with 0.100 M NaOH and the following titration curve was obtained:



The second trace (close to the x-axis) is the derivative of the pH graph; the maximum of the derivative shows the equivalence points. The presence of two equivalence points suggests that Sample I is maleic acid. The data in Table 1 can be obtained from the graph.

Table 1: Titration results of Sample I

Parameter	Equivalence Point #1	Equivalence Point #2
Equivalence point (mL)	5.00	10.00
Half-titration point (mL)	2.50	5.00 + (10.00 – 5.00)/2 = 7.50
pH at half-titration point	2.20	6.00
pK_a	2.20	6.00

The pK_a values determined from the graph are close to the theoretical values, confirming the presence of maleic acid. The percent error of this determination is

$$\text{Percent Error} = \left|\frac{\text{Theoretical Value} - \text{Experimental Value}}{\text{Theoretical Value}}\right| \times 100$$

$$\text{Percent Error} = \left|\frac{1.90 - 2.20}{1.90}\right| \times 100 = 16\%$$

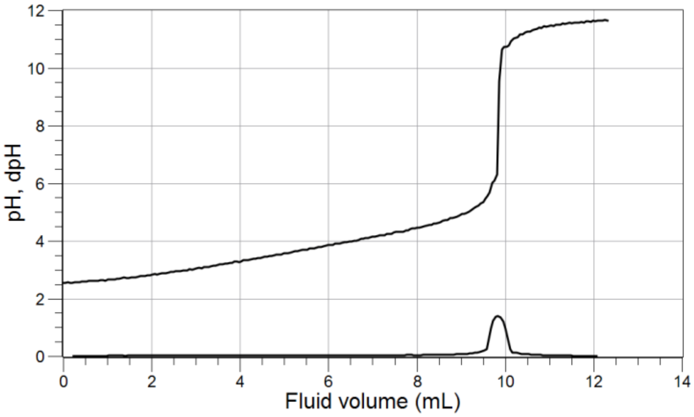
$$\text{Percent Error} = \left|\frac{6.07 - 6.00}{6.07}\right| \times 100 = 1.2\%$$

The concentration of that solution, using the first equivalence point, was

$$5.00\text{ mL NaOH}\left(\frac{0.100\text{ mol NaOH}}{1000\text{ mL NaOH}}\right)\left(\frac{1\text{ mol maleic acid}}{1\text{ mol NaOH}}\right)\left(\frac{1}{5.000 \times 10^{-2}\text{ L}}\right) = 0.0100\text{ M}$$

Sample II

A solution made from Sample II was analyzed next. 50.00 mL of solution was titrated with 0.100 M NaOH and the following titration curve was obtained:



The presence of only one equivalence point suggests that Sample II is fumaric acid. The data in Table 2 can be obtained from the graph.

Table 2: Titration results of Sample II

Parameter	Equivalence Point Values
Equivalence point (mL)	9.90
Half titration point (mL)	4.95
pH at half titration point	3.50
pK_a	3.50

The expected value of pK_a for fumaric acid is between pK_{a1} and pK_{a2}: (4.44 + 3.03)/2 = 3.74, so the percent error is

$$\text{Percent Error} = \frac{|3.74 - 3.50|}{3.74} \times 100 = 6.4\%$$

The concentration of Sample II, using the equivalence point, was:

$$9.90\text{ mL NaOH}\left(\frac{0.100\text{ mol NaOH}}{1000\text{ mL NaOH}}\right)\left(\frac{1\text{ mol fumaric acid}}{2\text{ mol NaOH}}\right)\left(\frac{1}{5.000 \times 10^{-2}\text{ L}}\right) = 9.90 \times 10^{-3}\text{ M}$$

The concentration of the solution of Sample II was also 9.90×10^{-3} M.

1. Explain the way the position of the second half-titration point for maleic acid was calculated.

The first equivalence point was at 5.00 mL. The NaOH solution used between 5.00 mL and 10.00 mL was to obtain the second equivalence point for the second hydrogen. The halfway point (where the pH will be equal to the pK_a) is

(10.00 mL – 5.00 mL)/2 = 2.50 mL

after the first equivalence point, so the point at which this happens is

5.00 mL+ 2.50 mL = 7.50 mL

2. Would we get a different result for the concentration of maleic acid if we used the second equivalence point instead of the first for the calculation?

No, we would have gotten the same results:

$$10.00\text{ mL NaOH}\left(\frac{0.100\text{ mol NaOH}}{1000\text{ mL NaOH}}\right)\left(\frac{1\text{ mol maleic acid}}{2\text{ mol NaOH}}\right)\left(\frac{1}{5.000 \times 10^{-2}\text{ L}}\right) = 0.0100\text{ M}$$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.027 M Maleic Acid:*** Dissolve 1.566 g of maleic acid in about 500 mL of distilled water in an Erlenmeyer flask. Place a stirring bar into the solution and on a hot plate gently heat and stir the solution until all solid dissolves. Allow the solution to cool to room temperature. Transfer the solution into a 2-L volumetric flask and fill it to the mark. Mix the solution well.

   Label the solution “Unknown I.”

2. ***0.027 M Fumaric Acid:*** Dissolve 1.566 g of fumaric acid in about 500 mL of distilled water in an Erlenmeyer flask. Place a stirring bar into the solution and on a hot plate gently heat and stir the solution until all solid dissolves. Allow the solution to cool to room temperature. Transfer the solution into a 2-L volumetric flask and fill it to the mark. Mix the solution well.

   Label the solution “Unknown II.”

3. ***0.500 M NaOH:*** Dissolve 20.00 g of NaOH in about 500 mL of distilled water in an Erlenmeyer flask. Allow the solution to cool to room temperature. Transfer the solution into a 1-L volumetric flask and fill it to the mark. Mix the solution well.

   Note: Standardize the solution and report the actual concentration to the students.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �$^{(1.2)}$

2. Connect a pH sensor to the data collection system. �$^{(2.1)}$

3. Calibrate the pH sensor. �$^{(3.6)}$

4. Assemble the titration apparatus, using the steps below and the illustration as a guide.

  a. Position the magnetic stirrer on the base of the ring stand.

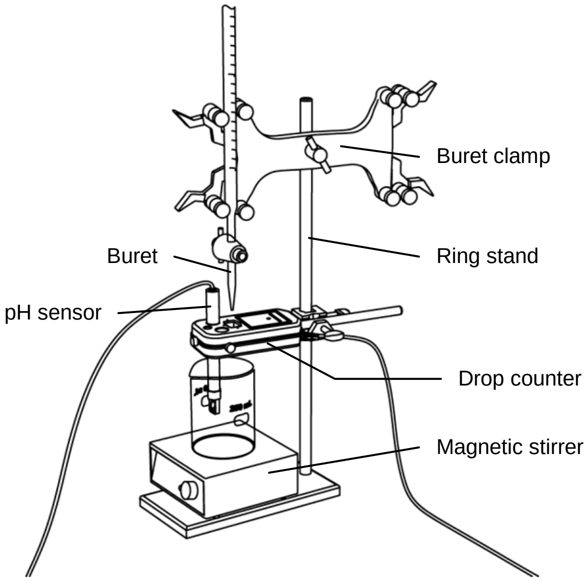
  b. Place a waste container (250-mL beaker) on the magnetic stirrer.

  c. Use the buret clamp to attach the buret to the ring stand.

  d. Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.

  e. Place the pH sensor through one of the slots in the drop counter.

Note: Do not connect the drop counter to the data collection system yet.



5. Rinse the buret with several milliliters of the 0.500 M NaOH solution:

  a. Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized NaOH solution.

  b. Open the stopcock on the buret and drain the rinse NaOH into the waste container.

  c. Repeat this process two more times.

6. Why is it necessary to rinse the buret with the NaOH solution?

If there is any residual water or contaminant in the buret, it will dilute the NaOH and change its concentration. Rinsing eliminates any such contamination.

7. Make sure the stopcock on the buret is in the “off” position and then use a funnel to fill the buret with about 50 mL of the 0.500 M NaOH solution (titrant).

8. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

9. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of NaOH. If this happens, the amount of titrant used will be inaccurate.

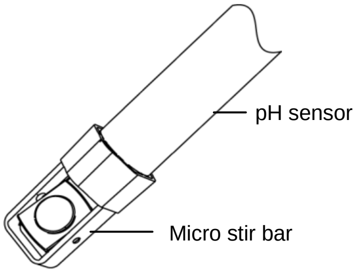
10. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

Note: Good control of the stopcock is important. Each drop should result in a blink of the LED on the drop counter. If the LED is continuously lit, you have opened the stopcock too far and you will have to start over**.**

11. Why will it be necessary to start your titration over again if you accidentally allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

12. Add the micro stir bar to the end of the pH sensor.



13. Why is it necessary to stir the solution during a titration?

Stirring thoroughly mixes the ions in the solution so that the recorded pH reflects the pH of the entire solution.

14. Add additional 0.500 M NaOH to the buret so the solution is above the zero mark. Allow some of the NaOH solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 3.

15. Remove the waste container.

16. Use the graduated cylinder to pour 100.0 mL of the Unknown I solution into a 250-mL beaker and set the beaker on the magnetic stirrer.

17. Lower the pH sensor into the solution.

18. Turn on the magnetic stirrer at a slow and steady rate.

19. Connect the drop counter to the data collection system. �(2.2)

20. Display the pH on the y-axis of a graph and Drop Count on the x-axis. �(7.1.1)

21. Clean the lens of the drop counter inside the opening through which the drops go with water and a cotton swab or tissue.

Collect Data

22. Start recording data. �(6.2)

23. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

24. Continue the titration past the equivalence point until the pH curve flattens.

Note: Not knowing which solution is fumaric or maleic acid, determine a strategy that will ensure the titration provides the necessary information for each.

25. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

26. How do you know when to stop the titration, not knowing how many equivalence points will be there?

The pH should level off around 12 when the titration is completed.

27. Stop recording data. �(6.2)

28. In Table 3, record the final drop count and the final reading of the titrant in the buret to a precision of 0.01 mL.

29. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 3.

Table 3: Titration data

Titration Information	Unknown I	Unknown II
Initial reading of HCl on the buret (mL)	0.00	0.00
Final reading of HCl on the buret (mL)	14.40	13.90
Volume of titrant (mL)	14.40	13.90
Final drop count	480	463

30. Calibrate the drop counter. �$^{(3.4)}$

31. On the graph, set the horizontal axis to the calculated volume. �$^{(7.1.9)}$

32. Record the volume of titrant used to reach each equivalence point in Table 4.

Note: The equivalence point will be where the slope of the titration curve is the steepest. Find the steepest slope of the data plot to determine this point. �$^{(9.3)}$

Note: For one of the unknowns, only one equivalence point will be detected, even though there are two. The one detected can be considered the second equivalence point.

33. Refill the buret over the zero mark with the NaOH solution.

a. Fill the buret above the zero mark and allow some of the NaOH solution to drip into a waste container until the bottom of the meniscus is lined up with the zero mark or just below.

b. Record the starting point in Table 3.

34. Clean the lens of the drop counter between runs with water and a cotton swab or tissue.

35. Rinse the pH probe tip with deionized water.

36. Remove the beaker and dispose of its contents according to the instructor's instructions.

37. Rinse the beaker with distilled water.

38. Use the graduated cylinder to pour 100.0 mL of the Unknown II solution into the 250-mL beaker and set the beaker on the magnetic stirrer.

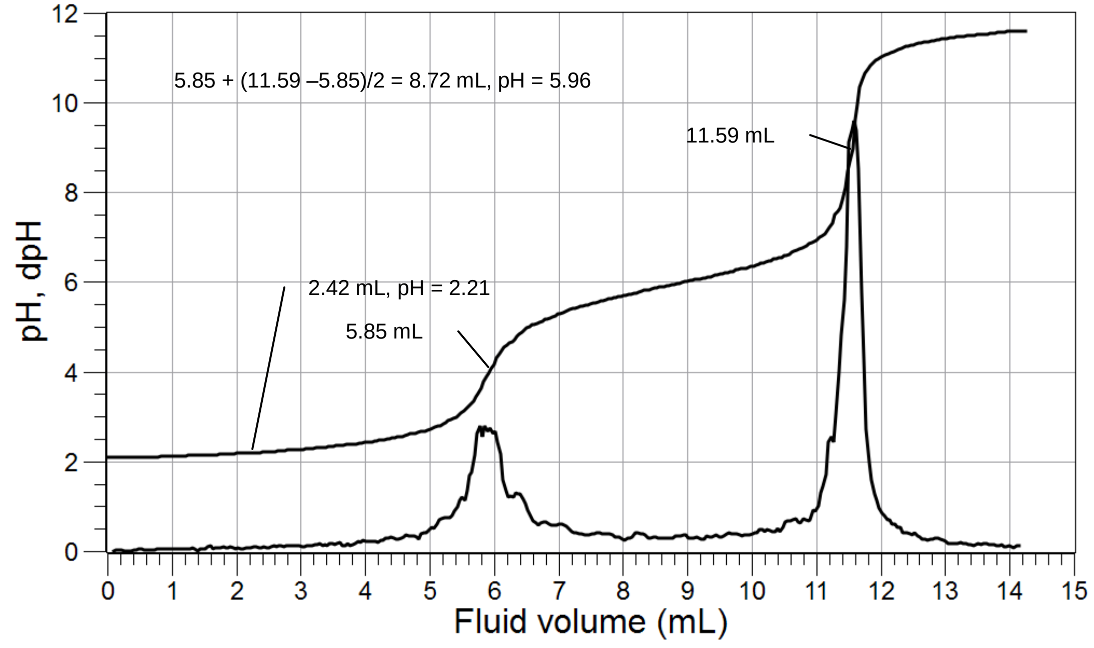
39. Lower the pH sensor into the solution.

40. Turn on the magnetic stirrer at a slow and steady rate.

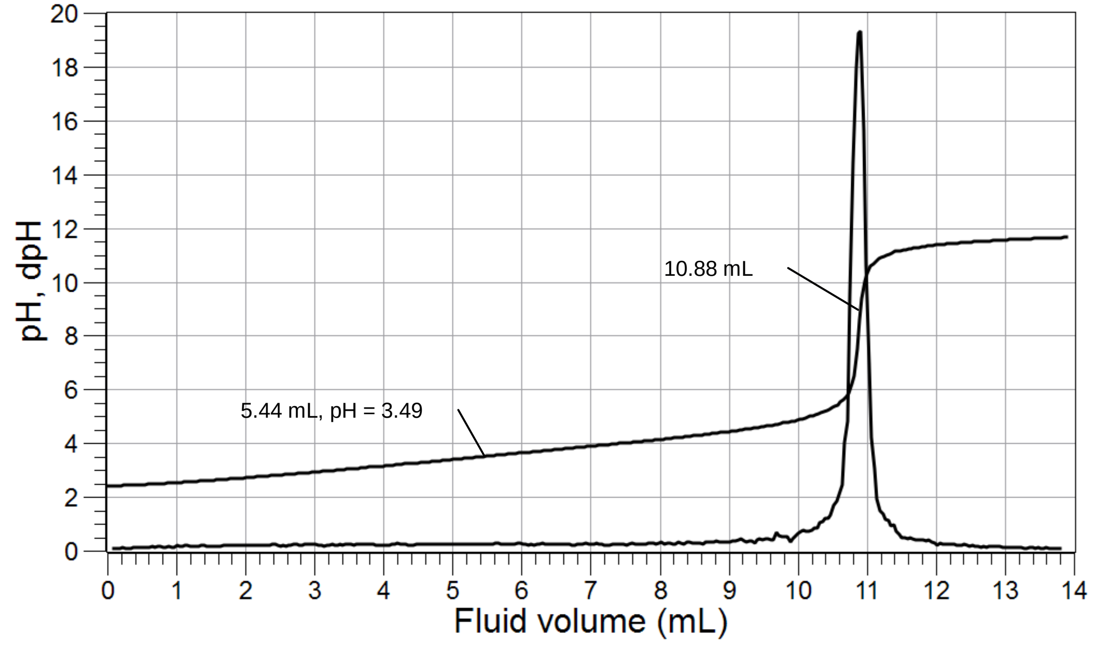
41. Return to the first step of the Collect Data section and repeat the titration with the Unknown II solution.

42. Save your experiment �(11.1) and clean up according to your instructor's instructions.

43. For each titration curve, sketch or print the graphs �(11.2) and paste them below. Identify which is fumaric and which is maleic acid.



Maleic acid



Fumaric acid

Data Analysis

1. Obtain the concentration of the NaOH solution from your instructor and record it in Table 4.

Table 4: Equivalence points of the unknown solutions

Parameter	Unknown I	Unknown II
Concentration of the NaOH solution (M)	0.5000	
Volume to the first equivalence point (mL)	5.85	
Volume to the second equivalence point (mL)	11.59	18.88

2. Which solution is maleic acid and which is fumaric acid?

Unknown I is maleic acid, as it has two distinct equivalence points. Unknown II is fumaric acid.

3. Copy the values in Table 4 to the appropriate column in Table 5.

4. Calculate the half-titration points for each equivalence point and record them in Table 4.

For maleic acid, the first half-titration point is at half the volume of the equivalence point (5.85 mL/2 = 2.42 mL). The second half-titration point is determined by adding half the volume of titrant used to the first equivalence point [5.85 mL + (11.59 mL – 5.85 mL)/2 = 8.72 mL].

For fumaric acid, the half-titration point is 10.88 mL/2 = 5.44 mL.

5. Use the graphs to determine the pH and p*K*a at the half-titration points and record these values in Table 5. �$^{(9.1)}$

For maleic acid, the pH is 2.21 and 5.96. The pK_a values are 2.21 and 5.96.

For fumaric acid, the pH is 3.40 and the pK_a is 3.40.

6. Record the published values of the p*K*a for maleic and fumaric acids in Table 5.

7. What is the percentage of error between the published values and the values you determined from the titration? Record these in Table 5.

For maleic acid and fumaric acid:

$$\text{Percent error} = \left|\frac{1.90 - 2.21}{1.9}\right| \times 100 = 16.3\%$$

$$\text{Percent error} = \left|\frac{6.07 - 5.96}{6.07}\right| \times 100 = 1.81\%$$

$$\text{Percent error} = \left|\frac{3.73 - 3.40}{3.73}\right| \times 100 = 8.85\%$$

8. Calculate the concentrations of the two solutions and determine the pK_a values. Record these values in Table 5.

$$5.85\text{ mL NaOH}\left(\frac{0.500\text{ mol NaOH}}{1000\text{ mL NaOH}}\right)\left(\frac{1\text{ mol maleic acid}}{1\text{ mol NaOH}}\right)\left(\frac{1}{100.0\times10^{-3}\text{ L}}\right) = 2.925\times10^{-2}\text{ M}$$

$$10.88\text{ mL NaOH}\left(\frac{0.500\text{ mol NaOH}}{1000\text{ mL NaOH}}\right)\left(\frac{1\text{ mol fumaric acid}}{2\text{ mol NaOH}}\right)\left(\frac{1}{100.0\times10^{-3}\text{ L}}\right) = 2.72\times10^{-2}\text{ M}$$

Table 5: Determination of acidity constants and concentration

Parameter	**Maleic Acid**		**Fumaric Acid**
Equivalence point	1	2	1–2
Equivalence point (mL)	5.85	11.59	10.88
Half-titration point (mL)	2.42	8.72	5.44
pH at half-titration point	2.21	5.96	3.40
pK_a	2.21	5.96	3.40
pK_a from literature	1.90	6.07	3.73 (avg)
Percent error (%)	16.3	1.81	8.85
Concentration (M)	2.92×10^{-2}		2.72×10^{-2}

Analysis Questions

1. Does your experimental data support the predicted values regarding the two acidity constants of maleic acid?

Yes, the two acidity constants came out close to the predicted values.

2. Does your experimental data support predicted values regarding the two acidity constants of fumaric acid?

The two acidity constants were determined as one, close to the average of the two.

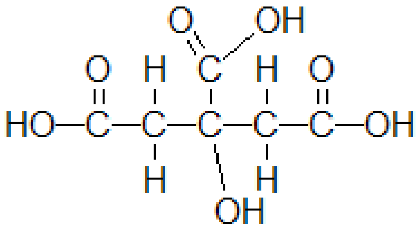
3. Why was only one equivalence point detected in the fumaric acid solution?

The two constants are too close to each other to be detected separately.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Consider citric acid, which is an important ingredient in lemons:



How many acidic hydrogen atoms can you identify?

There are three: the ones attached to oxygen atoms on carboxylic groups.

2. Predict how close the acidity constants (K_a) are to each other?

The acidity constants should be relatively close to each other, just like those of fumaric acid. Indeed, the three Ka values are: 7.41×10^{-2}, 1.74×10^{-5}, 2.72×10^{-7}.

3. Which acidity constant (K_a) of citric acid is smallest and why?

The third one, since the third positively -charged hydrogen would have to come off of a doubly negatively-charged ion.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Which statement is correct regarding the acidity constants of fumaric acid?

- **A. They are close to each other.**
- **B.** The first one is much larger than the second.
- **C.** The second one is much larger than the first one.
- **D.** Identical.

2. Which statement is correct regarding the acidity constants (K_a) of maleic acid?

- **A.** They are close to each other.
- **B. The first one is much larger than the second.**
- **C.** The second one is much larger than the first one.
- **D.** Identical.

3. What is the second acidity constant of maleic acid influenced by?

- **A.** It is influenced by the pH of the solution.
- **B.** **It is influenced by the formation of a stable structure after the dissociation of the first hydrogen ion**.
- **C.** It is affected by the first acidity constant.
- **D.** It is influenced by titrating solution.

4. The acidity constants of fumaric and maleic acids are different because:

- **A.** They have the same formula
- **B.** **They have the same formula but different structure**.
- **C.** They are both organic acids.
- **D.** They are not different.

Extended Inquiry Suggestions

Students can analyze a mixture of maleic acid and fumaric acid. There will be three equivalence points with the equivalence point for fumaric acid falling between the first and second equivalence points of maleic acid.

Acknowledgements

This experiment was adapted from the following work of Dr. Frazier Nyasulu:

Nyasulu, F. W.; Macklin, J. *Journal of Chemical Education*. 2006, *83* (5), 770–773.

Kinetics and Equilibrium

27. Determine the Equilibrium Constant for a Chemical Reaction

Objectives

Students determine the equilibrium constant for a chemical reaction using visible spectroscopy.

Procedural Overview

Students gain experience conducting the following procedures:

- Preparing solutions
- Using visible spectroscopy to determine the concentration of an absorbing species
- Calculating the equilibrium using Beer's law, known initial concentrations, and the mathematical relationship between the concentrations of the reactants and products

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Colorimeter and cuvette
- Extension cable
- Beaker (2), 50-mL
- Test tube (5),15-mL
- Test tube rack
- Graduated pipet (2), 10-mL
- Rubber pipet bulb
- 0.01 M Iron (Fe^{3+}), 20 mL[1]
- 0.00300 M Potassium thiocyanate (KSCN), 20 mL[2]
- Kimwipes®
- Deionized water, 40 mL
- Marker

[1-2] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- The concept of equilibrium
- Stoichiometry of a chemical reaction
- Reversible chemical reactions
- Le Chatelier's Principle
- Beer's Law

Related Labs in This Guide

Labs conceptually related to this one include:

- Absorption Spectra
- Colorimetric Analysis
- Determination of a Solubility Product

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting sensors to the data collection system �(2.1)
- Calibrating the colorimeter �(3.2)
- Using the colorimeter to collect data with blue light �(4.1)
- Monitoring live data without recording �(6.1)
- Starting and stopping data recording �(6.2)
- Saving your experiment �(11.2)

Background

In many chemical reactions the products of the reaction can react to reform the original reactants. The forward reaction occurs rapidly at first, but slows as the reactants are consumed. The reverse reaction occurs slowly at first and increases in rate as more products of the forward reaction become available. At some point the two reactions occur at the same rate, resulting in a constant amount of reactants and products. The state in which the concentrations of the reactants and products have no net change over time is known as chemical equilibrium.

The mathematical relationship between the concentrations of the reactants and products is given by the law of mass action, which states that the rate of a chemical reaction is proportional to the concentration of the reactants.

In general, for a reaction of the form,

$$\text{aA} + \text{bB} \rightleftharpoons \text{cC} + \text{dD}$$

the equilibrium constant K_{eq} is given by

$$K_{\text{eq}} = \frac{[\text{C}]^c[\text{D}]^d}{[A]^a[\text{B}]^b}$$

In this experiment, you use a colorimeter to help determine the equilibrium constant for the formation of $FeSCN^{2+}$. In dilute solutions, iron (III) nitrate, $Fe(NO_3)_3(aq)$, and potassium thiocyanate, KSCN(aq), are completely dissociated. When these two solutions are mixed, the following equilibrium is established:

$$\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$$

Pre-Lab Experiment

Setting the stage for the experiment

Of the five ions in solution, K^+(aq), NO_3^- (aq), and SCN^- (aq) are colorless, Fe^{3+}(aq) is nearly colorless, and $FeSCN^{2+}$(aq) is deep red. Changes in the concentration of $FeSCN^{2+}$(aq) are indicated by changes in the intensity of the color of the solution.

The equilibrium expression for the reaction is

$$K_{\text{eq}} = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]}$$

To calculate K_{eq} for this reaction, you need to determine the molar concentration of Fe^{3+}, SCN^-, and $FeSCN^{2+}$ at equilibrium.

The relationship between electromagnetic absorption and concentration of the absorbing species is given by Beer's law. Absorption of light is directly proportional to the distance that the light travels through an absorbing medium and the molar concentration of the absorbing species.

$$A = \varepsilon \times l \times c \qquad (1)$$

where

A = absorption
ε = absorptivity coefficient ($M^{-1}cm^{-1}$)
l = path length that light travels through the solution (cm)
c = molar concentration of the absorbing species (M).

Note: Equation 1 can also be written as "A = *a b c*" where *a* and *b* correspond to ε and *l*, respectively.

The absorptivity coefficient ε is a proportionality constant, and its value depends both on the nature of the absorbing species and on the wavelength of light chosen for the measurement. At a given wavelength and using a sample cell of constant path length, absorption is directly proportional to concentration. Thus, a measurement of A can be used to determine concentration. The red $FeSCN^{2+}$ ion absorbs blue light and will be analyzed at 468 nm.

Example calculation to try

In an experiment to determine the equilibrium constant for the reaction between Fe^{3+} and SCN^{-}, a student prepared a solution by mixing 1.00 mL of 0.0100 M Fe^{3+}, 1.00 mL of 0.00300 M SCN^{-} solution, and 8.00 mL of water. A portion of the solution was placed in a cell and the absorbance of the solution was measured. The cell path length l is 1.00 cm thick. The absorptivity coefficient ε is 5302 $M^{-1}cm^{-1}$ for $FeSCN^{2+}$.

The concentration of Fe^{3+} and SCN^{-} in the reaction solution before the reaction between Fe^{3+} and SCN^{-} occurs can be calculated by considering the dilution of the reactants.

$$c_i V_i = c_f V_f$$

where

c_i = initial concentration (M)
V_i = initial volume (mL)
c_f = final concentration (M)
V_f = final volume after the dilution (mL)

Using this equation, the concentration of Fe^{3+} in the reaction solution before the reaction occurs is $[Fe^{3+}]_0 (1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}) = (0.0100\text{ M})(1.00\text{ mL})$.

The calculated $[Fe^{3+}]_0$ is the concentration of iron(III) *after* the dilution (after mixing the reactants) but *before* the reaction starts.

Solving for $[Fe^{3+}]_0$ and doing the same to calculate the initial concentration of SCN^{-} results in the following:

$$[Fe^{3+}]_0 = \frac{1.00\text{ mL}}{1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}}(0.0100\text{ M}) = 1.00 \times 10^{-3}\text{ M}$$

$$[SCN^{-}]_0 (1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}) = (0.00300\text{ M})(1.00\text{ mL})$$

$$[SCN^{-}]_0 = \frac{1.00\text{ mL}}{1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}}(0.00300\text{ M}) = 3.00 \times 10^{-4}\text{ M}$$

To calculate the equilibrium constant, you need to calculate the equilibrium concentrations. The concentration of $FeSCN^{2+}$ at equilibrium is determined using the absorbance of the solution:

$$[FeSCN^{2+}] = \frac{A}{\varepsilon l} = \frac{0.293}{\left(5203\ M^{-1}\ cm^{-1}\right)(1.00\ cm)} = 5.63 \times 10^{-5}\ M$$

The equilibrium concentrations of Fe^{3+} and SCN^{-} are then the difference between their initial concentrations and the equilibrium concentration determined for $FeSCN^{2+}$.

$$[Fe^{3+}] = [Fe^{3+}]_0 - [FeSCN^{2+}] = (1.00 \times 10^{-3} M) - (5.63 \times 10^{-5} M) = 9.44 \times 10^{-4} M$$

$$[SCN^{-}] = [SCN^{-}]_0 - [FeSCN^{2+}] = (3.00 \times 10^{-4} M) - (5.63 \times 10^{-5} M) = 2.44 \times 10^{-4} M$$

Using the calculated concentrations, the equilibrium constant is:

$$K_{eq} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]} = \frac{(5.63 \times 10^{-5})}{(9.44 \times 10^{-4})(2.44 \times 10^{-4})} = 244$$

1. What kind of mathematical relationship exists between the absorbance *A* and the concentration of the absorbing species *c*?

The relationship is linear. That is, the absorbance is directly proportional to the concentration.

2. Looking at the equation (Equation 1) that describes the relationship between absorbance and the concentration, what would be the intercept on the plot of *A* versus *c*? Explain!

The intercept would be 0. This means that when the concentration is 0, so is the absorbance. This makes perfect sense: If there are no species absorbing light, the absorbance should be zero.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.0100 M Iron solution:*** In a 500-mL volumetric flask, dissolve 2.02 g of $Fe(NO_3)_3{\cdot}9H_2O$ in some distilled water, add 20 mL of concentrated HNO_3 and fill the flask to the mark with distilled water.
2. ***0.00300 M KSCN:*** In a 500-mL volumetric flask, dissolve 0.1383 g of KSCN in some distilled water and fill the flask to the mark with distilled water.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect the colorimeter to the data collection system using a sensor extension cable. �(2.1)

3. Display Blue absorbance (468 nm) in a digit display. �(7.3.1)

4. Set the data collection system to monitor live data without recording. �(6.1)

5. Label the first test tube “Blank” and the others from “1” to “4”.

6. Prepare the solutions in the labeled test tubes by combining the prescribed amounts of the reactants and water (see Table 1).

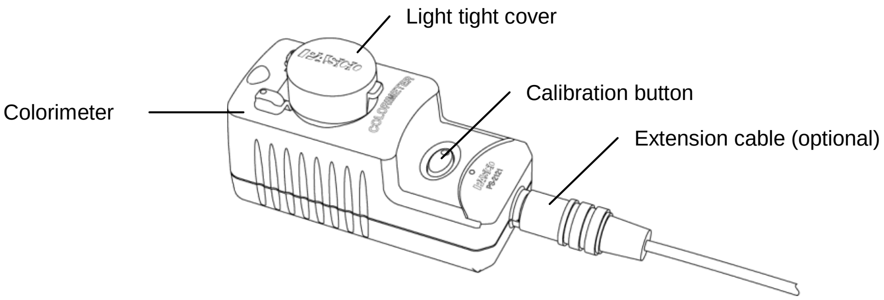
Table 1: Composition of solutions to study chemical equilibrium

Test Tube	**1.00×10^{-2} M $Fe_2(NO_3)_3$, acidic (mL)**	**3.00×10^{-3} M KSCN (mL)**	**Water (mL)**	***A***
Blank	1.00	0.00	9.00	
1	1.00	1.00	8.00	0.360
2	1.00	2.00	7.00	0.764
3	1.00	3.00	6.00	1.144
4	1.00	4.00	5.00	1.475

7. How do you think the intensity of the color changes among the solutions? Explain your prediction.

The intensity of the color increases with the concentration of the colorful species, KSCN. Therefore test tube #4 will have the most intense color.

8. Calibrate the colorimeter with the blank solution. �(3.2)



Important: Always make sure that the cell is clean and dry on the outside before placing it into the colorimeter.

9. Throughout this experiment, collect data using blue light (468 nm) in the colorimeter. �(4.1)

Collect Data

10. Measure the absorbance of the four solutions following the steps below.

- **a.** Rinse the cell with a small portion of the first solution and fill the cuvette two-thirds full. Wipe the cuvette clean and dry and place it into the colorimeter.
- **b.** Why do you have to rinse the cell with some of the solution?

If there is any residual water in the cuvette, it will dilute the concentration of the solution and falsify the data.

- **c.** After the reading stabilizes, record the absorbance in Table 1 and Table 2.
- **d.** Dispose of the solution and rinse the cell thoroughly with water.
- **e.** Why do you think it is important to rinse the cell thoroughly between measurements?

You need to rinse the cell to avoid contamination of the solutions.

11. Clean up according to your instructor's instructions. �(11.1)

Data Analysis

For your calculations, consider the product of absorptivity ε and the cell thickness l to be

$\varepsilon \times l = 5900\ \text{M}^{-1}$

1. Calculate and record in Table 2 the initial concentrations of Fe^{3+} and SCN^{-} in each test tube.

For Test Tubes 1 to 4 for $[Fe^{3+}]_0$ and for Test Tube 1 for $[SCN^{-}]_0$:

$$[Fe^{3+}]_0\left(1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}\right) = (0.0100\text{ M})(1.00\text{ mL})$$

$$[Fe^{3+}]_0 = \frac{1.00\text{ mL}}{1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}}(0.0100\text{ M}) = 1.00 \times 10^{-3}\text{ M}$$

$$[SCN^-]_0\left(1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}\right) = (0.00300\text{ M})(1.00\text{ mL})$$

$$[SCN^-]_0 = \frac{1.00\text{ mL}}{1.00\text{ mL} + 1.00\text{ mL} + 8.00\text{ mL}}(0.00300\text{ M}) = 3.00 \times 10^{-4}\text{ M}$$

2. Calculate the concentration of the $Fe(SCN)^{2+}$ ions from the absorbance measurements using Beer's Law and the above value of **ε × *l***. Record the values in Table 2.

The concentration of $Fe(SCN)^{2+}$ in the Test Tube 1:

$$[FeSCN^{2+}] = \frac{A}{\varepsilon l} = \frac{0.360}{5900\text{ M}^{-1}} = 6.10 \times 10^{-5}\text{ M}$$

3. Calculate the equilibrium concentration of the Fe^{3+} and SCN^- ions from the initial concentration of the ions and the amount of ions used to establish the equilibrium concentration of $FeSCN^{2+}$. Record the values in Table 2.

The concentration of Fe^{3+} and SCN^- ions in Test Tube 1:

$$[Fe^{3+}] = [Fe^{3+}]_0 - [FeSCN^{2+}] = (1.00 \times 10^{-3}\text{ M}) - (6.10 \times 10^{-5}\text{ M}) = 9.39 \times 10^{-4}\text{ M}$$

$$[SCN^-] = [SCN^-]_0 - [FeSCN^{2+}] = (3.00 \times 10^{-4}\text{ M}) - (6.10 \times 10^{-5}\text{ M}) = 2.39 \times 10^{-4}\text{ M}$$

4. Calculate the equilibrium constant from the equilibrium concentration of the $Fe(SCN)^{2+}$, Fe^{3+}, and SCN^- ions. Record the values in Table 2.

Performing the calculation for the first solution:

$$K_{eq} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(6.10 \times 10^{-5})}{(9.39 \times 10^{-4})(2.39 \times 10^{-4})} = 271$$

Table 2: Calculation of the equilibrium concentrations and the equilibrium constant

#	$[Fe^{3+}]_0$ (M)	$[SCN^-]_0$ (M)	A	$[FeSCN^{2+}]$ (M)	$[Fe^{3+}]$ (M)	$[SCN^-]$ (M)	K_{eq}
1	1.00×10^{-3}	3.00×10^{-4}	0.360	6.10×10^{-5}	9.39×10^{-4}	2.39×10^{-4}	271
2	1.00×10^{-3}	6.00×10^{-4}	0.764	1.29×10^{-4}	8.71×10^{-4}	4.71×10^{-4}	316
3	1.00×10^{-3}	9.00×10^{-4}	1.144	1.93×10^{-4}	8.06×10^{-4}	7.06×10^{-4}	341
4	1.00×10^{-3}	1.20×10^{-3}	1.475	2.500×10^{-4}	7.50×10^{-4}	9.50×10^{-4}	351

5. Calculate the average equilibrium constant and record the value below.

Average value of K_{eq}: 320

Analysis Questions

1. How did the absorbance change with increasing initial SCN^- concentration while the initial concentration of Fe^{3+} was kept constant? Why?

The absorbance increased because higher SCN^- concentration pushes the equilibrium of Equation 1 to the right, which results in more $FeSCN^-$ ions.

2. Why do you think the equilibrium constant remained virtually constant, within experimental error, even though you were changing the concentrations?

The equilibrium constant does not depend on the concentrations. On the contrary, concentrations adjust to satisfy the equilibrium constant by shifting the concentration of reactants and products in the appropriate direction.

3. How do you think your results would have been different if you used a cell with twice the path length?

The absorbance values would have been doubled. However, we would have obtained the same concentrations.

4. Beer's Law (the linear relationship between concentration and absorbance) is accurate to about $A = 1.5$. How would you modify the experiment if the absorbance readings were higher than 1.5?

The solutions would have to be diluted until the absorbance was within the acceptable range.

Synthesis Questions

Use available resources to help you answer the following questions.

1. Does the absorbance you measured come only from the $FeSCN^{2+}$ ion? Explain your answer.

Only the $FeSCN^{2+}$ ion absorbs appreciably at this wavelength. This is also proven by the fact that only the $FeSCN^{2+}$ ion is colored.

2. The Fe^{3+} ion can react with three SCN^- ions according to the following equilibrium equations to form $Fe(SCN)_2^+$ and $Fe(SCN)_3$. These products are also red.

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+} \qquad \text{(SQ1)}$$

$$FeSCN^{2+} + SCN^- \rightleftharpoons Fe(SCN)_2^+ \qquad \text{(SQ2)}$$

$$Fe(SCN)_2^+ + SCN^- \rightleftharpoons Fe(SCN)_3 \qquad \text{(SQ3)}$$

In light of these reactions, propose an explanation as to why this experiment uses a large excess of Fe^{3+} ions.

The experiment used a large excess of Fe^{3+} to suppress the products resulting from Equations SQ2 and SQ3, which require SCN^- ions. This ensures that the measured absorbance is completely attributed to $Fe(SCN)^{2+}$: according to Le Chatelier's Principle, the first reaction is shifted to the right, removing most of the SCN^- ions; the second and third reactions are shifted to the left to increase the concentration of SCN^- ions.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. The four measurements you made resulted in four substantially different equilibrium constants. Which statement could be correct?

- **A.** The equilibrium constant is determined by the concentrations. We used different concentrations, so the resulting equilibrium constants should be the same.
- **B.** The equilibrium of the second and third equations (SQ2 and SQ3) interfered with our measurements.
- **C.** The equilibrium constant depends on the temperature, so the fluctuation in room temperature might have interfered with our measurements.
- **D.** **There was an error in mixing the solutions, or one (or both) of the stock solutions had the wrong concentration**.

2. How do you think doubling the initial iron concentration of Fe^{3+} ions would affect the obtained value for K_{eq}?

- **A.** Doubling the initial concentration of Fe^{3+} ions will double K_{eq}, according to Le Chatelier's Principle.
- **B.** **Doubling the initial concentration of Fe^{3+} ions will not affect K_{eq}.**
- **C.** Doubling the initial concentration of Fe^{3+} ions will result in half of the value for K_{eq}.
- **D.** The effect of doubling the Fe^{3+} initial concentration is not predictable; you would need to actually perform the experiments.

3. The $FeSCN^{2+}$ ion is red, the other species are practically colorless. Would it interfere with your measurements if another species had color?

- **A.** No, we measure only $FeSCN^{2+}$.
- **B.** **If the other colored species does not absorb at 468 nm where we perform the experiment, it would not interfere with our measurements.**
- **C.** Yes, but we would need to divide the measured absorbance by 2 to get the absorbance from $FeSCN^{2+}$.
- **D.** The answer depends on which other species absorbs.

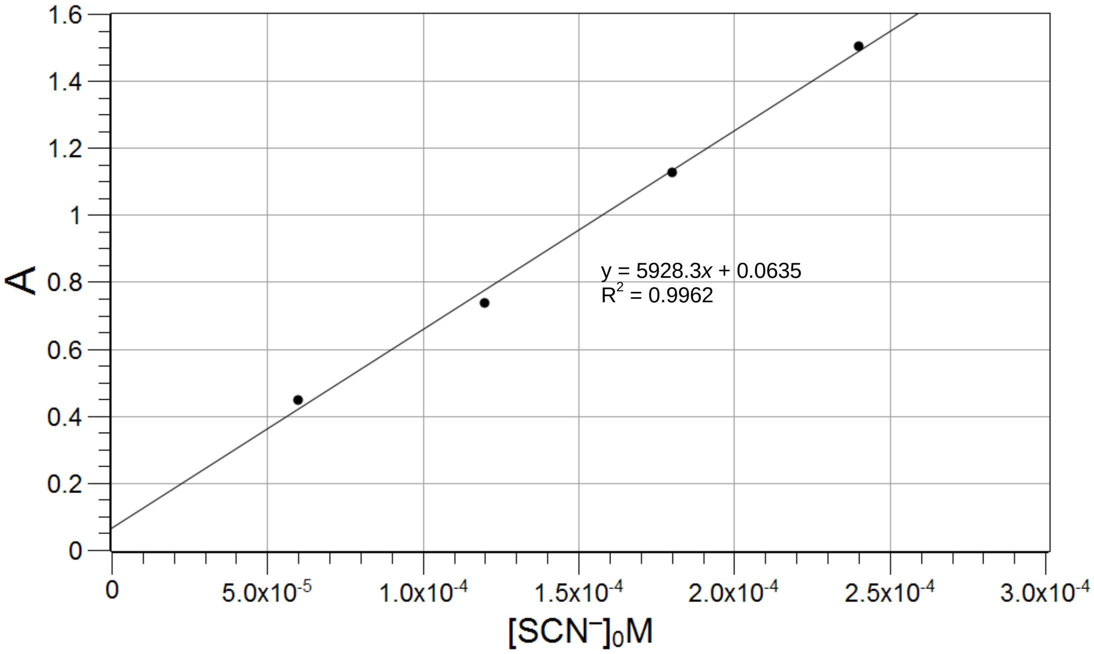
Extended Inquiry Suggestions

If time allows, ask your students to determine the product of absorptivity of the species and cell path length instead of giving them for the calculations. Please note that if the colorimeter is used, the path length is not well defined because the cell is round and not all of the photons pass through the same thickness of solution. Therefore, it is more appropriate to consider the product of absorptivity ε and cell path length l as one constant that relates the absorbance to the concentration.

The product of $\varepsilon \times l$ can be determined by preparing 4 solutions with Fe^{3+} ions in overwhelming excess. In this case, it is safe to assume that all Fe^{3+} ions are quantitatively converted to $FeSCN^{2+}$ (see the table below).

Absorptivity of the calibrating solutions

0.003 M KSCN (mL)	**0.1 M Fe^{3+} (mL)**	**Water (mL)**	**$[FeSCN^{2+}]$ (M)**	**A**
0.50	20.00	4.50	6.00×10^{-5}	0.446
1.00	20.00	4.00	1.20×10^{-4}	0.737
1.50	20.00	3.50	1.80×10^{-4}	1.126
2.00	20.00	3.00	2.40×10^{-4}	1.502



The product of absorptivity ε and path length *l* is 5.93×10^3 M^{-1} cm^{-1}.

28. Determination of the Rate of the Decomposition of Hydrogen Peroxide

Objectives

Students determine the rate constant of a chemical reaction.

Procedural Overview

Students gain experience conducting the following procedures:

- Using a catalyst to increase the rate of a reaction
- Measuring the pressure generated by the reaction in order to determine the change in concentration of a reactant
- Calculating the order of the reactants as a means to calculating the rate constant of the limiting reaction

Time Requirement

♦ Preparation time	50 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	90 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Absolute pressure sensor with quick-release connectors and plastic tubing
- Stainless steel temperature sensor
- Sensor extension cable
- Beaker (3), 100-mL
- Erlenmeyer flask, 250-mL
- Graduated pipet (3), 25-mL with rubber bulb
- Stopper with two holes for the Erlenmeyer flask
- Beaker, 50-mL
- Glycerin, several drops
- 0.1000 M Potassium iodide (KI), 60 mL[1]
- 3% Hydrogen peroxide (H_2O_2), 40 mL[2]
- Water, deionized, 100 mL
- Electrical tape, 60 in. (optional)

[1] To prepare the 0.1000 M KI solution usingsolid potassium iodide, refer to the Lab Preparation section.

[2] 3% hydrogen peroxide solution is readily available in pharmacies.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Titration
- Acid-base reactions
- Stoichiometry of chemical reactions
- Rate of chemical reaction
- Order of reactants and overall order of reactions

Related Labs in This Guide

Labs conceptually related to this one include:

- Molar Volume of a Gas
- Order of Reaction
- Identifying an Unknown Metal
- Exploring Gas Laws

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a temperature sensor and a pressure sensor to your data collection system �(2.2)
- Starting and stopping data recording �(6.2)
- Displaying data on a graph �(7.1.1)
- Displaying multiple data runs in a graph �(7.1.3)
- Finding the slope and an intercept of a best-fit line �(9.6)
- Saving your experiment �(11.1)
- Printing �(11.2)

Background

Hydrogen peroxide (H_2O_2) in aqueous solution decomposes very slowly under ordinary conditions. The equation for the decomposition is

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (1)$$

A catalyst such as potassium iodide, manganese dioxide, or catalase enzyme may be used to increase the rate of reaction. Conducting a catalyzed decomposition of H_2O_2 in a closed vessel enables the determination of the reaction rate based on the pressure increase from the production of oxygen gas. Every 2 H_2O_2 molecules yields one O_2 molecule; therefore, the rate at which H_2O_2 disappears is half the rate at which O_2 is formed:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Because the concentration of oxygen is proportional to its pressure, we can calculate the rate at which H_2O_2 decomposes by monitoring the rate of increase of the pressure due to the formation of oxygen. By varying the initial molar concentration of H_2O_2 solution, the rate law for the reaction can be determined.

There are two steps involved in the decomposition of hydrogen peroxide with potassium iodide as the catalyst:

$$H_2O_2 + I^- \rightarrow OI^- + H_2O$$

$$2OI^- \rightarrow O_2 + 2I^-$$

The first reaction determines the rate, that is, it goes much slower than the second reaction. The rate of the rate-determining reaction is calculated as follows:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = k_1[H_2O_2]^m[I^-]^n \qquad (2)$$

where

k_1 = the rate constant of the first reaction

m = the order of I^- in the first reaction

n = the order of H_2O_2 in the first reaction

In this experiment, we determine *n and m*, as well as k_1.

As O_2 is a gas, it makes more sense to work with the number of moles than with concentration to obtain the concentration of H_2O_2. For Equation 1,

$$-\frac{1}{2}\frac{\Delta n_{H_2O_2}}{\Delta t} = \frac{\Delta n_{O_2}}{\Delta t}$$

While we cannot measure the change of number of moles of O_2, using the ideal gas law we can calculate it from the change of pressure, which we can measure:

$$-\frac{1}{2}\frac{\Delta n_{H_2O_2}}{\Delta t} = \frac{V}{RT}\frac{\Delta P}{\Delta t}$$

where

V = the volume that the O_2 can occupy (L)

R = the gas constant (L kPa/mol K)

T = the temperature inside the flask (K)

P = the partial pressure of the O_2 generated by the reactions (kPa)

Now we can return to calculating the change of concentration for H_2O_2 as well:

$$V_s[H_2O_2] = n_{H_2O_2}$$

$$V_s\left(\Delta[H_2O_2]\right) = \Delta n_{H_2O_2}$$

$$-\frac{V_s}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{V}{RT}\frac{\Delta P}{\Delta t}$$

where

V_s = volume of the solution

We can rearrange the formula to get the rate of the reaction:

$$\frac{\Delta[H_2O_2]}{\Delta t} = -\frac{2V}{V_sRT}\frac{\Delta P}{\Delta t}$$

Substituting this into Equation 2, we can calculate the rate constant:

$$\frac{2V}{V_sRT}\frac{\Delta p}{\Delta t} = k_1[H_2O_2]^m[I^-]^n$$

$$k_1 = \frac{2V}{[H_2O_2]^m[I^-]^n V_sRT}\frac{\Delta P}{\Delta t} \tag{3}$$

To determine the order of the reactants, *n and m*, the reactions are performed according to the following table.

Table1: Concentration ratios between the two reactants

Reaction	**Conc. of H_2O_2**	**Conc. of I^-**
1	$[H_2O_2]$	$[I^-]$
2	$[H_2O_2]$	$2[I^-]$
3	$2[H_2O_2]$	$[I^-]$

Determining the rate for reactions 1 and 2:

$$Rate_1 = k_1[H_2O_2]^m[I^-]^n$$

$$Rate_2 = k_1[H_2O_2]^m\left(2[I^-]\right)^n$$

The ratio of the two rates yields

$$\frac{Rate_2}{Rate_1} = \frac{k_1[H_2O_2]^m\left(2[I^-]\right)^n}{k_1[H_2O_2]^m[I^-]^n}$$

$$\frac{Rate_2}{Rate_1} = 2^n$$

$$\ln\left(\frac{\mathrm{Rate}_2}{\mathrm{Rate}_1}\right) = \ln 2^n$$

$$\ln\left(\frac{Rate_2}{Rate_1}\right) = n\ln 2$$

$$n = \frac{\ln\left(\frac{Rate_2}{Rate_1}\right)}{\ln 2}$$

Using the same argument to derive *m* from reactions 1 and 3:

$$m = \frac{\ln\left(\frac{Rate_3}{Rate_1}\right)}{\ln 2}$$

The values of the order of the reactants, *m* and *n,* then will be used to determine k_1, using Equation 3.

Pre-Lab Experiment

Setting the stage for the experiment

You will perform the three reactions described above and monitor the change of pressure. This allows the respective rates to be calculated. From this calculation the rate constant of the rate determining step k_1 can be calculated. To calculate n *and* m, it is not necessary to calculate the actual rates because both n and m depend only on the ratio of the rates. Therefore, the ratio of the slopes of the pressure versus time graph is sufficient to determine n and m.

Example calculation to try

A commercially available 3% hydrogen peroxide solution was analyzed. After mixing the potassium iodide and hydrogen peroxide solutions, the volume of the solution V_s was 60.0 mL. The volume V that the O_2 gas could occupy was 242 mL, and the reaction temperature T was carried out at 303 K. Table 2 shows the results.

Table 2: Results of the 3 reactions

Reaction	$[H_2O_2]$ (M)	$[I^-]$ (M)	$\Delta P/\Delta t$ (kPa/s)	n	m
1	0.147	0.0250	0.0293	1	1
2	0.294	0.0250	0.0606		
3	0.147	0.0500	0.0616		

The following calculations determine n and m

$$n = \frac{\ln\left(\dfrac{6.06 \times 10^{-2}}{2.93 \times 10^{-2}}\right)}{\ln(2)} = 1.05 \approx 1$$

$$m = \frac{\ln\left(\dfrac{6.16 \times 10^{-2}}{2.93 \times 10^{-2}}\right)}{\ln(2)} = 1.07 \approx 1$$

Both n and m must be integers; the closest integer for each is 1.

Now we can calculate the rate constant. For instance, we can use reaction 1:

$$k_1 = \frac{(2)(0.242\ \text{L})}{\left(0.147\ \dfrac{\text{mol}}{\text{L}}\right)\left(0.0250\ \dfrac{\text{mol}}{\text{L}}\right)(0.0600\text{L})\left(8.314\ \dfrac{\text{L kPa}}{\text{mol K}}\right)(303\ \text{K})}\left(0.0293\ \frac{\text{kPa}}{\text{s}}\right) \tag{4}$$

$$k_1 = 2.55 \times 10^{-2}\ \frac{1}{\text{M s}}$$

1. Why is the unit for the volume of the solution inserted as “L” instead of “m^3”, the SI unit for volume?

The rate of a chemical reaction is given as the change of the concentration of a substance in mol/L divided by the time for that change. Therefore, the volume of the solution has to be in liters.

2. Why do both *n* and *m* have to be rounded to the closest integer, in this case 1?

Since both *n* and *m* are stoichiometric coefficients of the chemical equation, they must be integers.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.1000 M KI:*** Dissolve 8.300 g KI in some water in a 500-mL volumetric flask and then fill it to the mark with distilled water.
2. Commercially available 3% hydrogen peroxide can be used directly.

Safety

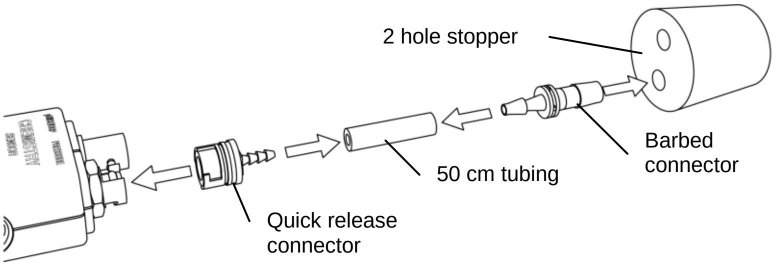
Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)
2. Place the barbed connector of the pressure sensor tightly into the rubber stopper and connect it to the pressure port of the sensor with a piece of tubing. If necessary, add a drop of glycerin onto the end of the connector that goes into the hole in the rubber stopper.

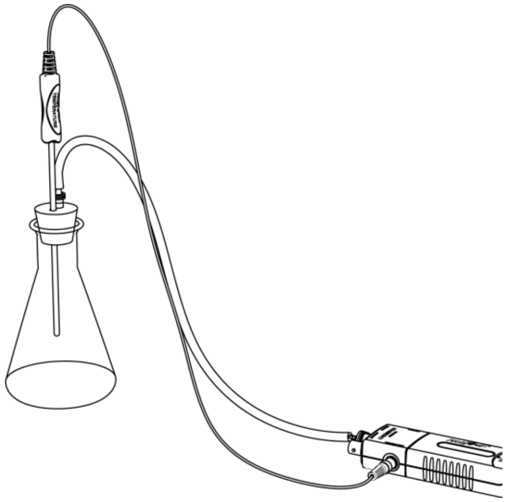


3. Insert the temperature sensor into the other hole in the rubber stopper. If necessary, add a drop of glycerin.

4. If electrical tape is available, wrap the Erlenmeyer flask with 10 to 15 rounds of electric tape. This is a preventive measure in case the flask cracks. The tape keeps the glass pieces together.

5. Connect the absolute pressure sensor to the data collection system using a sensor extension cable. �$^{(2.2)}$

6. Display Pressure on the y-axis with Time on the x-axis. �$^{(7.1.1)}$



Collect Data

Table 3: Reactant amounts to use for the three reactions

Reaction	3% H_2O_2 (mL)	0.1 M KI (mL)	Water (mL)
1	10.00	15.00	35.00
2	20.00	15.00	25.00
3	10.00	30.00	20.00

7 Perform each of the three reactions, using the measured amounts given in Table 3, according the steps listed below.

a. With graduated pipets, measure and transfer the water and potassium iodide solution into the 250-mL Erlenmeyer flask.

b. With a graduated pipet, measure and transfer the prescribed amount of H_2O_2 solution into the 50-mL beaker.

c. Pour the H_2O_2 solution into the Erlenmeyer flask and immediately insert the rubber stopper into the flask.

Important: Make sure that the stopper is sitting firmly in the flask. Pressure is building in the flask and a loose stopper might pop out. If that happens, you will need to repeat the experiment.

d. Start recording data. �$^{(6.2)}$

e. Continue to record the data for three minutes. Gently shake the Erlenmeyer flask constantly during data collection. Hold the stopper firmly during the experiment.

f. Why do you think it is necessary to shake the solution (Hint: what is the product of the reaction)?

We need to shake the solution to make sure that the oxygen generated quantitatively leaves the solution.

g. Stop recording data. �(6.2)

Note: The initial portion of the pressure versus time graph is not straight, which is attributed to the fact that the reaction does not begin immediately.

8. Display the three data runs on a graph. �(7.1.3)

9. Print the graph. �(11.2)

10. Save your experiment and clean up according to your instructor's instructions. �(11.1)

Data Analysis

1. Convert the percent by mass concentration to molarity for the different volumes of H_2O_2. Record the values in Table 4.

For Reaction 1 the 60.00 mL reaction mixture had

$$\left(\frac{3.00\text{ g }H_2O_2}{100\text{ mL}}\right)(10\text{ mL}) = 0.300\text{ g }H_2O_2$$

The number of moles of the H_2O_2 in the 60.00 mL solution is

$$\left(\frac{0.300\text{ g}}{34\,\frac{\text{g}}{\text{mol}}}\right) = 8.82\times10^{-3}\text{ mol }H_2O_2$$

The concentration of H_2O_2 is

$$\left(\frac{8.82\times10^{-3}\text{ mol}}{0.0600\text{ L}}\right) = 0.147\text{ M}$$

2. Find the slope of the best-fit line for each data run on the Absolute Pressure versus Time graph and enter the value below. �(9.6) Record the values in Table 4 using the appropriate units.

Slope_1 (kPa/s): 0.0244

Slope_2 (kPa/s): 0.0444

Slope_3 (kPa/s): 0.0482

3. Calculate the order of the two reactants from the respective rates.

$$n = \frac{\ln\left(\frac{0.0444}{0.0244}\right)}{\ln\ 2} = 0.864$$

$$m = \frac{\ln\left(\frac{0.0482}{0.0244}\right)}{\ln\ 2} = 0.982$$

4. Calculate the rate constants, using Equation 3, by substituting your respective experimental data (refer to Equation 4 as an example). Record the values in Table 4 and determine the average value of k_1.

Calculating the rate constant for Reaction 1:

$$k_1 = \frac{(2)(0.242\text{ L})}{\left(0.147\,\frac{\text{mol}}{\text{L}}\right)\left(0.0250\,\frac{\text{mol}}{\text{L}}\right)(0.06000\text{ L})\left(8.314\,\frac{\text{L kPa}}{\text{mol K}}\right)(303\text{ K})}\left(24.4\,\frac{\text{kPa}}{\text{s}}\right)$$

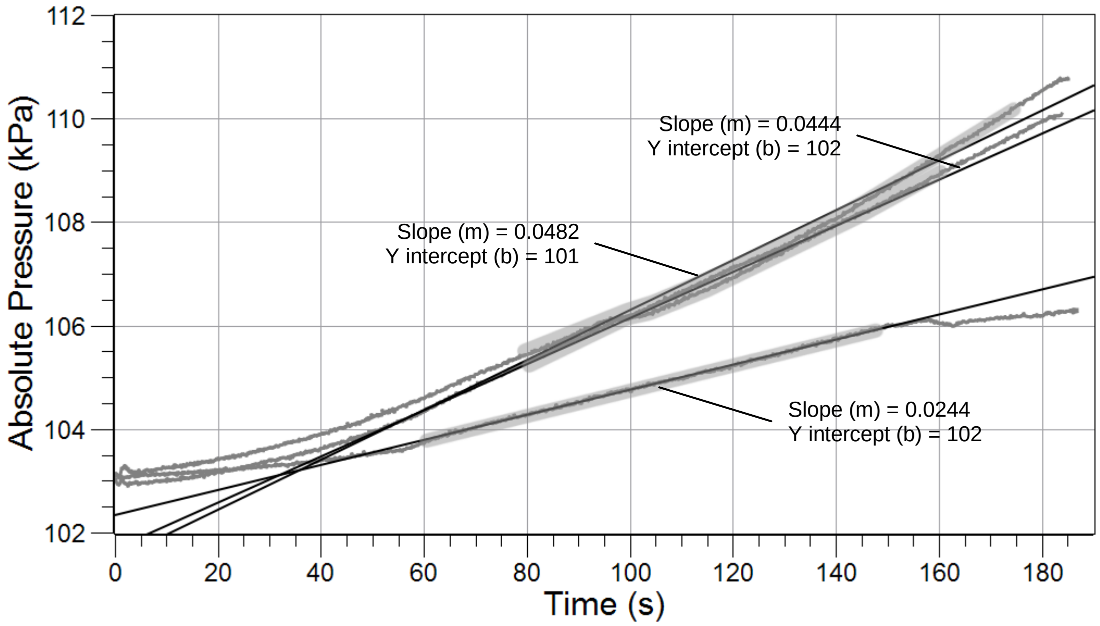
$$k_1 = 2.13 \times 10^{-2}\,\frac{1}{\text{M s}}$$

Table 4: Experimental data and data analysis

Reaction	$[H_2O_2]$ (M)	$[I^-]$ (M)	$\Delta P/\Delta t$ (kPa/s)	n	m	k_1 ($M^{-1}s^{-1}$)
1	0.147	0.025	0.0244	0.864	0.982	2.13×10^{-2}
2	0.294	0.025	0.0444			1.93×10^{-2}
3	0.147	0.050	0.0482			2.10×10^{-2}

Average k_1: $2.05 \times 10^{-2}\ M^{-1}\ s^{-1}$

5. Sketch or attach the graph showing the curves and specifying the slopes of the three reactions.



Analysis Questions

1. Why can we use the rate of change of pressure directly instead of the rate of change of concentration to calculate *n* and *m*?

We need to calculate only the ratio of the two rates. The conversion of rate of change of pressure to rate of change of concentration is achieved by multiplication and division with the same numbers for both rates (in the numerator and denominator). Therefore, they don't change the ratio and cancel out.

2. What might the reason be if the pressure starts to decrease instead of increase?

This would indicate there is a leak in the system. Most likely the stopper is not firmly placed.

3. Did the temperature increase? Why or why not?

Because the reaction is exothermic, it releases heat. This increases the temperature of the solution.

4. As you probably observed, the initial portion of the graphs may have curved a little due to the fact that there is an induction time for this reaction. Did that introduce any error into your measurement?

No, it did not introduce errors because we calculated the rate from the slope of the linear portion of the graph.

5. Based on the values of *n* and *m*, what is the overall order of the reaction?

The reaction is a second order reaction.

Synthesis Questions

Use available resources to help you answer the following questions.

1. How would the slope for the second reaction have changed (when we doubled the concentration of I^-), if *n* were 2?

Instead of doubling, it would have been increased 4-fold.

2. How would the slope have changed if *n* were 2 and we doubled both the I^- and H_2O_2 concentrations?

The slope would have increased 8-fold.

3. If you check the equations for the two consecutive reaction steps, you will notice that the I^- ions are recovered and not consumed in the reaction. How is that possible?

The I^- ions are catalysts and therefore do not change during the reaction.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. The order of H_2O_2 in the reaction is:

- **A.** The slope of the pressure versus time graph.
- **B.** 1
- **C.** 2
- **D.** The value of the rate constant, k_1

2. The rate constant of the decomposition was determined from:

- **A.** The concentration of the reactants.
- **B.** The ratio of the slopes of the pressure versus time graphs.
- **C. The slope of the pressure versus time graph.**
- **D.** The temperature versus time graph.

3. Since *n* or *m*, or both, probably did not come out to be an integer, which of the following statements is correct regarding this fact?

- **A.** There is an experimental error.
- **B.** You must round to the nearest integer.
- **C.** Both were determined experimentally.
- **D. All three statements are correct.**

Extended Inquiry Suggestions

The reaction can be performed at different temperatures to determine the activation energy of the reaction:

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$$

The activation energy (E_a) can be determined from the slope of the ln k versus 1/T plot.

Experimental data from an experiment performed at 298 K.

T = 298 K	$[H_2O_2]$ (M)	$[I^-]$ (M)	$\Delta P/\Delta t$ (kPa/s)	n	m	k_1 ($M^{-1}\,s^{-1}$)	
1	0.147	0.025	2.44×10^{-2}	0.864	0.902	0.0216	2.08×10^{-2}
2	0.294	0.025	4.44×10^{-2}			0.0197	
3	0.147	0.050	4.82×10^{-2}			0.0213	

Experimental data from an experiment performed at 303 K.

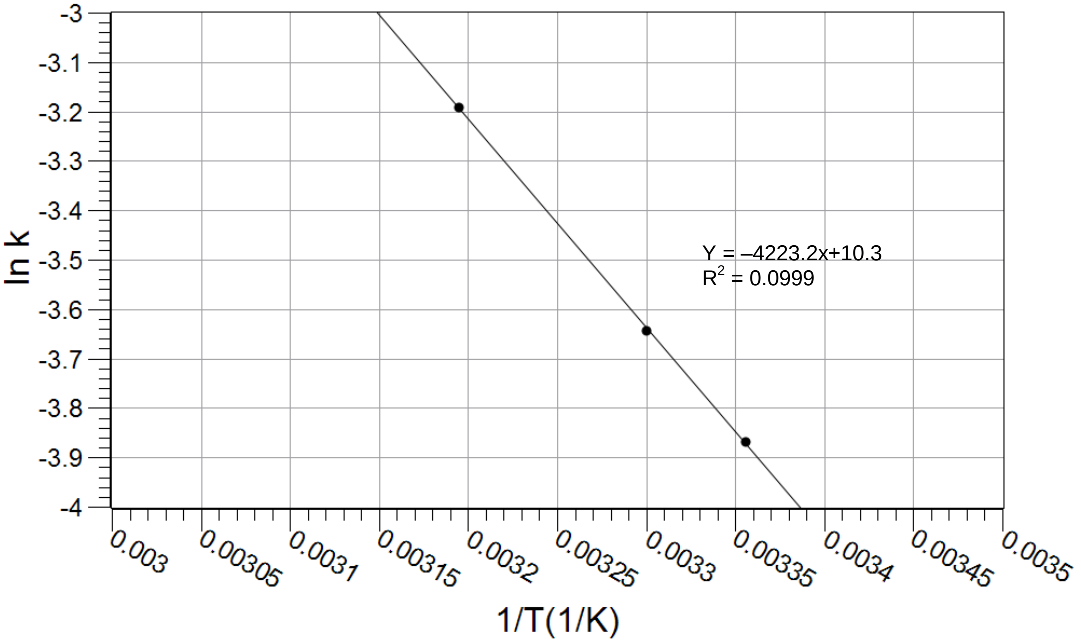
T = 303 K	$[H_2O_2]$ (M)	$[I^-]$ (M)	$\Delta P/\Delta t$ (kPa/s)	n	m	k_1 ($M^{-1}\,s^{-1}$)	
1	0.147	0.025	2.93×10^{-2}	1.07	1.04	0.0255	2.62×10^{-2}
2	0.294	0.025	6.16×10^{-2}			0.0268	
3	0.147	0.05	6.01×10^{-2}			0.0262	

Experimental data from an experiment performed at 313 K.

T = 313 K	$[H_2O_2]$ (M)	$[I^-]$ (M)	$\Delta P/\Delta t$ (kPa/s)	n	m	k_1 ($M^{-1}\,s^{-1}$)	
1	0.147	0.025	4.81×10^{-2}	1.08	0.971	0.0406	4.11×10^{-2}
2	0.294	0.025	1.02×10^{-1}			0.0430	
3	0.147	0.05	9.43×10^{-2}			0.0398	

Temperature dependence of k_1.

k (M^{-1} s^{-1})	ln k	T (K)	1/[T (K)]
2.08×10^{-2}	–3.86941	298	3.36×10^{-3}
2.62×10^{-2}	–3.64302	303	3.30×10^{-3}
4.11×10^{-2}	–3.19165	313	3.20×10^{-3}



The activation energy is

$$E_a = -(-4223.2\,\text{K})\left(8.314\frac{\text{J}}{\text{mol K}}\right) = 35{,}112\frac{\text{J}}{\text{mol}} = 35.1\frac{\text{kJ}}{\text{mol}}$$

29. Determination of a Solubility Product

Objectives

Students demonstrate a method of determining the solubility product constant of an ionic compound.

Procedural Overview

Students will gain experience conducting the following procedures:

- Through titration and calculations, determine the solubility product of calcium hydroxide

Time Requirement

Preparation time	15 minutes (plus 3 hours solution preparation)
Pre-lab discussion and experiment	15 minutes
Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- pH sensor
- Drop counter and micro stir bar
- Ring stand
- Clamp, buret
- Clamp, right-angle
- Beaker, 100-mL
- Beaker (2), 150-mL
- Beaker (2), 25-mL
- Pipet, graduated or volumetric, 50-mL
- Rubber bulb
- Buret, 50-mL
- Filter flask, 250-mL
- Büchner funnel
- Pipet, transfer
- Filter paper
- Magnetic stirrer
- 0.1000 M Hydrochloric acid (HCl), 200 mL[1]
- Calcium hydroxide ($Ca(OH)_2$), saturated, 200 mL[2]
- Buffers, pH 4 and pH 10, 10 mL
- Wash bottle with distilled water
- Parafilm® or aluminum foil
- Cotton swab or tissue

[1,2] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Molarity
- Acid-Base reactions
- Titration
- pH
- Chemical equilibria
- Le Chatelier's principle

Related Labs in This Guide

Labs conceptually related to this one include:

- Acid–Base Titration
- Standardizing a Solution of Sodium Hydroxide
- Determining K_{a} by Half-Titration of a Weak Acid
- Conductometric Titration
- Determination of the K_{a} Values of Two Isomer Multi-Protic Acids

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connect a sensor to the data collection system �(2.1)
- Connecting multiple sensors to the data collection system �(2.2)
- Calibrating a drop counter �(3.4)
- Calibrating a pH sensor �(3.6)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)

- Changing the variable on the x-axis and y-axis of a graph �$^{(7.1.9)}$

- Printing the graph �$^{(11.2)}$

Background

The ability of a compound to dissolve in a solvent is called solubility. The solubility of an ionic compound refers to the maximum amount of substance (solute) that can dissolve in a given amount of solvent at standard temperature and pressure. The solution of an ionic compound containing the maximum amount of solute is known as a saturated solution and is in a state of equilibrium between dissolved and undissolved solute. The equation below describes the equilibrium of a saturated solution of calcium carbonate in water:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

Calcium carbonate dissolves into the solution (forward reaction) and at the same time calcium carbonate precipitates from the solution (reverse reaction). When both reactions occur at the same rate, a state of equilibrium is established. The solubility product constant, K_{sp}, is a temperature-dependent constant that refers to this state. If a salt, M_xA_y, dissociates into cations $[M^{m+}]$ and anions $[A^{a-}]$ the expression for the solubility product will be

$$K_{sp} = [M^{m+}]^x [A^{a-}]^y$$

Pre-Lab Experiment

Setting the stage for the experiment

In this lab, you will determine the K_{sp} of calcium hydroxide. It will not be necessary to determine the concentration of both Ca^{2+} and OH^- because there is a fixed relationship between the two quantities. It will only be necessary to find the concentration of one, since the other can be easily calculated from it.

Example calculation to try

To determine the molar concentration of dissolved hydroxide ions, about 10 g of solid $Ba(OH)_2$ was placed into a 500-mL Erlenmeyer flask with about 300 mL of water. A stirring bar was placed into the solution and the flask was placed on a magnetic stirrer. The solution was stirred for 2 hours, during which time the solution became saturated with $Ba(OH)_2$.

About 100 mL of the solution was filtered and 50.00 mL of the filtrate was pipetted into a 150-mL beaker. A stirring bar was placed into the solution and the beaker was set onto a magnetic stirrer. A pH electrode was calibrated and mounted in the solution. A 50-mL buret was filled with 0.2000 M HCl solution.

The saturated $Ba(OH)_2$ solution was titrated with the HCl solution. A sharp jump occurred after 20.50 mL (equivalence point) and the titration was continued until 25.00 mL HCl solution was added.

The chemical reaction that occurred was:

$$Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O$$

The amount of HCl solution added until the equivalence point was:

$$(20.50\ \text{mL})\left(\frac{0.2000\ \text{mol HCl}}{1000\ \text{mL}}\right) = 4.100 \times 10^{-3}\ \text{mol HCl}$$

Based on the stoichiometry of the reaction between H_3O^+ and OH^- ions, the same amount of OH^- ions were in the solution as H_3O^+ ions were in HCl. The concentration of the OH^- ions is:

$$\left(\frac{4.100 \times 10^{-3}\ \text{mol OH}^-}{5.000 \times 10^{-2}\ \text{L}}\right) = 8.200 \times 10^{-2}\ \text{M OH}^-$$

Based on the stoichiometry, the Ba^{2+} concentration is:

$$[Ba^{2+}] = \frac{[OH^-]}{2} = \frac{(8.200 \times 10^{-2}\ \text{M})}{2} = 4.100 \times 10^{-2}\ \text{M}$$

Substituting the concentrations into the expression for K_{sp} yields:

$$K_{sp} = [Ba^{2+}][OH^-]^2 = \left(4.100 \times 10^{-2}\right)\left(8.200 \times 10^{-2}\right)^2 = 2.760 \times 10^{-4}$$

Experimental data and calculated solubility product for $Ba(OH)_2$

Parameter	Value
Volume of 0.2000 M HCl until equivalence point (mL)	20.50
Amount of HCl added until the equivalence point (mol)	4.100×10^{-3}
Amount of OH^- ions that were present in the solution (mol)	4.100×10^{-3}
Concentration of OH^- ions in the solution (M)	8.200×10^{-2}
Concentration of Ba^{2+} ions in the solution (M)	4.100×10^{-2}
Calculated solubility product	2.760×10^{-4}
Known value	2.55×10^{-4}

1. Do you think it matters how much solid $Ba(OH)_2$ is used to make the saturated solution? Explain your answer!

As long as there is a sufficient amount to leave some undissolved $Ba(OH)_2$ after the solution is made, it doesn't matter.

2. List three additional, chemically different solutions, and their concentrations, that would be appropriate to determine the OH^- concentration in the saturated $Ba(OH)_2$ solution.

Any strong acid solution would be appropriate: acids with one hydrogen ion, H^+, such as HNO_3 would have to have about the same concentration (0.2 M), acids with two hydrogen ions, such as H_2SO_4, would need half of the concentration (0.1 M), acids with three hydrogen ions, such as H_3PO_4 would have to have a third of the concentration (0.07 M).

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.1000 M HCl:*** Carefully add 8.4 mL of 36% (concentrated) HCl to some distilled water in a 1-L volumetric flask. Fill the flask to the mark.

Note: This method prepares a solution with an approximate concentration. Standardization is necessary to determine the exact concentration of the solution using a standardized NaOH solution or any appropriate primary standard.

2. ***Saturated $Ca(OH)_2$:*** Place about 2 g of $Ca(OH)_2$ in a 1-L Erlenmeyer flask and fill it to about the 1-L mark with distilled water. Place a stirring bar in the flask and place the flask on a magnetic stirrer. Stir for about three hours to saturate the solution.

Safety

Add these important safety precautions to your normal laboratory procedures:

- In case of contact with skin, HCl should be washed off with large amounts water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)

2. Connect a pH sensor to the data collection system. �(2.1)

3. Connect the drop counter to the data collection system. �(2.2)

4. Display the pH on the y-axis of a graph and Drop Count on the x-axis. �(7.1.1)

5. Calibrate the pH sensor. �$^{(3.6)}$

6. Assemble the titration apparatus, using the steps below and the illustration as a guide.

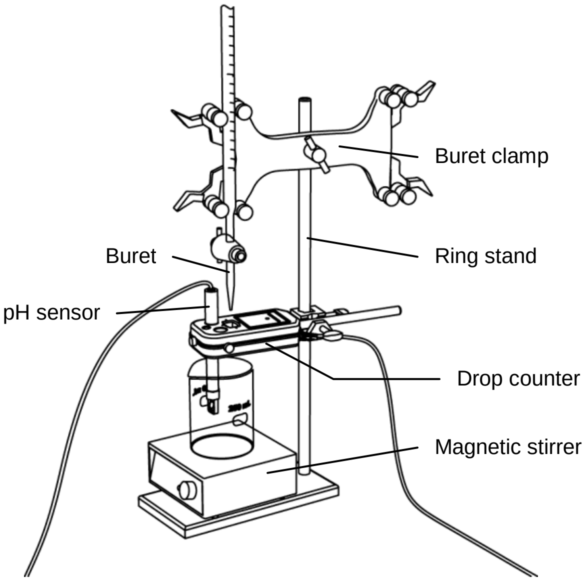
a. Position the magnetic stirrer on the base of the ring stand.

b. Place a waste container on the magnetic stirrer.

c. Use the buret clamp to attach the buret to the ring stand.

d. Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.

e. Place the pH sensor through one of the slots in the drop counter.



7. Rinse the buret with several milliliters of the 0.1 M HCl solution:

a. Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized HCl solution.

b. Open the stopcock on the buret and drain the rinse HCl into the waste container.

c. Repeat this process two more times.

8. Why is it necessary to rinse the buret with the HCl solution?

If there is any residual water or contaminant in the buret, it will dilute the HCl and change its concentration. Rinsing eliminates any such contamination.

9. Make sure the stopcock on the buret is in the "off" position, and then use a 100-mL beaker to fill the buret with about 50 mL of the 0.1000 M HCl solution (titrant).

10. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

11. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of HCl. If this happens, the final amount of titrant used will be inaccurate.

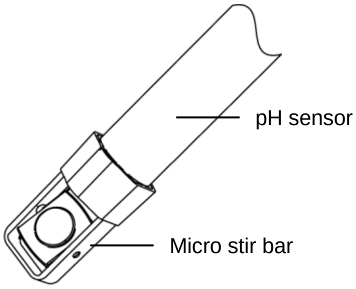
12. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

Note: Good control of the stopcock is important. If you accidentally open the stopcock too far and the HCl flows out (as opposed to coming out in drops), you will have to start over.

13. Why will it be necessary to start your titration over again if you accidentally allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

14. Add the micro stir bar to the end of the pH sensor.



15. Why is it necessary to stir the solution during a titration?

Stirring thoroughly mixes the ions in the solution so that the recorded pH is for the entire solution.

16. Add additional HCl solution to the buret so it is above the zero mark. Allow some of the solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the starting volume in Table 1.

17. Remove the waste container.

18. Cover the beaker containing the remaining titrant solution with a piece of Parafilm® or aluminum foil.

Perform the titration of saturated $Ca(OH)_2$ solution three times, following the steps below.

19. Analyte preparation:

- **a.** Filter about 80 mL of the saturated $Ca(OH)_2$ solution through a Büchner funnel (with the filter paper covering the holes) connected to a 250-mL filtering flask and an aspirator pump.
- **b.** Why do you think the filtration is necessary?

Filtration is necessary to remove the solid particles which, if left in the solution, would react with the titrant and introduce a significant error.

- **c.** How do you know if the solution is saturated?

If the solution was allowed to equilibrate with solid $Ca(OH)_2$, then it became saturated.

- **d.** Pipet 50.00 mL of the filtered solution into a clean, 150-mL beaker and place it on the magnetic stirrer. Add enough water to the solution to ensure the bulb of the pH sensor is fully submerged.
- **e.** Propose a way to precisely measure 50.00 mL of solution.

For the most precise measurement, a 50-mL volumetric pipet should be used. A 50-mL graduated cylinder can provide sufficient accuracy as well.

20. Turn on the magnetic stirrer at a slow and steady rate.

Collect Data

21. Clean the lens of the drop counter inside the opening through which the drops are going with water and a cotton swab or tissue.

22. Start recording data. �(6.2)

23. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

Note: Do not allow the titrated solution to be exposed to air for an extended period of time.

24. Why do you think prolonged exposure of the titrated solution would introduce an error? (Hint: What can the solution absorb from the air and what chemical reaction can occur as a result?)

Carbon dioxide can be absorbed and turn some of the $Ca(OH)_2$ to $CaCO_3$:

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

25. Do you expect a pH jump or a pH drop at the equivalence point? Explain your answer.

The pH initially was high, since the solution was alkaline. After the equivalence point, when HCl is in excess, the pH should be low. Therefore, at the equivalence point, a pH drop is expected.

26. Continue the titration past the equivalence point until the pH curve flattens.

27. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

28. Stop recording data. �(6.2)

29. In Table 1, record the final drop count and the final volume of the titrant in the buret to a precision of 0.01 mL.

30. Calculate the volume of titrant (final volume minus initial volume) and record this value in Table 1.

Table 1: Titration data

Titration Information	Trial 1	Trial 2	Trial 3
Initial reading of HCl on the buret (mL)	4.00	0.00	0.00
Final reading of HCl on the buret (mL)	29.81	25.72	25.64
Volume of titrant (mL)	25.81	25.72	25.64
Final drop counts	549	558	561

31. Calibrate the drop counter. �(3.4)

32. Set the horizontal axis to the calculated volume. �(7.1.9)

33. In Table 2, record the volume of titrant used to reach the equivalence point.

34. Remove the beaker and dispose of its contents according to the instructor's instructions.

35. Rinse the beaker with distilled water.

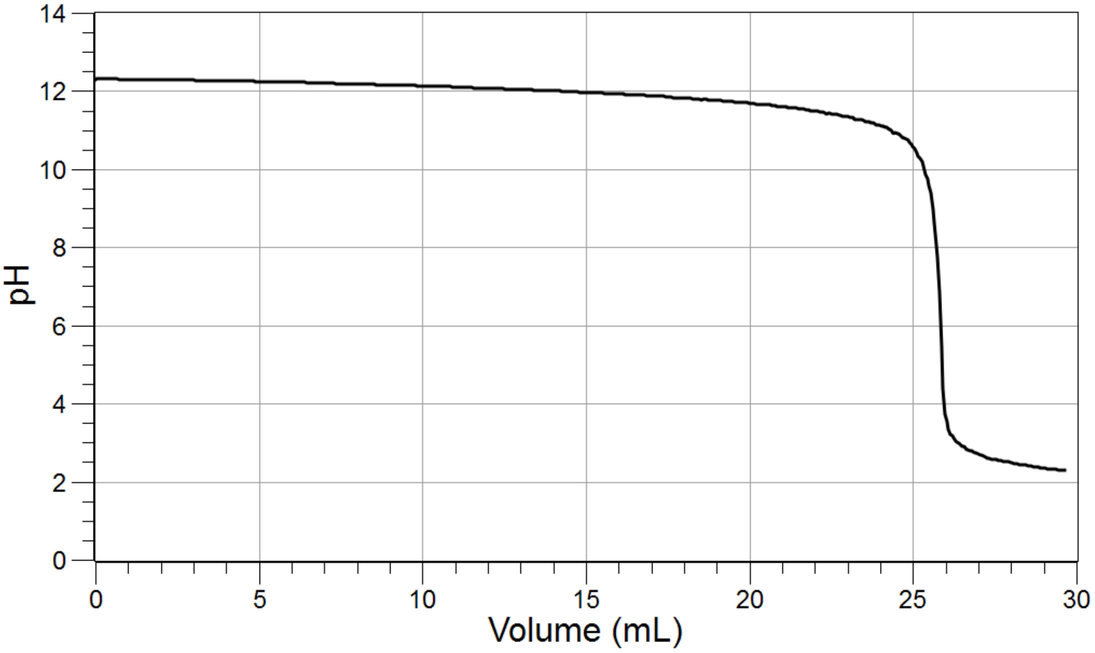
36. Refill the buret over the zero mark with the HCl solutions.

- **a.** Fill the buret over the zero mark and allow some of the HCl solution to drip into a waste container until the bottom of the meniscus is lined up with the zero mark or just below.
- **b.** Record the initial reading in Table 1.

37. Repeat the procedure two more times, beginning with the analyte preparation.

38. Save your experiment �(11.1) and clean up according to your instructor's instructions.

39. For each titration curve, sketch the graphs or print the graphs �(11.2) and paste them below.



Data Analysis

1. Calculate the amount of HCl added to reach the equivalence point for each run and enter your answers in Table 2.

For Trial 1:

$$(25.81\text{ mL titrant})\left(\frac{0.09600\text{ mol HCl*}}{1000\text{ mL}}\right) = 2.478 \times 10^{-3}\text{ mol HCl}$$

* A standardized HCl solution with 0.09600 M concentration was used for the test experiments.

2. How can you determine the amount of OH^- ions present in the saturated solution? Enter the number of OH^- ions for each run in Table 2.

Based on the stoichiometry of the reaction between H^+ and OH^- ions, the same number of OH^- ions was in the $Ca(OH)_2$ solution as H_3O^+ ions were in HCl.

3. Calculate the concentration of OH^- ions in the solution for each run and enter your answers in Table 2.

For Trial 1:

$$[OH^-] = \left(\frac{2.478 \times 10^{-3}\text{ mol}}{0.05000\text{ L}}\right) = 4.956 \times 10^{-2}\text{ M OH}^-$$

4. Calculate the concentration of Ca^{2+} ions in the solution for each run and enter your answers in Table 2.

For Trial 1:

$$[Ca^{2+}] = \frac{[OH^-]}{2} = \frac{(4.956 \times 10^{-2}\ M)}{2} = 2.478 \times 10^{-2}\ M$$

5. Calculate the solubility product of calcium hydroxide for each run and enter your answers in Table 2.

$$K_{sp} = [Ca^{2+}][OH^-]^2 = \left(2.478 \times 10^{-2}\right)\left(4.956 \times 10^{-2}\right)^2 = 6.080 \times 10^{-5}$$

Table 2: Determination of the solubility product of $Ca(OH)_2$

Parameter	Trial 1	Trial 2	Trial 3
Volume of 0.1 M HCl to reach the equivalence point (mL)	25.81	25.72	25.64
Amount of HCl added to reach the equivalence point (mol)	2.478×10^{-3}	2.470×10^{-3}	2.461×10^{-3}
Amount of OH^- ions present in the saturated solution (mol)	2.478×10^{-3}	2.470×10^{-3}	2.461×10^{-3}
Concentration of OH^- ions in the solution (M)	0.04956	0.04938	0.04923
Concentration of Ca^{2+} ions in the solution (M)	0.02478	0.02469	0.02461
Solubility product	6.08×10^{-5}	6.02×10^{-5}	5.96×10^{-5}
Average value of solubility product	6.02×10^{-5}		
Known value of the solubility product	5.02×10^{-6}		

6. How different is your calculated solubility product from the published value? What accounts for the difference?

Significantly higher solubility product than the known value can be attributed to imperfect filtration which resulted in the presence of $Ca(OH)_2$ particles. These particles yield higher acid consumption which in turns will cause higher OH^- and Ca^{2+} concentrations. If the solubility appears to be lower, the solution may not have been saturated.

Analysis Questions

1. How would the experimental value of the solubility product change if the solution was not saturated?

Lower concentrations would yield a lower solubility product.

2. Sometimes in the filtered solution white precipitate appears. Propose a possible explanation. (Hint: The filtering flask is connected to a vacuum which may promote faster evaporation of water from the filtered solution.)

Since the amount of solvent would decrease, the saturated solution would become super-saturated. The excess $Ca(OH)_2$ would precipitate out.

3. Does the filtered precipitate or the solution that is captured by the filter paper have any effect on your results? If so, what?

No, it does not. We measure the volume of the saturated solution after the filtration and not before.

4. Prolonged exposure of the saturated solution to air may result in the appearance of a white precipitate other than calcium hydroxide. What could it be? What reaction is taking place? (Hint: What gases are in the air that can initiate a chemical reaction in the solution?)

CO_2 can dissolve in the solution and produce calcium carbonate, $CaCO_3$, which is less soluble than $Ca(OH)_2$ and therefore will precipitate:

$$Ca^{2+}(aq) + CO_2(aq) + 2OH^-(aq) \rightarrow CaCO_3(s) + H_2O$$

Synthesis Questions

Use available resources to help you answer the following questions.

1. The solubility product of lead chloride, $PbCl_2$, is rather large ($K_{sp} = 1 \times 10^{-5}$). Propose a method to decrease the solubility of lead ions in a saturated $PbCl_2$ solution. (Hint: Use the Le Chatelier principle.)

Since the saturation process is an equilibrium process, shifting the equilibrium backwards will decrease the lead concentration. According to Le Chatelier's principle, increasing the concentration of the products will shift the equilibrium back. Increasing the Cl^- ion concentration will provide the desired effect. Therefore, adding Cl^- from a sodium chloride solution will reduce the lead ion concentration:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

2. $Mg(OH)_2$ has a solubility product, K_{sp}, of 5.6×10^{-12}. How would you change the pH to help the dissolution of $Mg(OH)_2$? (Hint: Use the Le Chatelier principle.)

Lowering the pH would remove some of the OH^- ions which, in turn, would shift the equilibrium to the right, allowing more $Mg(OH)_2$ to dissolve.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

3. Would you have been able to measure the solubility constant for $Ca(OH)_2$ if the saturated $Ca(OH)_2$ solution was made in a 0.01 M NaOH solution instead of water?

No. The HCl titrant solution simply measures the OH^- concentration. The OH^- concentration would no longer be related to the Ca^{2+} concentration through stoichiometry if the $Ca(OH)_2$ was made in a NaOH solution because OH^- ions would come from two sources. We would have no way of measuring or calculating the Ca^{2+} concentration, which is necessary for the computation of K_{sp}.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Solubility of Ca^{2+} and OH^{-} ions in a saturated $Ca(OH)_2$ solution

- **A.** depends on the volume of water that was used to make the solution.
- **B.** depends on the amount of solid $Ca(OH)_2$ that was used to make the solution.
- **C. does not depend on the amount of solid $Ca(OH)_2$ or the amount of water that was used as long as there was enough solid to make a saturated solution.**
- **D.** depends on both the amount of solid $Ca(OH)_2$ and the amount of water that was used.

2. The filtration process will introduce an error if

- **A.** any of the solution is absorbed by the filter paper.
- **B.** any of the solid $Ca(OH)_2$ is captured on the paper.
- **C. the paper is damaged and allows some solid $Ca(OH)_2$ particles to go through.**
- **D.** the room temperature is too low.

3. Adding NaOH solution to a saturated $Ca(OH)_2$ solution will

- **A.** have no effect on the solubility of $Ca(OH)_2$.
- **B. result in a lower solubility of $Ca(OH)_2$.**
- **C.** result in a higher solubility of $Ca(OH)_2$.
- **D.** result in precipitation of NaOH.

4. How would the obtained value for the solubility constant change if you used 100.00 mL of the saturated solution instead of 50.00 mL?

- **A.** The value of the solubility constant would double.
- **B.** The value of the solubility constant would be half of what we obtained with 50.00 mL.
- **C. The value of the solubility constant would be the same.**
- **D.** The value of the solubility constant would be the same if the concentration of the titrant, HCl solution, was also doubled.

Extended Inquiry Suggestions

The solubility product of $CaSO_4$ ($K_{sp} = 5 \times 10^{-5}$) can be determined using conductivity titration with $BaCl_2$ solution. Since the solubility product of $BaSO_4$ ($K_{sp} = 1.08 \times 10^{-10}$) is much less than the solubility product of $CaSO_4$, the excess SO_4^{2-} ions will be removed by Ba^{2+} ions. The process can be monitored with a conductivity sensor (see Conductometric Titration).

30. Order of Reaction

Objectives

Students determine the order of reaction by analyzing the reaction rate of crystal violet and NaOH.

Procedural Overview

Students gain experience conducting the following procedures:

- Using spectroscopic methods to analyze the reaction rate for a pseudo first-order reaction
- Calculating the order of reaction using the initial rate method and a graph of the concentration of crystal violet over time
- Determining the equation needed to obtain a straight-line plot

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	80 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Colorimeter
- Sensor extension cable
- Cuvette
- Beaker (3), 50-mL
- Syringe (3), 5-mL
- Watch glass, 4 in
- 0.1 M Sodium hydroxide (NaOH), 20 mL[1]
- 1.2×10^{-5} M Crystal violet, 20 mL[2]
- Water, deionized, 30 mL
- Marking pen
- Kimwipes®

[1, 2] To prepare the solutions, refer to the Lab Preparation section

Concepts Students Should Already Know

Students should be familiar with the following concepts:

♦ Molarity

♦ Beer's Law

♦ Rate of chemical reactions

Related Labs in This Guide

Labs conceptually related to this one include:

♦ Determining the Equilibrium Constant for a Chemical Reaction

♦ Determination of the Rate of the Decomposition of Hydrogen Peroxide

♦ Absorption Spectra

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

♦ Starting a new experiment on the data collection system �(1.2)

♦ Connecting a sensor to the data collection system �(2.1)

♦ Calibrating the colorimeter �(3.2)

♦ Monitoring live data without recording �(6.1)

♦ Starting and stopping data recording �(6.2)

♦ Recording a manually sampled data point �(6.3.2)

♦ Finding the values of a point in a graph �(9.1)

♦ Creating calculated data �(10.3)

Background

Kinetics and Reaction Order

Kinetics is the area of chemistry that deals with how quickly or how slowly reactions take place. By studying the rate of a reaction, valuable information can be gained about how the reaction proceeds—the reaction mechanism. In general, the rate of a reaction depends on the concentration of the reactants and can be expressed mathematically as the “rate law.”

The rate law for a chemical reaction is an equation that relates the rate of the disappearance of reactants or the rate of appearance of products to the concentration of the reactants. Consider the following reaction:

$$\text{bB} + \text{cC} \rightarrow \text{Products}$$

Generally, the rate law is expressed in terms of the concentrations of reactants and products in the form of

$$Rate = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = -\frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = k[\mathrm{B}]^m[\mathrm{C}]^n \ldots \tag{1}$$

where

k = the rate constant

m and n = the individual reaction orders for each reactant

The individual reactant reaction orders (that is, the exponents) in Equation 1 must be determined by experiment because they are not necessarily based on the mole ratio in the balanced equation. The sum of the individual orders is the “overall order” of the reaction.

The order of a reaction is commonly zero order, first order, or second order. A zero-order reaction is one in which the rate is *independent* of the concentration of reactants. A first-order reaction is one where the rate depends only on the concentration of one reactant, and in which $m = 1$. A second-order reaction can be one in which the reaction rate depends on the concentration of two different reactants (where $m = 1$ and $n = 1$), or where the reaction rate depends on the concentration of one reactant (where $m = 2$). These options are shown in the "Rate" column in Table 1.

Table 1: Characteristics of reaction order

Overall Reaction Order	Reactants and Products	Rate	Equation to Obtain a Straight-Line Plot (Integrated Rate Equations)
Zero order	B → Products	k	$[\mathrm{B}] = -kt$
First order	B → Products	$k[\mathrm{B}]$	$\ln[\mathrm{B}] = \ln[\mathrm{B}]_0 - kt$
Second order	B + C → Products	$k[\mathrm{B}][\mathrm{C}]$	$\ln\left(\frac{[\mathrm{C}]/[\mathrm{C}]_0}{[\mathrm{B}]/[\mathrm{B}]_0}\right) = \left([\mathrm{C}]_0 - [\mathrm{B}]_0\right)kt$
	2B → Products	$k[\mathrm{B}]^2$	$\frac{1}{[\mathrm{B}]} = \frac{1}{[\mathrm{B}]_0} + kt$

Determining the Rate of Reaction

The equation to show the dependence of the concentration of the reactant as a function of time, also called "integrated rate equation," depends on the order of the reactant. These integrated rate equations are shown for different reaction orders in Table 1. (The zero index on the concentrations references initial condition.)

Creating a graph of concentration versus time is one method that can be used to determine the order of a reaction with respect to a particular reactant. If the reaction is zero-order, a plot of concentration versus time will result in a straight line with the slope = $-k$. If the reaction is first-order, a straight-line plot will result from a graph of the natural log of concentration versus time, with the slope equal to $-k$. If the reaction is second-order, a plot of 1/concentration versus time will result in a straight line with the slope equal to $+k$.

A more rigorous approach is the "initial rate method." This method relies on the fact that we know the concentrations of the reactants at $t = 0$ seconds and the order of the reactants can be calculated from the measured rate starting at this time. We will be using the latter approach in this experiment.

To measure the rate of a reaction, we monitor the change of the concentration of one of the reactants or products:

$$Rate = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t}$$

The negative sign accounts for the fact that the change of the concentration of a reactant is negative—the negative sign turns the rate positive. We scale the rate with the stoichiometric coefficient so that the rate calculated for any species involved in the reaction is the same.

For second-order reactions where the rate depends on the concentration of two species and the concentration of one of the species is in large excess, the concentration of the species in excess will not change appreciably and can be considered constant. Therefore, the reaction behaves like a first-order reaction. We designate this as a "pseudo first-order reaction" (this assumes $[\mathrm{B}] >> [\mathrm{C}]$):

$$Rate = k[\mathrm{B}][\mathrm{C}] \approx k'[\mathrm{C}]$$

where

$k' = k[\mathrm{B}]$, the pseudo rate constant

Pre-Lab Experiment

Setting the stage for the experiment

In this lab you will monitor the concentration of a reactant in a chemical reaction using a spectroscopic method and applying Beer's Law:

$$A = \varepsilon\, l\, c \qquad (2)$$

where

A = absorption

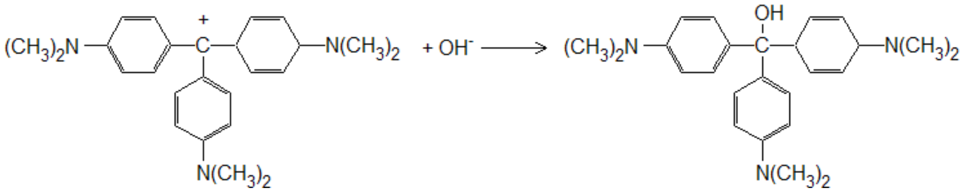
ε = molar absorption coefficient at 565 nm; the published value is 5×10^4 $\text{cm}^{-1}\,\text{M}^{-1}$

l = path length of solution the light passes through (the width of the container with the solution)

c = concentration of the absorbing species

(This equation is also expressed as $A = a\, b\, c$; where a and b correspond to ε and l, respectively.)

The chemical reaction is between crystal violet (CV^+), a dye with an intense blue color (therefore it absorbs light in the visible range), and OH^- ions:



$CV^+ + OH^- \longrightarrow CVOH$

The product is colorless. The absorption is attributed completely to the reactant present in the solution.

Initial Rate Method

One way to determine the order of the reactants in a reaction is to utilize the “initial rate method.” Applying this technique, one measures the initial rate of the reaction under carefully chosen conditions and then applies the rate equation (in terms of the rate constant and the concentration of the reactants) under two different conditions.

Applying Equation 1 (with subscripts 1 and 2 to indicate the two sets of conditions) the rate, concentration of CV^+, and the concentration of OH^- for the two conditions will be:

$$Rate_1 = k[\mathrm{CV}^+]_1^m[\mathrm{OH}^-]_1^n$$

$$Rate_2 = k[\mathrm{CV}^+]_2^m[\mathrm{OH}^-]_2^n$$

In order to eliminate one of the variables, we divide the first equation by the second one:

$$\frac{Rate_1}{Rate_2} = \frac{k[CV^+]_1^m[OH^-]_1^n}{k[CV^+]_2^m[OH^-]_2^n} \tag{3}$$

If the initial concentrations are set so that $[CV^+]_1 = [CV^+]_2$ and $[OH^-]_2 = 2[OH^-]_1$, Equation 3 becomes:

$$\frac{Rate_1}{Rate_2} = \frac{[OH^-]_1^n}{[OH^-]_2^n} = \frac{[OH^-]_1^n}{\left(2[OH^-]_1\right)^n} = \frac{1}{2^n} \tag{4}$$

Since n is the exponent, it is logical to take the logarithm of both sides of Equation 4:

$$\ln\left(\frac{Rate_1}{Rate_2}\right) = \ln\left(\frac{1}{2^n}\right) = \ln(2^{-n}) = -n\ln 2 \tag{5}$$

Multiplying both sides of Equation 5 by (– 1) yields:

$$-\ln\left(\frac{Rate_1}{Rate_2}\right) = n\ln 2 \tag{6}$$

For convenience, we eliminate the negative sign in front of the logarithmic term in Equation 6 with the following two steps:

$$\ln\left(\frac{Rate_1}{Rate_2}\right)^{-1} = n\ln 2$$

$$\ln\left(\frac{Rate_2}{Rate_1}\right) = n\ln 2$$

Equation 6 can then be rearranged to solved for n:

$$n = \frac{\ln\left(\frac{Rate_2}{Rate_1}\right)}{\ln 2}$$

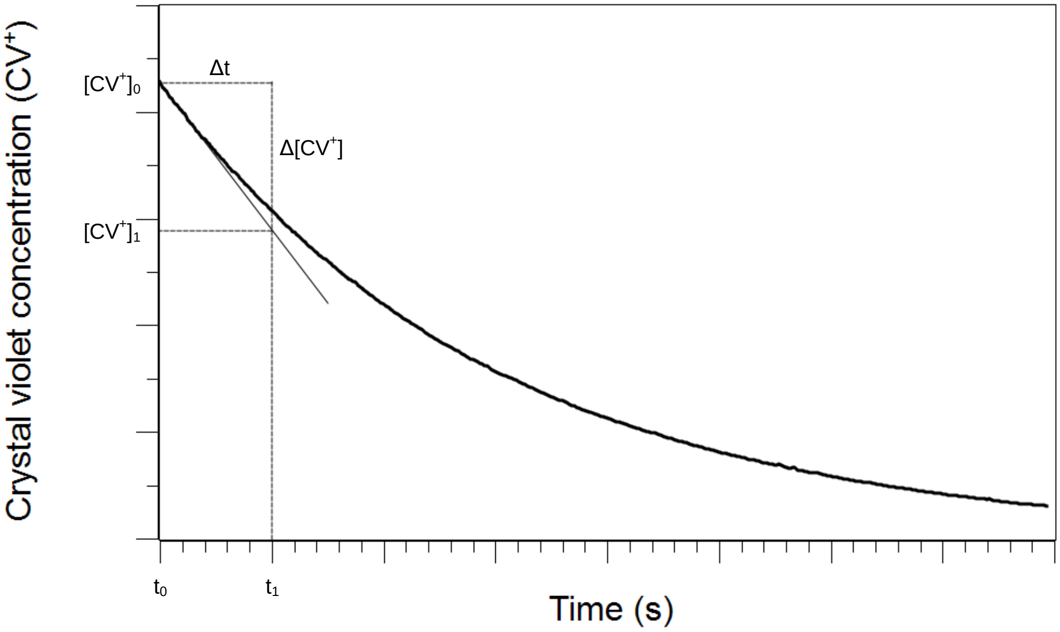
To determine the order m of CV^+, we design a third experiment which we will label with the subscript "3," with the initial conditions: $[CV^+]_3 = 2[CV^+]_1$ and $[OH^-]_3 = [OH^-]_1$. The same derivation can be performed as before and the following expression can be obtained for m:

$$m = \frac{\ln\left(\frac{Rate_3}{Rate_1}\right)}{\ln 2}$$

By measuring the rates of the three reactions with the concentrations as defined, both n and m can be determined.

Measuring the Reaction Rates

To measure the rate, we will utilize the fact that the rate is the value of the slope at every point of the Crystal Violet concentration versus Time graph:



The initial rate is determined as the slope of the line drawn from the initial concentration point to the concentration at the point corresponding to t_1, $[CV^+]_1$.

Once the orders of the reactants are obtained, we can determine the value of *k* by using the appropriate rate representation from Table 1.

Example calculation to try

In an experiment, the following concentrations were prepared for CV^+ and OH^-:

Table 2: Concentration of reactants for 3 trials

Trial	**$[CV^+]$ (M)**	**$[OH^-]$ (M)**
1	3.0×10^{-6}	2.5×10^{-2}
2	6.0×10^{-6}	5.0×10^{-2}
3	6.0×10^{-6}	2.5×10^{-2}

For each run, the reactants were mixed and the reaction mixture was transferred into a spectroscopic cell. Without any delay, the cell was placed into a colorimeter. The absorbance data was collected at 565 nm until the absorbance dropped below 0.1. The absorbance data was then converted to concentration data:

Repeating Equation 2,

$$A = \varepsilon\, l\, c$$

and solving for c (concentration),

$$[CV^+] = \frac{A}{\varepsilon\, l}$$

From the slopes of the curves on the $[CV^+]$ versus Time graph, the initial rates were determined (shown by the straight lines) and listed in Table 3.

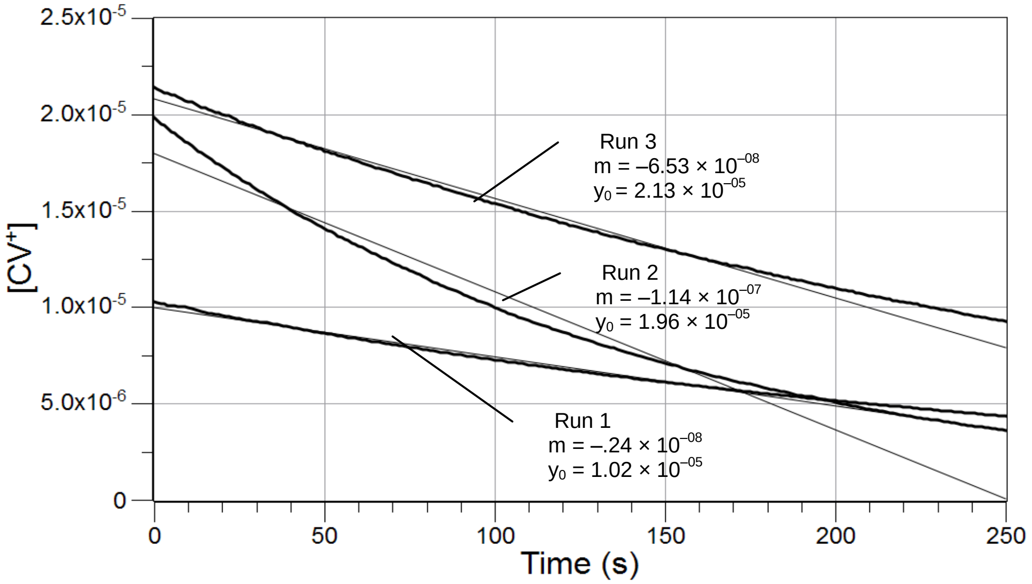


Table 3: Initial rates

Trial	Initial Rate (M/s)
1	3.2×10^{-8}
2	1.1×10^{-7}
3	6.5×10^{-8}

In Trial 3, the concentration of CV^+ was prepared to be twice as much as in Trial 1: $[CV^+]_3 = 2[CV^+]_1$:

$$\frac{Rate_1}{Rate_3} = \frac{[\mathrm{CV}^+]_1^m}{[\mathrm{CV}^+]_3^m} = \frac{[\mathrm{CV}^+]_1^m}{\left(2[\mathrm{CV}^+]_1\right)^m} = \frac{1}{2^m}$$

Taking the logarithm of this equation and multiplying both sides by (–1) yields:

$$\ln\left(\frac{Rate_1}{Rate_3}\right) = \ln\left(\frac{1}{2^m}\right) = \ln\left(2^{-m}\right) = -m\ln 2$$

$$\ln\left(\frac{Rate_3}{Rate_1}\right) = m\ln 2$$

Solving this equation for m gives the following results:

$$m = \frac{\ln\left(\frac{Rate_3}{Rate_1}\right)}{\ln 2} = \frac{\ln\left(\frac{6.5\times10^{-8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}{3.2\times10^{-8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}\right)}{\ln 2} = \frac{0.708}{0.693} = 1.010 \approx 1.0$$

In Trial 2, the concentration of OH^- was twice as much as in Trial 3: $[OH^-]_2 = 2[OH^-]_3$:

$$\frac{Rate_3}{Rate_2} = \frac{[\mathrm{OH}^-]_3^n}{[\mathrm{OH}^-]_2^n} = \frac{[\mathrm{OH}^-]_3^n}{\left(2[\mathrm{OH}^-]_3\right)^n} = \frac{1}{2^n}$$

Taking the logarithm of this equation and multiplying both sides by (–1) yields:

$$\ln\left(\frac{Rate_3}{Rate_2}\right) = \ln\left(\frac{1}{2^n}\right) = \ln\left(2^{-n}\right) = -n\ln 2$$

$$\ln\left(\frac{Rate_2}{Rate_3}\right) = n\ln 2$$

Solving this equation for n gives the results:

$$n = \frac{\ln\left(\frac{Rate_2}{Rate_3}\right)}{\ln 2} = \frac{\ln\left(\frac{1.1\times10^{-7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}{6.5\times10^{-8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}\right)}{\ln 2} = \frac{0.526}{0.693} = 0.759 \approx 1$$

It appears that the order of both reactants is 1, so the overall order (the sum of the individual orders) is 2. Since the concentration of OH^- is much greater than the concentration of CV^+, the concentration of OH^- will not change appreciably, which makes the reaction a *pseudo first-order reaction*:

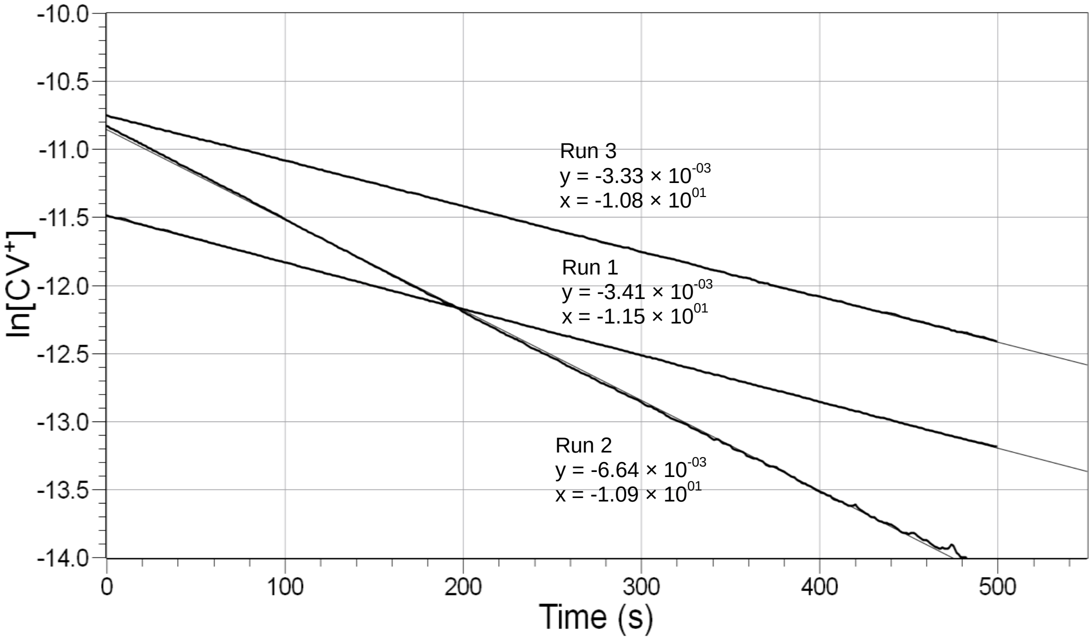
$$Rate = k[\mathrm{OH}^-][\mathrm{CV}^+] \approx k'[\mathrm{CV}^+]$$

Therefore, the applicable rate law is

$$\ln[\mathrm{CV}^+] = \ln[\mathrm{CV}^+]_0 - k't$$

The plot of $\ln[\mathrm{CV}^+]$ versus Time gave a straight line for each run. From the slope, the rate constant k can be calculated:

$$k = \frac{k'}{[\mathrm{OH}^-]}$$



The following data was obtained and the rate constant calculated.

Table 4: Determination of the reaction rate constant

Trial	**k' (M s^{-1})**	**[OH$^-$] (M)**	**k (s^{-1})**
1	3.4×10^{-3}	2.5×10^{-2}	0.14
2	6.6×10^{-3}	5.0×10^{-2}	0.13
3	3.3×10^{-3}	2.5×10^{-2}	0.13

Using the results from Trial 1:

$$k = \frac{k'}{[\mathrm{OH}^-]} = \frac{3.4 \times 10^{-3}\ \mathrm{s}^{-1}}{2.5 \times 10^{-2}\ \mathrm{M}} = 0.14\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

1. What does the value of the intercept represent on the $\ln[\mathrm{CV}^+]$ versus time graph?

The intercept represents $\ln[\mathrm{CV}^+]_0$.

2. Why do the initial rates have to be measured (as opposed to measuring the rate at any other time point) in order to calculate the order of the reactants? (Hint: what are the concentrations of the reactants in the beginning of the reaction and what are they later?)

The rates have to be determined in the beginning because that is the only point where we know the concentrations of the reactants. As the reaction progresses, we no longer know the concentrations of the reactants to use in the equations to calculate *n* or *m*.

3. If at t_0 = 0 seconds $[CV^+]_0 = 5.0 \times 10^{-6}$ M and at t_1 = 10 seconds, $[CV^+]_1 = 2.0 \times 10^{-6}$ M, what is the initial rate of the reaction?

$$Rate = -\frac{\Delta[CV^+]}{\Delta t} = -\frac{[CV^+]_1 - [CV^+]_0}{t_1 - t_0} = -\frac{\left(2.0 \times 10^{-6}\ \mathrm{M}\right) - \left(5.0 \times 10^{-6}\ \mathrm{M}\right)}{\left(10\ \mathrm{s}\right) - \left(0\ \mathrm{s}\right)} = 3.0 \times 10^{-7}\ \frac{\mathrm{M}}{\mathrm{s}}$$

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.1 M NaOH:*** Dissolve 0.4 g of NaOH in some distilled water in a 100-mL volumetric flask. Fill the flask to the mark and mix well.
2. ***1.2×10^{-5} M Crystal Violet:*** Dissolve 0.0472 g of crystal violet in some distilled water in a 100-mL volumetric flask. Fill the flask to the mark and mix the solution well. Make sure there are no solid particles on the bottom after the solution rests for a few minutes. Pipet 10.00 mL of this solution into a 1-L volumetric flask. Fill the flask to the mark and mix the solution well.

Safety

Add these important safety precautions to your normal laboratory procedures:

- In case of contact with skin, NaOH should be washed off with a large amount of water.
- Use care when handling crystal violet as it is a stain.

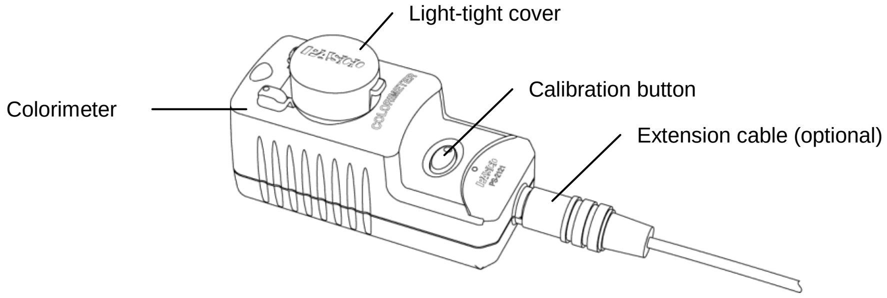
Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Start a new experiment on the data collection system. �(1.2)
2. Connect the colorimeter to the data collection system using the extension cable. �(2.1)

3. Calibrate the colorimeter. �(3.2)



4. Put about 20 mL of the crystal violet solution, the sodium hydroxide solution, and the distilled water in separate 50-mL beakers. Label the beakers.

5. Cover the NaOH solution with a watch glass.

6. Why is it necessary to cover the NaOH solution with a watch glass?

NaOH absorbs CO_2 from air and forms $NaHCO_3$.

7. Label one syringe "CV", one "NaOH", and one "Water".

8. For the first run, fill the three syringes with the volume of liquids specified in Table 5, Trial 1.

9. Eliminate the air bubbles from the syringes by holding the syringe over a sink, pointing upward, knocking gently on the syringe and pushing the plunger in until all the air is expelled. Draw in more solution as needed.

Table 5: Initial volumes and concentrations

Trial	**Initial Concentration (M)**		**Volume (mL)**			
	$[CV^+]$	**$[OH^-]$**	**Crystal Violet 1.2×10^{-5} M**	**NaOH 0.10 M**	**Water**	**Total**
1	3.0×10^{-6}	2.5×10^{-2}	1.50	1.50	3.00	6.00
2	6.0×10^{-6}	5.0×10^{-2}	3.00	3.00	0.0	6.00
3	6.0×10^{-6}	2.5×10^{-2}	3.00	1.50	1.50	6.00

Collect Data

10. Perform the experiment for each of the three runs as follows:

a. Deliver the water and sodium hydroxide solutions from the syringes into a clean cuvette.

b. Display Green (565 nm) Absorbance on the y-axis with Time on the x-axis. �$^{(7.1.1)}$

c. As quickly as possible, add the crystal violet solution to the cuvette, close the cuvette, invert it a few times, wipe it dry and clean and place it into the colorimeter.

Note: This should be done as quickly as possible to minimize the error arising from the delay of collecting data after mixing the reactants.

d. Immediately close the lid on the colorimeter and start data recording. �$^{(6.2)}$

e. Why do you think the cuvette should be clean on the outside?

The wall should be free of fingerprints and other marks because contamination introduces error in the detection of absorption.

f. Continue taking readings until the absorbance drops below 0.1.

g. Stop data recording �$^{(6.2)}$ and clean the cuvette.

h. For the next run, fill the three syringes with the volume of liquids specified for the next trial (in Table 5) and eliminate air bubbles, as before. Repeat the process for each of the next two runs.

11. Print the graph. �$^{(11.2)}$

12. Save your experiment �$^{(11.1)}$and clean up according to your instructor's directions.

Data Analysis

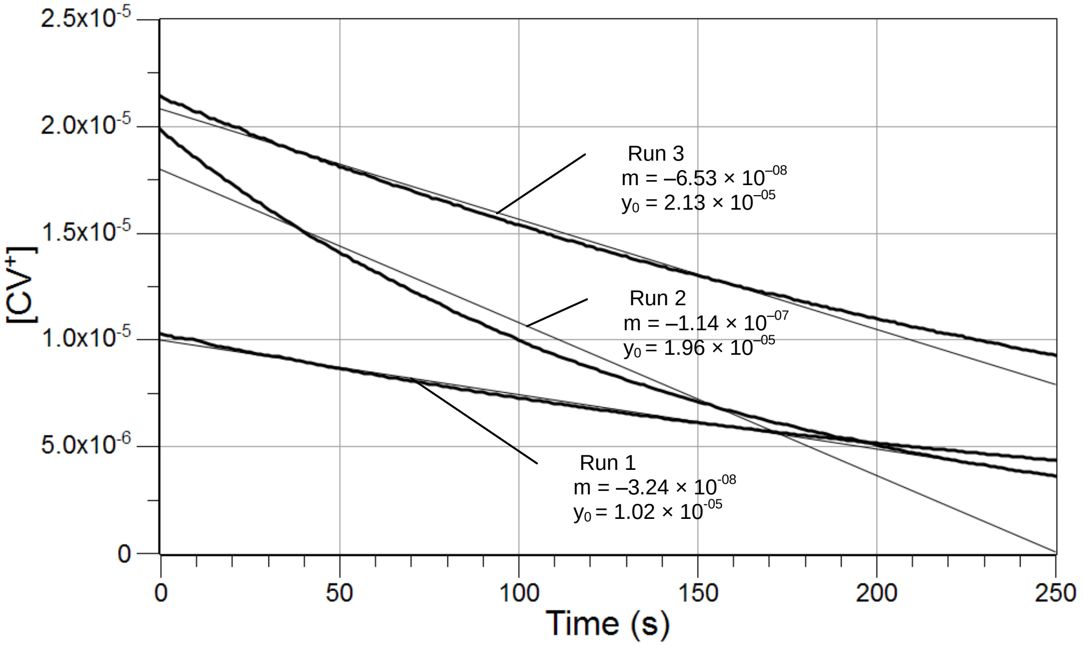
1. In the data collection system, create a calculated data set to obtain the concentrations as a function of time for each trial using Beer's Law �$^{(10.3)}$ knowing the path $l = 1.65$ cm and $\varepsilon = 5 \times 10^4\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.

2. Display the concentration data set on the y-axis with Time on the x-axis. �$^{(7.1.1)}$

3. Find the slope and intercept of the best-fit line. �$^{(9.6)}$

4. Print the graph. �$^{(11.2)}$

5. Sketch or attach the Concentration versus Time graph, showing the slopes.



6. Find the slope of the best-fit line over the first 20 to 25 points to determine the initial rate on your graphs. �$^{(9.6)}$ Consider those points which are still lined up on a straight line. Record the slopes of those lines (which actually are the rates for the reactions) in Table 6.

Table 6: Initial rates

Trial	Initial Rate (M/s)
1	3.2×10^{-8}
2	1.1×10^{-7}
3	6.5×10^{-8}

7. With these values of the rates, calculate *m* from the rates of Trial 1 and Trial 3.

$$m = \frac{\ln\left(\frac{Rate_3}{Rate_1}\right)}{\ln 2} = \frac{\ln\left(\frac{6.5 \times 10^{-8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}{3.2 \times 10^{-8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}\right)}{\ln 2} = 1$$

8. With these values of the rates, calculate *n* from the rates of Trial 2 and Trial 3.

$$n = \frac{\ln\left(\frac{Rate_2}{Rate_3}\right)}{\ln 2} = \frac{\ln\left(\frac{1.1 \times 10^{-7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}{6.5 \times 10^{-8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}}\right)}{\ln 2} = \frac{0.526}{0.693} = 0.759 \approx 1$$

9. With these values of *n* and *m*, what is the rate expression in terms of the concentrations of the reactants?

$Rate = k[CV^+][OH^-]$

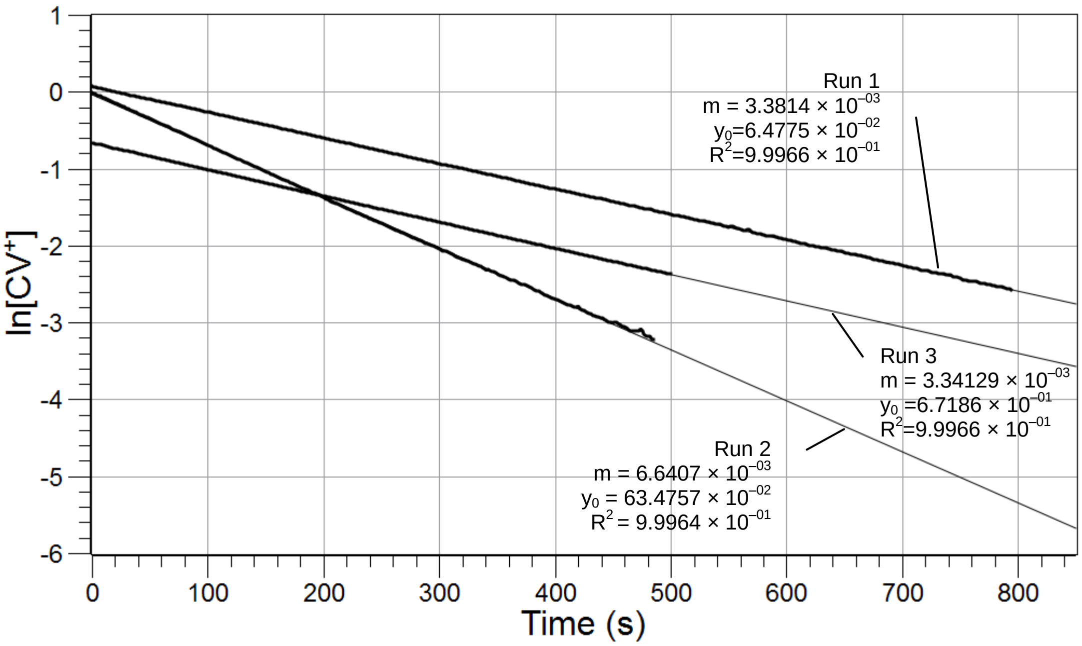
10. Consider that $[OH^-] >> [CV^+]$ and won't change appreciably during the reaction. The OH^- concentration can be considered "constant" and can be combined with *k* to form *k'*, which is a pseudo rate constant. What is the value of the pseudo rate constant in terms of the rate constant and the concentration of OH^-?

$k' = k[OH^-]$

11. What is the rate expression using the pseudo rate constant instead of the rate constant and the concentration of OH^-?

$Rate = k'[CV^+]$

12. Based on the order determined for the two reactants, display a graph with the appropriate representation of your data ($\ln[CV^+]$ or $1/[CV^+]$ versus Time) �(7.1.1). Sketch or print�(11.2) and paste the resulting curve for each trial below.



13. From the graph above, calculate the rate constant, k, from the values of the pseudo rate constant, k'.

For Trial 1:

$$k = \frac{k'}{[\mathrm{OH^-}]}$$

$$k = \frac{3.4 \times 10^{-3}\ \mathrm{M\,s^{-1}}}{2.5 \times 10^{-2}\ \mathrm{M}} = 0.14$$

Table 7: Determination of the reaction rate constant

Trial	k' (M $\mathrm{s^{-1}}$)	[$\mathrm{OH^-}$] (M)	k ($\mathrm{s^{-1}}$)
1	3.4×10^{-3}	2.5×10^{-2}	0.14
2	6.6×10^{-3}	5.0×10^{-2}	0.13
3	3.3×10^{-3}	2.5×10^{-2}	0.13

Analysis Questions

1. What values did you get for *n* and *m*? What is the overall order of the reaction?

Both *n* and *m* should be 1. Therefore, the overall order of the reaction is second order.

2. What is the average value of the rate constant that you obtained with standard deviation?

$k = 0.14 \pm 0.01\ \mathrm{s^{-1}}$

3. How did the color of the solution change during the reaction? Explain!

The color intensity decreased since the concentration of the absorbing species was decreasing.

4. How do you think the rate would change if we doubled the concentration of both reactants?

The rate would increase four fold.

Synthesis Questions

Use available resources to help you answer the following questions.

1. **Iodine reacts with acetone to form iodo-acetone according to the following reaction:**

$$I_2 + CH_3\text{–}CO\text{–}CH_3 \rightarrow HI + CH_2I\text{–}CO\text{–}CH_3$$

Iodine is brown; the acetone, hydrogen iodide, and iodo-acetone are colorless. The order of both reactants is 1. Propose a method to measure the rate constant for this reaction.

The reaction can be monitored by measuring the absorbance of iodine. From the absorbance, the iodine concentration can be calculated the same way we calculated it in this experiment for the crystal violet.

2. **When only one species is absorbing it is easy to follow the reaction. However, if there are two species involved in absorption, the situation is somewhat more complicated. Consider the following hypothetical reaction:**

$$A + B \rightarrow C + D$$

where A absorbs in the blue range and C absorbs in the yellow range of the visible spectrum. Do you think the reaction can be monitored by monitoring the absorption of the solution? If so, how? Explain!

Since the colors are substantially different, both species can be monitored simultaneously. The blue species absorbs around 440 nm while the yellow absorbs around 500 nm.

3. **How would your strategy be different from this experiment if you were to monitor the concentration of C in the previous example? (Hint: how would the absorption of C change as the reaction progresses?)**

Instead of the consumption of a reactant being monitored, one could monitor the accumulation of one of the products which is numerically the same (because of the stoichiometry). However, they have opposite signs.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. The rate of the reaction between CV^+ and OH^- depends:

- **A.** Only on the concentration of the reactants.
- **B.** Only on the rate constant, *k*.
- **C. On the concentrations of the reactants and the rate constant, *k*.**
- **D.** On the ratio of the concentrations of the reactants and the rate constant, *k*.

2. In the reaction between CV^+ and OH^-, doubling the concentration of CV^+:

- **A.** Will not change the reaction rate.
- **B.** Will double the rate constant.
- **C. Will double the reaction rate.**
- **D.** Will not have an affect on the reaction at all.

3. Generally in a chemical reaction, changing the concentration of a reactant:

- **A.** Will always change the rate of the reaction.
- **B. Will always change the rate of the reaction except if the order of that reactant is zero-order.**
- **C.** Will always change the rate of the reaction except if the order of that reactant is first-order.
- **D.** Will always change the rate of the reaction except if the order of that reactant is second-order.

4. The absorbance is:

- **A.** Not related to the concentration of the absorbing species.
- **B.** Proportional to the concentration of the absorbing species only.
- **C. Proportional to the concentration of the absorbing species and the path length of solution the light passes through.**
- **D.** Proportional only to the path length through which the light has to pass.

Extended Inquiry Suggestions

An Arrhenius analysis can be performed with this reaction. If the cuvette is kept in a water bath at various temperatures, the reaction can be performed at different temperatures to determine the activation energy of the reaction:

$$k = Ae^{-E_a / RT}$$

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$$

Electrochemistry

31. Oxidation–Reduction Titration

Objectives

Students use the change in potential during an oxidation-reduction reaction to determine the concentration of a commercial, nominally 3% hydrogen peroxide solution.

Procedural Overview

Students gain experience conducting the following procedures:

- Applying titration skills to oxidation-reduction reactions; using an oxidation reduction potential electrode
- Applying oxidation-reduction equations to obtain the stoichiometric ratio between the titrant and analyte
- Using the equivalence point volume of the titrant to calculate the concentration of the hydrogen peroxide solution

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Chemistry sensor[1]
- Oxidation reduction potential (ORP) electrode
- Drop counter
- Magnetic stirrer and stir bar
- Buret, 50-mL
- Beaker (2), 150-mL
- Volumetric pipet with rubber bulb, 10-mL
- Graduated cylinder, 50-mL
- Clamp, right-angle
- Clamp, buret
- Ring stand
- Hydrogen peroxide, approximately 3%, 1:20 dilution, 40 mL[2]
- 1.000×10^{-2} M Potassium permanganate ($KMnO_4$), 100 mL[3]
- 4 M Sulfuric acid (H_2SO_4), 70 mL[4]
- Water, deionized, 250 mL
- Wash bottle with deionized water

[1] The PASPORT High Resolution pH/ORP/ISE Amplifier with Temperature Sensor can also be used.
[2-4] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- ♦ Conversion between molarity and percent by mass
- ♦ Redox reactions
- ♦ Titration

Related Labs in This Guide

Labs conceptually related to this one include:

- ♦ Acid–Base Titration
- ♦ Determination of the Rate of the Decomposition of Hydrogen Peroxide
- ♦ Determination of Electrochemical Series
- ♦ Electroplating

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- ♦ Starting a new experiment on the data collection system �(1.2)
- ♦ Connecting a sensor to the data collection system. �(2.1)
- ♦ Connecting multiple sensors to your data collection system �(2.2)
- ♦ Calibrating the drop counter �(3.4)
- ♦ Starting and stopping data recording �(6.2)
- ♦ Displaying data in a graph �(7.1.1)
- ♦ Adjusting the scale of a graph �(7.1.2)
- ♦ Changing the variable on the x-axis and y-axis of a graph �(7.1.9)

- Finding the slope at a point on the data plot �(9.3)

- Saving your experiment �(11.1)

- Printing the graph. �(11.2)

Background

Hydrogen peroxide is a commonly used oxidizing agent in a broad range of situations ranging from medical applications to propellant materials in rockets. A 3% solution of hydrogen peroxide is available in pharmacies. It is used as a common topical disinfectant solution.

Solutions with higher concentrations of hydrogen peroxide are used in industrial processes (60% to 70%) and in rocket propellants (90%). While hydrogen peroxide is a desired oxidizing agent in industrial processes because the product of the reactions is water, hydrogen peroxide solutions are highly unstable. Particularly at higher concentration, they can decompose explosively.

Even though the 3% hydrogen peroxide solution is stable, it decomposes slowly; the actual concentration may differ from the value printed on the label.

Pre-Lab Experiment

Setting the stage for the experiment

Hydrogen peroxide, in most reactions, acts as an oxidizer. It picks up electrons.

$$\mathrm{H_2O_2} + 2e^- \rightarrow \mathrm{2OH^-}$$

When the reaction is performed in an acidic medium, the product is water.

$$\mathrm{H_2O_2} + \mathrm{2H^+} + 2e^- \rightarrow \mathrm{2H_2O}$$

If, however, it is mixed with a stronger oxidizer, it can act as a reducing agent; that is, it loses electrons.

$$\mathrm{2H_2O_2} \rightarrow \mathrm{O_2} + \mathrm{2H_2O} + 2e^-$$

Potassium permanganate ($KMnO_4$) is a stronger oxidizer than hydrogen peroxide. Therefore, it oxidizes the H_2O_2.

$$\mathrm{2MnO_4^-} + \mathrm{5H_2O_2} + \mathrm{6H^+} \rightarrow \mathrm{2Mn^{2+}} + \mathrm{5O_2} + \mathrm{8H_2O} \tag{1}$$

This reaction provides a means to determine the precise concentration of a 3% H_2O_2 solution.

The titration of the H_2O_2 solution of unknown concentration is performed with 0.01 M $KMnO_4$ solution. The reaction can be followed using the ORP sensor (also referred to as an ORP electrode), which monitors the reduction-oxidation (redox) potential in the solution. (This is similar to a pH sensor monitoring the pH in a solution.)

The titration curve looks similar to one obtained with a pH sensor during an acid-base titration. The curve is the steepest at the equivalence point, when all the H_2O_2 molecules have reacted. Also, the $KMnO_4$ solution is purple and the products of the reaction are colorless. When there is no more H_2O_2 for a reaction to continue, the first extra drop of $KMnO_4$ colors the titrated solution.

Example calculation to try

A 50.00 mL solution, nominally 3% H_2O_2, was titrated with a 1.000 M $KMnO_4$ solution. The volume of $KMnO_4$ needed to reach the equivalence point was 21.50 mL. The number of moles of $KMnO_4$ necessary for the titration was

$$(21.50\text{ mL KMnO}_4)\frac{(1.000\text{ mol KMnO}_4)}{(1000\text{ mL KMnO}_4)} = 0.02150\text{ mol KMnO}_4$$

According to the stoichiometric equation (see Equation 1), 2 moles of $KMnO_4$ reacts with 5 moles of H_2O_2. Applying this ratio to determine the number of moles of hydrogen peroxide that reacted with the permanganate gives

$$(0.02150\text{ mol KMnO}_4)\frac{(5\text{ mol H}_2\text{O}_2)}{(2\text{ mol KMnO}_4)} = 0.05375\text{ mol H}_2\text{O}_2$$

Therefore, the 50.00 mL sample contained 5.375×10^{-2} mol H_2O_2. The concentration of the sample was

$$(0.05375\text{ mol})\frac{(1000.00\text{ mL})}{(50.00\text{ mL})} = 1.075\text{ M}$$

The number of grams of H_2O_2 in 1000 mL of solution is:

$$(1.075\text{ mol})\left(34.00\ \tfrac{\text{g}}{\text{mol}}\right) = 36.55\text{ g}$$

Therefore, the number of grams of H_2O_2 in 100 mL of this solution is 3.655 g. Since the density of the solution is assumed to be 1.000 g/mL, the 100 mL solution has the mass of 100 g. With 3.655 g of H_2O_2 in a 100 g solution, the result is a 3.655% H_2O_2 solution.

1. Why is H_2O_2 a preferred oxidizing agent these days in industrial processes? (Hint: consider one of the most important concerns in today's society.)

H_2O_2 is preferred because the products are environmentally friendly.

2. Oxidizing agents gain electrons while reducing agents lose electrons in a reaction. What do you know about the number of transferred electrons in a reaction (that is, the number of lost electrons and the number of gained electrons)?

The number of lost electrons should be the same as the number of gained electrons; electrons are neither created nor destroyed in a redox reaction.

3. How can H_2O_2 be a reducing agent when it is known as one of the strongest oxidizing agents?

Being either an oxidizing or reducing agent is not absolute. It always depends on the partner in the reaction. Since the $KMnO_4$ is a stronger oxidizer, it forces the hydrogen peroxide to lose electrons, which are taken by the $KMnO_4$. The $KMnO_4$ is reduced. In this case the hydrogen peroxide is a reducing agent.

4. Which method is better to follow the titration: using an ORP electrode or using the $KMnO_4$ as an indicator, since it is purple and the products of the titration are colorless? Explain.

The ORP electrode provides an objective way of following the reaction. Determining the color is subjective. Therefore, using the sensor is more accurate.

5. In this reaction, how many electrons does the Mn gain in MnO_4^-? How many electrons does an H_2O_2 molecule lose?

Manganese gains 5 electrons and each H_2O_2 molecule loses 2 (each O loses one).

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.15% H_2O_2:*** A 3% hydrogen peroxide solution is readily available from any pharmacy. Measure 25 mL of a 3% hydrogen peroxide solution and pour it into a 0.5 L volumetric flask. Fill the flask to the mark with distilled water.
2. ***1.000×10^{-2} M $KMnO_4$:*** Measure 0.8 g of $KMnO_4$ and transfer it into a 0.5 L volumetric flask, fill to the mark with distilled water and dissolve all the crystals.

   Note: Because the solution is dark, make sure that all the crystals dissolve before filling the flask to the mark.

   Note: This method prepares a solution with an approximate concentration. Standardization is necessary to determine the exact concentration of the solution using an appropriate primary standard.
3. ***4 M H_2SO_4:*** Measure 109 mL of 96 to 98% sulfuric acid solution. Add about 0.25 L of distilled water to an empty 0.5-L Erlenmeyer flask and s*lowly* add the sulfuric acid solution to the water while constantly mixing.

   Important: Do *not* perform a dilution of sulfuric acid in a volumetric flask. The solution may heat up excessively and crack it. Volumetric flasks are usually not heat resistant.

Safety

Add these important safety precautions to your normal laboratory procedures:

- Wash any $KMnO_4$ solution that comes in contact with your skin with large amounts of water. $KMnO_4$ can cause brown discoloration of the skin.
- Wash any H_2O_2 solution or H_2SO_4 solution that comes in contact with your skin with large amounts of water. H_2O_2 can cause white discoloration of the skin. H_2SO_4 can cause burns.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

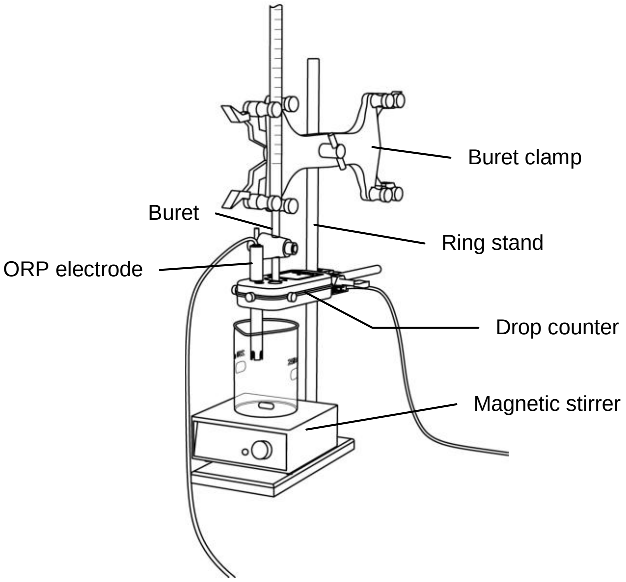
1. Start a new experiment on the data collection system. �$^{(1.2)}$

2. Connect the chemistry sensor, with the oxidation reduction potential (ORP) electrode attached, to the data collection system. �$^{(2.1)}$

Note: No calibration procedure is needed for this experiment. You do not use the numerical redox value; you use the electrode to determine the point at which there is a jump in the redox potential.

3. Assemble the titration apparatus, using the steps below and the illustration as a guide.

- **a.** Position the magnetic stirrer on the base of the ring stand.
- **b.** Place a waste container (150-mL beaker) on the magnetic stirrer.
- **c.** Use the buret clamp to attach the buret to the ring stand.
- **d.** Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.
- **e.** Place the ORP electrode through one of the slots in the drop counter.



Note: Do not connect the drop counter to the data collection system yet.

4. Rinse the buret with several milliliters of the 1.000×10^{-2} M $KMnO_4$ solution:

- **a.** Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized $KMnO_4$ solution.
- **b.** Open the stopcock on the buret and drain the rinse $KMnO_4$ solution into the waste container.
- **c.** Repeat this process two more times.

5. Why is it necessary to rinse the buret with the $KMnO_4$ solution?

If there is any residual water or contaminant in the buret, it will dilute the $KMnO_4$ and change its concentration. Rinsing eliminates any such contamination.

6. Make sure the stopcock on the buret is in the "off" position and then use a funnel to fill the buret with about 50 mL of the $KMnO_4$ solution (titrant).

7. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

8. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of $KMnO_4$. If this happens, the amount of titrant used will be inaccurate.

9. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

Note: Good control of the stopcock is important. Each drop should result in a blink of the LED on the drop counter. If the LED is continuously lit, you have opened the stopcock too far and you will have to start over.

10. Why will it be necessary to start your titration over again if you accidentally allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

11. Add additional 1.000×10^{-2} M $KMnO_4$ to the buret so the solution is above the zero mark. Allow some of the $KMnO_4$ solution to drip into the waste container until the top of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 1.

12. Why are you instructed to set the top of the meniscus to the zero mark instead of the bottom of the meniscus?

$KMnO_4$ solution has a deep purple color which makes it difficult to read the bottom of the meniscus.

13. Remove the waste container.

Perform the titration of a H_2O_2 solution three times, following the steps below.

14. Use the volumetric pipet to transfer 10.00 mL of the H_2O_2 solution into a 150-mL beaker.

15. Using the graduated cylinder, transfer 20.00 mL of the 4 M H_2SO_4 into the same 150-mL beaker.

Note: Handle sulfuric acid carefully.

16. Add enough deionized water to the beaker so the tip of the ORP electrode is covered with solution.

17. Add the magnetic stir bar to the beaker.

18. Turn on the magnetic stirrer at a slow and steady rate.

19. Connect the drop counter to the data collection system. �$^{(2.2)}$

20. Display the Potential on the y-axis of a graph and Drop Count on the x-axis. �$^{(7.1.1)}$

Collect Data

21. Clean the lens of the drop counter inside the opening through which the drops are going with water and a cotton swab or tissue.

22. Start recording data. �$^{(6.2)}$

23. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

24. Continue the titration past the equivalence point until the ISE voltage curve flattens.

25. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

26. Stop recording data. �$^{(6.2)}$

27. In Table 1, record the final drop count and the final reading of the titrant in the buret to a precision of 0.01 mL.

28. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 1.

Table 1: Titration data for drop counter calibration

Titration Information	Trial 1	Trial 2	Trial 3
Initial reading of $KMnO_4$ on the buret (mL)	0.00	0.00	0.00
Final reading of $KMnO_4$ on the buret (mL)	21.00	18.80	17.90
Volume of titrant (mL)	21.00	18.80	17.90
Final drop count	428	386	357

29. Calibrate the drop counter. �(3.4)

30. Set the horizontal axis to the calculated volume. �(7.1.9)

31. In Table 2, record the volume of $KMnO_4$ (to a precision of 0.01 mL) used to reach the equivalence point. The equivalence point will be where the slope of the titration curve is the steepest. Find the steepest slope of the data plot to determine this point. �(9.3)

32. Refill the buret above the zero mark with the $KMnO_4$ solution.

- **a.** Fill the buret above the zero mark and allow some of the $KMnO_4$ solution to drip into a waste container until the top of the meniscus is lined up with the zero mark or just below.
- **b.** Record the starting point in Table 1.

33. Rinse the ORP electrode tip with deionized water.

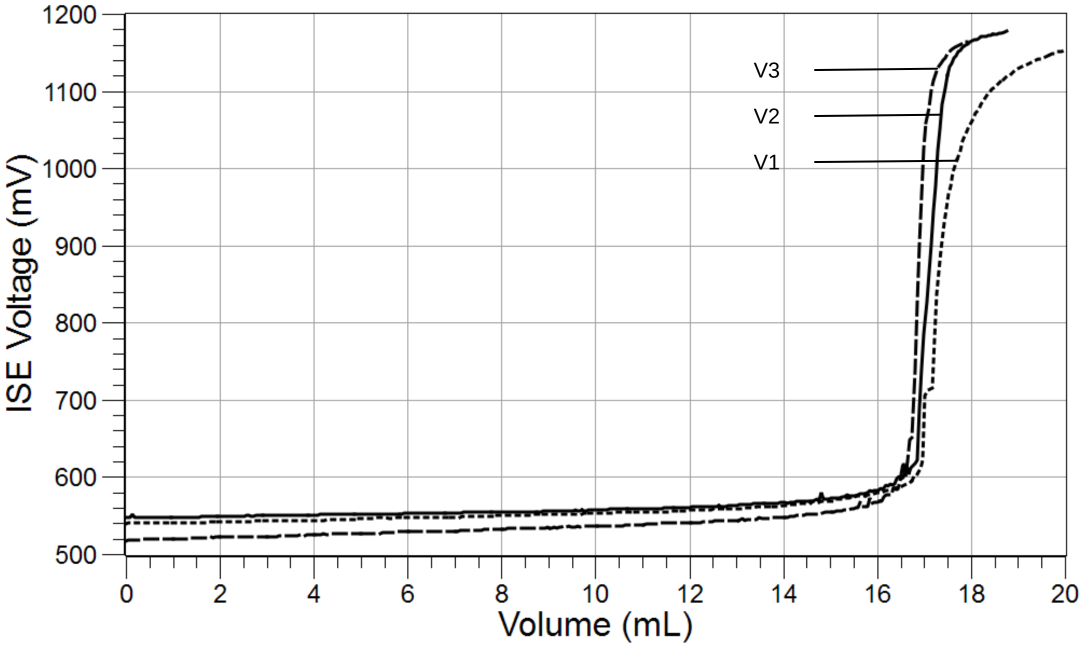
34. Remove the beaker and dispose of its contents according to the instructor's instructions.

35. Rinse the beaker with distilled water.

36. Repeat the titration procedure with two more H_2O_2 samples.

37. Save your experiment �(11.1) and clean up according to your instructor's instructions.

38. For each titration curve, sketch the graphs or print the graphs �(11.2) of oxidation reduction potential, measured as ISE Voltage verses Volume, and paste them below.



Data Analysis

1. Calculate the number of moles of $KMnO_4$ added to reach the equivalence point. Record this value in Table 2.

For Trial 1:

$$(17.32 \text{ mL KMnO}_4)\frac{(1.000 \times 10^{-2} \text{ mol KMnO}_4)}{(1000 \text{ mL KMnO}_4)} = 1.732 \times 10^{-4} \text{ mol KMnO}_4$$

2. Calculate the number of moles of H_2O_2 in the 10.00 mL sample. Record this value in Table 2.

According to the stoichiometric equation (Equation 1), 2 mol of $KMnO_4$ reacts with 5 mol of H_2O_2:

For Trial 1:

$$(1.732 \times 10^{-4} \text{ mol KMnO}_4)\frac{(5 \text{ mol H}_2\text{O}_2)}{(2 \text{ mol KMnO}_4)} = 4.330 \times 10^{-4} \text{ mol H}_2\text{O}_2$$

3. Determine the concentration of the H_2O_2 solution. Record these values in Table 2.

For Trial 1: The 10.00 mL sample contained 4.330×10^{-4} mol H_2O_2. The concentration of the sample is

$$(4.330 \times 10^{-4} \text{ mol})\frac{(1000.00 \text{ mL})}{(10.00 \text{ mL})} = 4.330 \times 10^{-2} \text{ M}$$

4. How many grams of H_2O_2 are in 1000 mL of this solution?

For Trial 1:

$(4.330 \times 10^{-2} \text{ M}) \times (34.00 \text{ g/mol}) = 1.472 \text{ g H}_2\text{O}_2\text{/L}$

5. Determine the percent concentration of the H_2O_2 solution. What is the average concentration, based on the three trials. (The density of the solution is assumed to be 1.000 g/mL, so the mass of 1000 mL is 1000 g.)

For Trial 1:

$$\frac{1.472\text{ g } H_2O_2}{1000\text{ g solution}} \times 100 = 0.1472\%$$

6. Since the hydrogen peroxide solution was a 1:20 dilution of the 3% hydrogen, calculate the percent concentration of the original solution. Record this value in Table 2.

Using the average:

0.1458% × 20 = 2.916%

Table 2: Determine the concentration of H_2O_2

Parameter	Trial 1	Trial 2	Trial 3
Expected concentration of H_2O_2 (%)	3%		
Volume of $KMnO_4$ added to reach the equivalence point (mL)	17.32	17.10	17.05
Amount of $KMnO_4$ added to reach the equivalence point (mol)	1.732×10^{-4}	1.710×10^{-4}	1.705×10^{-4}
Amount of H_2O_2 in 10.00 mL sample (mol)	4.330×10^{-4}	4.275×10^{-4}	4.263×10^{-4}
Concentration of H_2O_2 solution (M)	4.330×10^{-2}	4.275×10^{-2}	4.263×10^{-2}
Concentration of H_2O_2 solution (%)	0.1472	0.1453	0.1449
Average concentration of H_2O_2 solution (%)	0.1458		
Concentration of original H_2O_2 solution (M)	2.916		

Analysis Questions

1. If you were given a sample of H_2O_2 from an old bottle of hydrogen peroxide to determine its concentration by titration, do you expect a greater or lesser volume of $KMnO_4$ needed to reach the equivalence point than if it were from a new bottle? Explain.

A lesser volume of $KMnO_4$ is expected because H_2O_2 slowly decomposes, resulting in less H_2O_2 content.

2. Does the fact that you set the top of the meniscus to the zero mark and take your final reading at the top of the meniscus introduce an error? Explain.

No, because it helps assure accuracy when finding the difference between the two readings. The volume of the solution between the tops of the two menisci and the bottoms of the two menisci are the same.

Synthesis Questions

Use available resources to help you answer the following questions.

1. If you were to adapt this titration method to determine the amount of iron(II) ions in an unknown solution, what would be the balanced chemical equation between MnO_4^- and Fe^{2+} in the presence of H_2SO_4 (H_3O^+)? (Hint: the products of this reaction are Mn^{2+}, Fe^{3+}, and H_2O.)

$$MnO_4^- + 5Fe^{2+} + 8H_3O^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 12H_2O$$

2. H_2O_2 is a strong enough oxidizer to oxidize iron(II) as well. What would be the balanced chemical equation between H_2O_2 and Fe^{2+} in the presence of H_2SO_4 (H_3O^+)? (Hint: the products of this reaction are Fe^{3+} and H_2O.)

$$H_2O_2 + 2Fe^{2+} + 2H_3O^+ \rightarrow 2Fe^{3+} + 4H_2O$$

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Glass surfaces are known to help the spontaneous decomposition of H_2O_2. How does the use of a buret, a pipet, and a beaker influence the $KMnO_4$ consumption?

- **A.** It would not affect the $KMnO_4$ consumption since the glass has no effect on $KMnO_4$.
- **B.** It would result in the consumption of more $KMnO_4$ because the product of the decomposition of H_2O_2, O_2, would also consume some $KMnO_4$.
- **C.** **Less H_2O_2 in the solution in the glass beaker would result in less $KMnO_4$ consumption.**
- **D.** It depends on the contamination of H_2O_2.

2. What is the electron change in MnO_4^- and H_2O_2?

- **A.** **MnO_4^- gains 5 electrons and H_2O_2 loses 2 electrons.**
- **B.** MnO_4^- gains 2 electrons and H_2O_2 loses 5 electrons.
- **C.** MnO_4^- loses 5 electrons and H_2O_2 gains 2 electrons.
- **D.** MnO_4^- loses 2 electrons and H_2O_2 gains 5 electrons.

Extended Inquiry Suggestions

$KMnO_4$ is not a stable chemical in solution. Because it readily oxidizes many materials, its precise concentration has to be determined with a primary standard before each use. Sodium oxalate ($Na_2C_2O_4$) is such a standard.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H_3O^+ \rightarrow 2Mn^{2+} + 10CO_2 + 24H_2O$$

If there is time available, it is worth performing the standardization of the $KMnO_4$ titrant with $Na_2C_2O_4$:

> Measure 0.8375 g of $Na_2C_2O_4$ (FW = 134 g/mol) and put it into a 100-mL beaker. Add 5 mL of 4 M H_2SO_4. Titrate the solution at 80 °C using the color of $KMnO_4$ to determine the end of the reaction.

Important: Do not use the ORP electrode. The high temperature will ruin it. The high temperature is necessary to eliminate the produced CO_2.

32. Determination of Electrochemical Series

Objectives

Students determine the half-reactions that relate to the anode and cathode of a galvanic cell. They also calculate the electromotive force for a battery, knowing the electrode materials used, by comparing the reduction potentials of metals.

Procedural Overview

Students gain experience conducting the following procedures:

- Constructing electrochemical cells
- Measuring the voltage produced in electrochemical cells with different metals and salt solutions as the anode and cathode

Time Requirement

Preparation time	15 minutes
Pre-lab discussion and experiment	15 minutes
Lab experiment	50 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Voltage sensor
- Beaker (6), 50-mL
- Glass plate (5 × 5 in)
- Disposable droppers (6), 1 mL
- Iron strip, 1-cm × 1-cm
- Lead strip, 1-cm × 1-cm
- Copper strip, 1-cm × 1-cm
- Silver wire, 1-cm
- Zinc strip, 1-cm × 1-cm
- Circular filter paper, 11-cm diameter
- 1.0 M Zinc sulfate ($ZnSO_4$), 10 mL[1]
- 1.0 M Iron sulfate ($FeSO_4$), 10 mL[2]
- 1.0 M Copper sulfate ($CuSO_4$), 10 mL[3]
- 1.0 M Silver nitrate ($AgNO_3$),10 mL[4]
- 1.0 M Lead nitrate ($Pb(NO_3)_2$), 10 mL[5]
- 1.0 M Sodium nitrate ($NaNO_3$), 20.0 mL[6]
- Sand paper
- Scissors

[1-6] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Redox (oxidation-reduction) reactions
- Redox potential
- Electrolytes
- Conductivity
- Molarity

Related Labs in This Guide

Labs conceptually related to this one include:

- Oxidation–Reduction Titration
- Electroplating

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to your data collection system �(2.1)
- Monitoring live data without recording it �(6.1)

Background

The basis for an electrochemical cell is an oxidation-reduction (or "redox") reaction. This reaction can be divided into two half-reactions:

Oxidation half-reaction (loss of electrons) takes place at the anode, which is the positive electrode that the anions migrate to (hence the name anode).

Reduction half-reaction (gain of electrons) takes place at the cathode, which is the negative electrode that the cations migrate to (hence the name cathode).

Due to the difference in the electric potential between the two electrodes, an electrical current can be generated. The difference in potential is a result of the differences between the individual potentials of the metal electrodes with respect to the electrolyte, which is an electrically conductive ionic solution. The electric potential also varies with temperature, concentration of electrolyte, and pressure.

The standard electrode potential, $E°$, is the measure of potential of any electrode at standard ambient conditions (temperature at 298 K, solutes at 1 M, and gases at 101.3 kPa). Since the oxidation potential of a half-reaction is the negative of the reduction potential in a redox reaction, it is adequate to calculate either one of the potentials. The standard electrode potential is commonly written as the standard reduction potential.

In this experiment, students will compare the potentials of five different metals: copper, zinc, lead, silver, and iron, by measuring combinations of their half reactions.

Pre-Lab Experiment

Setting the stage for the experiment

Standard potential is defined as the potential of an electrode that consists of a metal and the 1 M solution of the salt of that metal. The representation of an electrode is always "oxidation/reduction." For example, Zn^{2+}/Zn represents a zinc electrode.

If the solution portion of two electrodes is connected electrically, we have a galvanic cell. The potential measured between the two metals is the electromotive force. In one electrode, spontaneous reduction occurs; in the other, spontaneous oxidation occurs. For example, if a Zn^{2+}/Zn electrode and a Cu^{2+}/Cu electrode are connected, copper will oxidize zinc since the zinc is located above the copper (that is, zinc has lower reduction potential than copper, according to the table below).

In the table below, metals are arranged in increasing reduction (or decreasing oxidation) potential from top to bottom. That is, for a metal further down in the table, the greater its reduction potential is since it is easier to reduce it. The opposite is true as well: the higher up a metal is in the table, the greater its “oxidation potential,” since it is easier to oxidize it.

In this experiment, you will compare the oxidation and reduction potential of five metals. The point of reference will be copper and the other four metals are iron, lead, zinc, and silver. Metals located above the copper are expected to reduce copper (since for those, copper has the highest reduction potential). Metals located below the copper have higher reduction potential. Therefore, those will be reduced and the copper will be oxidized.

Table 1: Standard reduction potentials ($E°$) for selected metals

Metal	Reduction Half-Reaction	$E°$ (V)
Lithium	$Li^+ + e^- \rightarrow Li(s)$	– 3.04
Cesium	$Cs^+ + e^- \rightarrow Cs(s)$	– 3.03
Rubidium	$Rb^+ + e^- \rightarrow Rb(s)$	– 2.98
Potassium	$K^+ + e^- \rightarrow K(s)$	– 2.93
Barium	$Ba^{2+} + 2e^- \rightarrow Ba(s)$	– 2.91
Strontium	$Sr^{2+} + 2e^- \rightarrow Sr(s)$	– 2.90
Calcium	$Ca^{2+} + 2e^- \rightarrow Ca(s)$	– 2.87
Sodium	$Na^+ + e^- \rightarrow Na(s)$	– 2.71
Magnesium	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	– 2.37
Berium	$Be^{2+} + 2e^- \rightarrow Be(s)$	– 1.85
Aluminum	$Al^{3+} + 3e^- \rightarrow Al(s)$	– 1.66
Manganese	$Mn^{2+} + 2e^- \rightarrow Mn(s)$	– 1.18
Zinc	$Zn^{2+} + 2e^- \rightarrow Zn(s)$	– 0.76
Chromium	$Cr^{3+} + 3e^- \rightarrow Cr(s)$	– 0.74
Iron	$Fe^{2+} + 2e^- \rightarrow Fe(s)$	– 0.44
Cadmium	$Cd^{2+} + 2e^- \rightarrow Cd(s)$	– 0.40
Nickel	$Ni^{2+} + 2e^- \rightarrow Ni(s)$	– 0.25
Tin	$Sn^{2+} + 2e^- \rightarrow Sn(s)$	– 0.13
Lead	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	– 0.13
Hydrogen	$2H^+ + 2e^- \rightarrow H_2(s)$	0.00
Bismuth	$Bi^{3+} + 3e^- \rightarrow Bi(s)$	+0.32
Copper	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.34
Silver	$Ag^+ + e^- \rightarrow Ag(s)$	+0.80
Mercury	$Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$	+0.80
Mercury	$Hg^{2+} + 2e^- \rightarrow Hg(l)$	+0.85
Palladium	$Pd^{2+} + 2e^- \rightarrow Pd(s)$	+0.91
Platinum	$Pt^{2+} + 2e^- \rightarrow Pt(s)$	+1.19
Cerium	$Ce^{4+} + e^- \rightarrow Ce^{3+}(s)$	+1.44
Gold	$Au^+ + e^- \rightarrow Au(s)$	+1.83

Example calculation to try

A galvanic cell is assembled from a Zn^{2+}/Zn and a Cu^{2+}/Cu electrode:

$$Zn(s)\,|\,Zn^{2+}(aq)\,|\,|\,Cu^{2+}(aq)\,|\,Cu(s)$$

where the single vertical bars represent the junction between solid and liquid, and the double vertical bars represent the junction between the two solutions.

By definition, the cathode is on the right and the anode is on the left. Therefore, in the right electrode there is reduction and in the left electrode there is oxidation. In this example, the zinc is oxidized and the copper is reduced (copper has the greater reduction potential). The standard reduction potentials of these electrodes are as follows:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E_1 = +0.34\,V$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E_2 = -0.76\,V$$

The electromotive force can be calculated as:

$$E = \text{(Potential of Cathode)} - \text{(Potential of Anode)}$$

$$E = E_1 - E_2 = (+0.34\,V) - (-0.76\,V) = +1.10\,V$$

This would be the potential shown by a voltmeter. A galvanic cell assembled in this fashion is called a Daniell cell and can be represented by the following diagram:

$Zn(s)\,|\,Zn^{2+}(aq)\,|\,|\,Cu^{2+}(aq)\,|\,Cu(s)$

1. Would silver form a galvanic cell with copper? Explain your answer.

Yes, it would, because the standard potential of the two metals are different.

2. If your answer is "yes" to the question above, which electrode would be the cathode and which one would be the anode? Explain.

Since copper has a lower reduction potential than silver, silver will oxidize copper; therefore, silver will be reduced. The cathode is the electrode where the reduction takes place, therefore the cathode will be the Ag^+/Ag electrode and the anode will be the Cu^{2+}/Cu electrode.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***1.0 M $ZnSO_4$:*** Dissolve 71.89 g of $ZnSO_4 \cdot 7H_2O$ in some distilled water in a 250-mL volumetric flask and fill it to the mark.
2. ***1.0 M $FeSO_4$:*** Dissolve 69.50 g of $FeSO_4 \cdot 7H_2O$ in some distilled water in a 250-mL volumetric flask and fill it to the mark.
3. ***1.0 M $CuSO_4$:*** Dissolve 62.42 g of $CuSO_4 \cdot 5H_2O$ in some distilled water in a 250-mL volumetric flask and fill it to the mark.
4. ***1.0 M $AgNO_3$:*** Dissolve 42.46 g of $AgNO_3$ in some distilled water in a 250-mL volumetric flask and fill it to the mark.
5. ***1.0 M $Pb(NO_3)_2$:*** Dissolve 82.80 g of $Pb(NO_3)_2$ in some distilled water in a 250-mL volumetric flask and fill it to the mark.
6. ***1.0 M $NaNO_3$:*** Dissolve 85.00 g of $NaNO_3$ in some distilled water in a 250-mL volumetric flask and fill it to the mark.

Safety

Add these important safety precautions to your normal laboratory procedures:

- Dispose of solutions properly.
- Wear safety goggles throughout this experiment.
- In case of contact with skin, chemicals should be washed off with large amounts of water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Draw five small circles with connecting lines on a piece of circular filter paper (11-cm diameter), as shown in Figure 1. Label the circles M_1, M_2, M_3, M_4, and M_5.

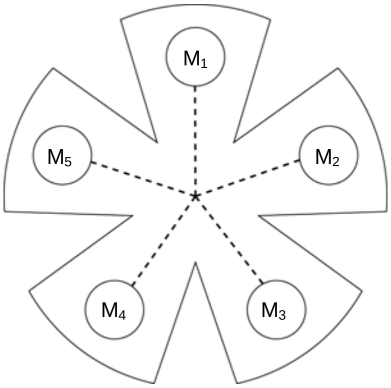


Figure 1: Filter paper diagram

2. Using a pair of scissors, cut wedges between the circles as shown.

3. Place the filter paper on top of the glass plate.

4. Obtain pieces of each of the five test metals. Sand each piece of metal on both sides so that a good electrical connection can be made.

5. Using a separate dropper for each solution, place three drops of each metal ion solution on the appropriate circle (M_1, M_2 etc.). Then, according to Table 2, place the corresponding piece of metal on the spot with its respective cation. The top side of the metal should be kept dry. These are the electrodes.

Table 2: Metals and salt solutions for setting up each half-cell

Material	**M_1**	**M_2**	**M_3**	**M_4**	**M_5**
Metal	Copper	Zinc	Lead	Silver	Iron
Salt Solution	Copper sulfate	Zinc sulfate	Lead nitrate	Silver nitrate	Iron sulfate

6. Based on the table above, complete Table 3a and 3b with your predictions of which metals will be oxidized and which ones reduced when coupled with copper. Provide the oxidation/reduction half-reaction for each metal and for the copper!

Table 3a: Predicted oxidation and reduction processes

Copper reduced	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
Other metals oxidized	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$

Table 3b: Predicted oxidation and reduction processes

Copper oxidized	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
Other metals reduced	$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$ $Ag^{+}(aq) + 2e^{-} \rightarrow Cu(s)$

7. Add enough 1.0 M sodium nitrate ($NaNO_3$) solution to make a continuous trail along a line drawn between each circle and the center of the filter paper. You may have to dampen the filter paper with more $NaNO_3$ during the experiment.

Note: The $NaNO_3$ trace is the liquid-to-liquid junction between the electrodes. Any two of the electrodes coupled represent a galvanic cell.

8. Why do you think the $NaNO_3$ solution is being used?

The $NaNO_3$ trace is the liquid-to-liquid junction between the electrodes. Any two of the electrodes coupled represent a galvanic cell. The $NaNO_3$ is the salt bridge that allows for ion flow between the electrodes.

Collect Data

Use M_1 (copper) as the reference metal. You will measure the potential of four cells by connecting M_1 to M_2 (copper to zinc), M_1 to M_3 (copper to lead), M_1 to M_4 (copper to silver), and M_1 to M_5 (copper to iron).

9. Start a new experiment on the data collection system. �(1.2)

10. Connect a voltage sensor to the data collection system. �(2.1)

11. Monitor live data without recording. �(6.1)

12. Touch the tip of the red (+) wire of the voltage sensor to one metal sample (for example, M_1) and the tip of the black (–) wire to the other metal sample (for example, M_2). If the voltage reading is below 0.00 V, reverse the ends of the voltage sensor, that is, switch the red (+) end of the sensor to M_2 and the black (–) end of the sensor to M_1.

13. When the voltage reading stabilizes, record the voltage for the half-cell (half-reaction) combination and the color of the lead, or clip that is touching each of the metals, in Table 4 in the Data Analysis section.

14. Use the same procedure to measure the potential of the other three "half cells" with copper, M_1, as the reference electrode.

Note: If you get a voltage reading of 0.00 V or a fluctuating reading, add more $NaNO_3$ solution along the lines connecting the metal spots.

15. Analyze your data for copper and make predictions about the other possible half-cell combinations using the same metals and solutions you used in this experiment.

Data Analysis

1. Complete the table below with your data. Use the Standard Reduction Potential table to calculate the expected potential difference between the two electrodes.

Note: *E* = (Potential of Cathode) – (Potential of Anode)

Table 4: Comparison of measured and calculated cell electromotive force

Half-cell Combination	Half-cell Standard Reduction Potential		Half-cell Standard Reduction Potential		Potential Using Standard Reduction Table	Measured Voltage
	Cathode (Red Wire) (+)	Voltage	Anode (Black Wire) (–)	Voltage		
M_1, M_2	M_1	0.34 V	M_2	–0.76 V	1.10 V	1.10 V
M_1, M_3	M_1	0.34 V	M_3	–0.13 V	0.47 V	0.47 V
M_1, M_4	M_4	0.80 V	M_1	0.34 V	0.46 V	0.45 V
M_1, M_5	M_1	0.34 V	M_5	–0.44 V	0.78 V	0.71 V

2. The red lead represents the cathode, where reduction takes place. The black lead represents the anode, where oxidation takes place. By arranging the clips so a positive voltage is obtained, you have determined that the metal at the red clip is more easily reduced than the one at the black clip.

Which metals were reduced by copper? Which metals oxidized copper?

Silver was reduced by copper and all other metals were oxidized by copper.

3. Based on your results, arrange the five metals (including copper, M_1) in order of reduction potential from the highest reduction potential at the top to the lowest reduction potential at the bottom.

(Hint: In relation to copper, a metal that has a higher reduction potential will result in a higher potential of the cell. The metals that reduced copper are more easily oxidized than copper, so their reduction potentials will be lower. Also, if a metal has a higher oxidation potential, it will have a lower reduction potential.)

Zinc, iron, lead, copper, silver

Analysis Questions

1. Which metal turned out to be the easiest to oxidize?

The easiest to oxidize was Zn.

2. Which metal was the most difficult to oxidize?

The most difficult to oxidize was silver.

3. Which electrode combination gave the most electromotive force?

The potential between the metal with the largest reduction potential and the metal with the smallest reduction potential gives the largest electromotive force. Therefore, the two metals are zinc and silver.

4. What is the cell diagram representation of a galvanic cell assembled from Zn^{2+}/Zn and Fe^{2+}/Fe?

Since zinc has more negative reduction potential than iron in the reduction potential series, iron will oxidize zinc which means iron will be the cathode (listed on the right) and zinc the anode (listed on the left):

$Zn(s) \,|\, Zn^{2+}(aq) \,||\, Fe^{2+}(aq) \,|\, Fe(s)$

Synthesis Questions

Use available resources to help you answer the following questions.

1. Can you think of any metal that is more difficult to oxidize than silver? What are the consequences of a metal being difficult to oxidize in terms of the properties of the metal?

Gold, platinum, and mercury have an even lower reduction potential than silver. The fact that a metal is hard to oxidize means that the metal form is more stable than the ion form of that specific metal. Metals that are hard to oxidize do not easily react, which is a common property of precious metals.

2. Do you think you would have obtained different potential readings if the nitrate salt of the metals would have been used instead of the sulfate salts?

No, the potential only depends on the redox properties of the metals.

3. If you were to assemble a Daniell cell from bigger pieces of copper and zinc, and light a light bulb by placing it between the two metals until the galvanic cell was depleted, what would happen to the pieces of copper and zinc?

Since the Cu^{2+} ions are reduced, some copper would be deposited on the surface of the copper electrode, and since the zinc is oxidized, some zinc would go into the solution and the piece of zinc would be smaller.

4. In lead acid batteries, which are used in cars to start the engine, the half-reactions for the two connected electrodes are:

$$\mathrm{PbO_2(s)} + 4\mathrm{H^+(aq)} + \mathrm{SO_4^{2-}(aq)} + 2e^- \rightarrow \mathrm{PbSO_4(s)} + 2\mathrm{H_2O} \qquad E_1 = +1.70\,\mathrm{V}$$

$$\mathrm{Pb^{2+}(aq)} + 2e^- \rightarrow \mathrm{Pb(s)} \qquad E_2 = -0.13\,\mathrm{V}$$

4a. Which electrode is the cathode and which is the anode? Explain your answer!

The redox potential is less for the second reaction. Therefore it will be the oxidation half-reaction which means the first reaction will be the reduction half-reaction. Since the cathode is where the reduction occurs, the first electrode will be the cathode and the second one will be the anode.

4b. What is the electromotive force of this cell?

The electromotive force of the galvanic cell will be, since the second reaction will be occurring in reverse:

$$E_{cell} = E_1 - E_2 = (+1.70\text{ V}) - (-0.13\text{ V}) = +1.83\text{ V}$$

It is worth mentioning that six of these cells are connected in series to provide the approximate 12 V that car batteries provide. Also, the process is reversible and goes backwards when the battery is being charged.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. In the Fe^{2+}/Fe and Cu^{2+}/Cu electrode pair:

- **A.** The Cu will be the anode
- **B.** The $CuSO_4$ solution will be the anode
- **C. The Cu will be the cathode**
- **D.** The $CuSO_4$ solution will be the cathode

2. The chemical reaction on the cathode is:

- **A.** The oxidation of the metal plate
- **B.** The reduction of the metal plate
- **C. Reduction of the metal ion**
- **D.** Oxidation of the metal ion

3. Copper could oxidize:

- **A.** All of the other four metals
- **B. All of the other metals except silver**
- **C.** All of the other metals except silver and lead
- **D.** Only zinc

4. A metal can oxidize any other metal that has a:

- **A.** More negative oxidation potential
- **B.** Less negative reduction potential
- **C.** More positive reduction potential
- **D. Less positive reduction potential**

Extended Inquiry Suggestions

An excellent demonstration of an electrochemical series is the method of preventing corrosion of steel structures:

Take two small sections of a steel or iron pipe. Connect a piece of zinc to one of them so there is an electrical connection between the zinc and the pipe. Place both sections of pipe into diluted (~0.01 M) HCl solution for one week.

What students should see is that the pipe without the zinc corrodes while the zinc pipe doesn't. Students should, however, also notice that the piece of zinc gets smaller. Steel structures do not corrode until there is no zinc present, therefore, the zinc plate has to be replaced periodically.

33. Electroplating

Objectives

Students construct an electrochemical cell that deposits copper onto another metal surface. They also apply Faraday's law to relate the total electric charge to the mass of metal deposited.

Procedural Overview

Students gain experience conducting the following procedures:

- Determining the change of mass of each electrode due to electroplating
- Comparing the experimental changes in mass at each electrode to the expected change in mass due to the total electrical charge, calculated using Faraday's law

Time Requirement

Preparation time	15 minutes
Pre-lab discussion and experiment	15 minutes
Lab experiment	120 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Voltage/current sensor
- DC power supply
- Banana plug cords, red (2) and black (1)
- Alligator clips, red (1) and black (1)
- Ring stand
- Clamps (2)
- Beaker, 100-mL
- Magnetic stir plate and stir bar
- Balance
- Metal object (key or spoon)
- Copper strip or heavy gauge copper wire (3 in)
- 1.0 M Copper sulfate ($CuSO_4$), 50 mL[1]
- Sand paper
- Electrical tape
- Paper towel, 1 sheet

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[1] To prepare the solution, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Redox reactions
- Redox potential
- Electrolytes
- Conductivity
- Molarity

Related Labs in This Guide

Labs conceptually related to this one include:

- Oxidation–Reduction Titration
- Determination of Electrochemical Series

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to your data collection system �(2.1)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Finding the area under a curve �(9.7)

Background

Electroplating is the process of coating an electrically conductive object with a layer of metal using an electric current. The process, also known as electrodeposition, is used to improve the appearance and increase hardness and corrosion resistance of the plated objects.

The cathode (article to be plated) in the electroplating cell is connected to the negative terminal of a direct current power supply. The anode is connected to the positive terminal of the power supply. The cathode and anode are immersed in an electrolyte, which is an electrically conductive ionic solution. When the power supply is turned on, the metal at the anode is oxidized from the 0 valence electron state to form positively charged cations. These cations migrate through the solution toward the negatively charged cathode. At the cathode, the cations are reduced and are deposited in their metallic, 0 valence electron state onto the surface of the cathode.

The electricity generated by the moving electrons can be measured as a rate of electric current flow in amperes, A. An ampere is equal to 1 coulomb, C, of charge per second. You can calculate the total amount of charge Q in coulombs by multiplying the current flow I by the amount of time t the current is flowing:

$$Q = It$$

1 mol of a metal with +1 charge requires 96,485 C to be reduced to neutral state:

$$F = (1.6 \times 10^{-19}\ \text{C})\left(6.02 \times 10^{23}\ \frac{1}{\text{mol}}\right) = 96,485\ \frac{\text{C}}{\text{mol}}$$

where:

F = Faraday's constant (96,485 C/mol)

1.6×10^{-19} C = the charge of one electron

$6.02 \times 10^{23}\ \text{mol}^{-1}$ = Avogadro's number

The relationship between the charge that passes through the solution and the amount of metal ion (in our case Cu^{2+} ion) neutralized is

$$It = zF\frac{m}{\text{AW}}$$

$$m = \frac{It\,\text{AW}}{zF}$$

where:

m = mass of neutralized ion or deposited metal (g)

I = current (A)

t = time of electroplating (s)

AW = molar mass of copper (g/mol)

z = charge of copper (+2)

F = Faraday constant (96,485 C)

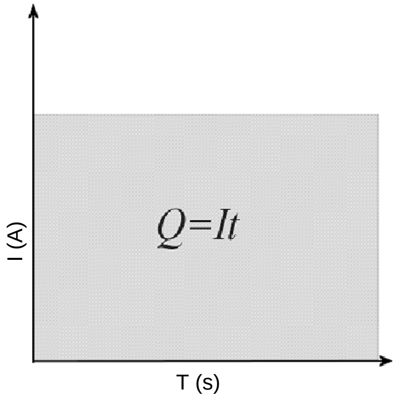
Pre-Lab Experiment

Setting the stage for the experiment

Students will assemble an electroplating cell from $CuSO_4$ solution, a key or spoon, and a piece of copper strip. The key or spoon will be connected to the negative terminal of the power supply (the cathode). The positive terminal of the power supply will be connected to the positive terminal of the current sensor. The negative terminal of the current sensor will be connected to the copper plate.

The two metal objects will then be immersed in the $CuSO_4$ solution. The flow of electrons moves from the negative to the positive terminal of the power supply. From the negative terminal, the electrons flow to the surface of the key or spoon where they get picked up by the Cu^{2+} ions and the neutralized copper is deposited onto the surface of the object. On the other electrode, copper atoms lose two electrons and go into solution as Cu^{2+} ions. The electrons left by the copper ions flow back into the power supply.

The current and the time of the electroplating will be monitored with a current sensor.



Total charge is shown as the area of current × time

The total charge used for electroplating can be calculated as the product of the current and time. This is the area shown on the graph of current versus time. If the current is kept constant, the total charge is simply the area of a rectangle. If the current is inconsistent, determine the area under the line using the area tool from the data collection system.

Example calculation to try

The mass of a silver spoon was measured and found to be 15.456 g. It was mounted in an electroplating cell as the cathode. A piece of copper strip (4.556 g) was mounted as the anode. The cell was filled with 1 M $CuSO_4$ solution. Wiring was completed from the negative terminal of the power supply to the spoon, from the copper plate to the negative terminal of a current sensor, and from the positive terminal of the current sensor to the positive terminal of the power supply.

The power supply was turned on and the current was maintained at 1.1 A for 30 min. The spoon was then removed, washed and dried. The mass of the spoon was found to be 16.066 g. The copper strip was washed and dried, and was found to be 4.010 g. This indicates that 0.546 g of copper dissolved:

$$4.556\text{ g} - 4.010\text{ g} = 0.546\text{ g}$$

The charge that passed through the cell was

$$Q = It = (1.1\ \text{A})(1{,}800\ \text{s}) = 1{,}980\ \text{A s} = 1{,}980\ \text{C}$$

The mass of copper equivalent to the total charge that passed through the cell is

$$m = \frac{It\,\text{AW}}{zF} = \frac{(1.1\ \text{A})(1{,}800\ \text{s})(63.55\ \frac{\text{g}}{\text{mol}}\ \text{Cu})}{(2)(96{,}485\ \frac{\text{A s}}{\text{mol}})} = 0.652\ \text{g Cu}$$

The actual amount of deposited copper was

16.066 g – 15.456 g = 0.610 g

Table 1: Compare the theoretical and actual amounts of copper deposited

	Electroplated Object	**Copper Strip**
Original mass (g)	15.456	4.556
Mass after electroplating (g)	16.066	4.010
Change of mass (g)	+0.610	–0.546
Theoretical change of mass (g)	0.652	–0.652
Yield (%)*	93.5	83.7

*The percent yield compares the experimental to the theoretical amount of copper deposited or dissolved.

1. Do you think it matters how much of the surface of the metal objects is in contact with the solution and if so, why?

More ions interact with the surface of the electrode when a greater surface area contacts the solution within a certain amount time, producing a larger current.

2. Why do you think the experimental quantity is less than the theoretical?

Due to the electrical resistance of the solution and secondary chemical processes, the utilization of the electricity is less than 100%.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***1.0 M $CuSO_4$:*** Dissolve 62.42 g of $CuSO_4 \cdot 5H_2O$ in some distilled water in a 250-mL volumetric flask and fill it to the mark.

Safety

Add this important safety precaution to your normal laboratory procedures:

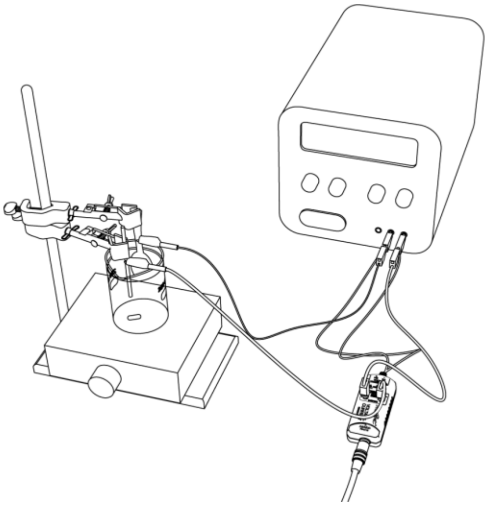
- In case of contact with skin, $CuSO_4$ solution should be washed off with large amounts water.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Place the beaker containing the copper sulfate solution on a magnetic stir plate and add a magnetic stirring bar.



2. Start a new experiment on the data collection system. �(1.2)

3. Connect a voltage/current sensor to the data collection system. �(2.1)

4. Carefully clean and dry the copper wire and spoon or key with steel wool.

5. Obtain the mass of the wire and spoon or key to the nearest 0.001 g and record the mass in Table 3.

6. Use a red alligator clip to attach one end of the red banana plug patch cord to one end of the heavy gauge copper wire.

7. Use a black alligator clip to attach one end of the black banana plug patch cord to the end of the handle of the metal spoon or key.

8. Wrap electrical tape around the spoon or key and copper wire near one end to provide insulation. Mount clamps on a support rod and clamp the wire and spoon or key in place by the insulated portion.

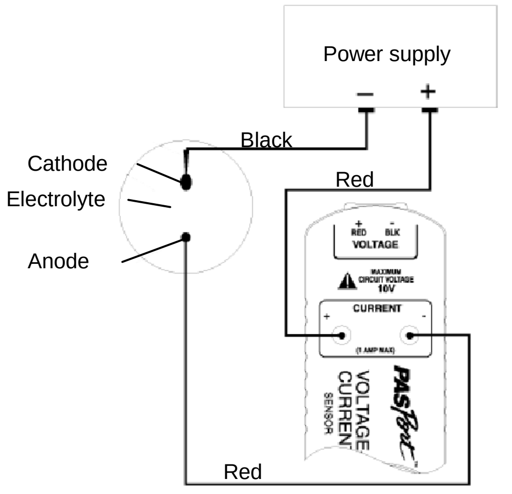
9. Position the end of the heavy gauge copper wire and the spoon or key so that they are immersed in the solution in the beaker.

10. Plug the black patch cord from the spoon or key into the negative (black) terminal of the power supply.

11. Connect the red patch cord from the positive (red) terminal of the power supply to the positive (+) jack on the current input of the voltage/current sensor.

12. Connect the red patch cord connected to the heavy gauge copper wire to the negative (–) jack on the voltage/current sensor.

Note: The Voltage Sensor leads are not used during this experiment.



Circuit diagram

13. What would the consequences be if you switched the leads on the power supply?

Switching the leads on the power supply would reverse the sign of the current and therefore the electroplating process would be reversed: the spoon or key would dissolve while copper would be deposited on the surface of the copper plate.

Collect Data

14. Display current on the y-axis of a graph with time on the x-axis. �$^{(7.1.1)}$

15. Start data recording. �$^{(6.2)}$

16. Turn on the power supply and adjust the current and voltage until the current reads 0.2 A.

17. Adjust the magnetic stirrer to achieve a reasonable amount of mixing; be sure to avoid splashing. Make sure the stir bar does not hit either of the electrodes.

18. Run the electroplating process for at least an hour, but no longer than two.

19. Stop the data recording�$^{(6.2)}$ and turn off the power supply.

20. Find the area under the Current versus Time curve. �$^{(9.7)}$ Record the value, in coulombs, in Table 2.

21. Carefully remove the metal spoon or key and the copper wire, very carefully rinse it with distilled water, and place them on a paper towel. Gently blot and air dry the spoon or key and the wire.

Note: Do not rub the surface of the spoon or key as the deposited copper is loosely attached to the surface.

22. Measure again the mass of the copper wire and metal spoon or key to the nearest 0.001 g and record these values in Table 3.

Data Analysis

1. Calculate the mass of copper equivalent to the total charge (area under *I* versus *t* curve) that passed through the cell and enter it in Table 2.

$$Q = It = (0.210\ \text{A})(4637\ \text{s}) = 974\ \text{A s} = 9.74 \times 10^{2}\ \text{C}$$

$$m = \frac{It\,\text{AW}}{zF} = \frac{(0.210\ \text{A})(4637\ \text{s})(63.55\ \frac{\text{g}}{\text{mol}}\ \text{Cu})}{(2)(96{,}485\ \frac{\text{A s}}{\text{mol}})} = 0.321\,\text{g Cu}$$

Table 2: Theoretical amount of copper deposited due to the total charge

Parameters	Calculated Values
Total charge (area under *I* versus *t* curve)(C):	974
Theoretical amount of Cu deposited (g):	0.321

2. Complete Table 3. Calculate the percent yield based on the theoretical and experimental amount of copper deposited.

The actual amount of deposited copper was: 13.996 g – 13.685 g = 0.311 g

The amount of dissolved copper was: 13.736 g – 13.422 g = 0.314 g

Table 3: Compare the theoretical and actual amounts of copper deposited and dissolved

	Electroplated Object	**Copper Strip**
Original mass (g)	13.685	13.736
Mass after electroplating (g)	13.996	13.422
Change of mass (g)	+ 0.311	– 0.314
Theoretical change of mass (g)	0.321	– 0.321
Yield (%)*	96.9	97.8

*The percent yield compares the experimental to the theoretical amount of copper.

3. Calculate the percent yield of copper deposited and copper dissolved.

The percent yield of copper deposited is:

$$\frac{\text{0.311 g of copper (experimental)}}{\text{0.321 g of copper (theoretical)}} \times 100 = 96.9\%$$

The percent yield of copper dissolved is:

$$\frac{\text{0.314 g of copper (experimental)}}{\text{0.321 g of copper (theoretical)}} \times 100 = 97.8\%$$

Analysis Questions

1. Propose an explanation for the less than 100 % yield.

The solution has some electrical resistance. Therefore, some of the charge was lost to the solution.

2. Was the amount of copper lost from the copper wire the same as the amount of copper gained on the metal object? If not, propose an explanation. (Hint: what other ions can migrate to the anode and what reaction can they become part of?)

The loss of copper from the wire was slightly greater than the gain of copper on the metal object. Some of the charge could have been used for other reactions, like the oxidation of the OH^- ions which are present inherently from the dissociation of the water molecules:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

3. The color of the deposited copper is slightly different from the original color of the object. (Hint: Consider the difference between the particle size in the original object and the deposited copper)

In the copper strip, the copper is "molded," while the deposited copper is formed from atomic-sized copper atoms. The different particle size results in different color.

4. Earlier we identified one parameter that could change the current. Can you think of changing another parameter of the cell (that is, the two metal electrodes, the solution, or the beaker) that can potentially increase the current? (Hint: reducing the electrical resistance of the solution would increase the current)

Moving the electrodes closer reduces the electrical resistance of the solution.

Synthesis Questions

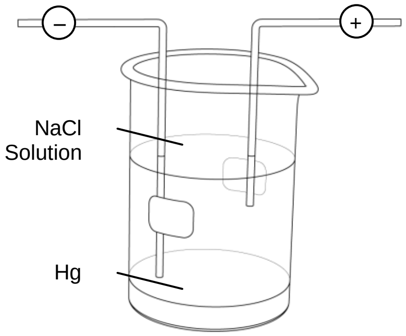
Use available resources to help you answer the following questions.

1. Can you propose a setup to silver plate a spoon?

The same cell configuration with a silver strip instead of a copper strip and the object to be silver plated mounted in the place of the copper object with $AgNO_3$ solution in the cell.

2. Electrolysis is a commonly used industrial technique. The diagram of the cell below shows how NaOH is produced by the electrolysis of NaCl solution. Mercury is used to promote the reduction of Na^+ ions on the cathode (–) in the form of Na^0. The neutral sodium will then dissolve in mercury as NaHg (called sodium amalgam).

Hydrolysis of NaHg yields the desired NaOH solution. What do you think is happening on the anode during the electrolysis? (Hint: what anions could get oxidized in the NaCl solution?)



Of the two anions, OH^- and Cl^-, the Cl^- ion gets oxidized to form chlorine gas: $2Cl^- \rightarrow Cl_2 + 2e^-$

3. All components of hot rods and Harley Davidson bikes that have a shiny chrome "finish" are made using electroplating. Are those components mounted as anodes or cathodes in the electroplating cells?

They are located in place of the copper object which was the cathode.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Copper on the anode will:

- **A.** Get reduced.
- **B. Get oxidized.**
- **C.** Not react. It will only get reduced on the cathode to form the copper deposit.
- **D.** Not react. It will only get oxidized on the cathode to form the copper deposit.

2. If you mount an iron object instead of a copper one as the cathode, with the copper strip as the anode:

- **A.** The copper won't be deposited on the surface of the iron object.
- **B.** The iron object will dissolve.
- **C. The copper will be deposited on the iron object the same way as on the surface of a copper object.**
- **D.** There will be no redox reaction as the metal for a Cu/Cu^{2+} electrode is missing.

3. Using $Cu(NO_3)_2$ instead of $CuSO_4$:

- **A.** Will result in a different anode reaction and prevent the copper from being deposited.
- **B.** Will result in a different cathode reaction and prevent the copper from being deposited.
- **C.** Will result in forming $(NO_3)_2$ gas on the anode.
- **D. Will not make a difference in the process of copper deposition on the cathode.**

4. Changing the concentration of the solution will:

- **A.** Prevent the deposition of copper on the cathode.
- **B.** Prevent the reduction of copper on the electrode.
- **C. Influence the electrical resistance of the solution and, therefore, the efficiency of the electrolysis.**
- **D.** Not make any difference.

Extended Inquiry Suggestions

Have students apply electro-oxidation (also called “anodizing”) to an aluminum object. Electro-oxidation is commonly used as a method to colorize aluminum objects. The process is based on the fact that aluminum objects are covered and protected by a thin oxide layer. Mounting the aluminum object as an anode exposes the aluminum object to the process:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

In this process, atomic oxygen is formed first. This is a very strong oxidant (the same as ozone). Atomic oxygen can oxidize aluminum in a special way. If the oxidation is taking place in a solution that is colored, due to the oxidation by atomic oxygen, the color of the solution becomes embedded in the porous surface of the aluminum metal. For example, for orange color, $K_2Cr_2O_7$ solution is commonly used. It is quite intriguing to electrolyze an aluminum object in a $K_2Cr_2O_7$ solution to turn the object orange. The object would have to be mounted as the anode (+). Take appropriate safety precautions when handling potassium dichromate.

34. The Breathalyzer™ Test for Alcohol

Objectives

Students understand the chemical oxidation of ethanol by acidic dichromate, as used in Breathalyzer tests for alcohol, and determine the concentration of an ethanol solution.

Procedural Overview

Students gain experience conducting the following procedures:

- Carrying out a reaction between ethanol and potassium chromate that uses a catalyst and hot water bath to increase the rate of reaction
- Developing a calibration curve using spectroscopic measurements to use for calculating the concentration of an ethanol solution
- Advanced preparation of solutions

Time Requirement

♦ Preparation time	60 minutes
♦ Pre-lab discussion and experiment	30 minutes
♦ Lab experiment	90 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Colorimeter
- Cuvette
- Sensor extension cable
- Erlenmeyer flask (7), 125-mL
- Volumetric flask, 100-mL
- Graduated pipet, 10-mL
- Graduated pipet, 5-mL
- Pipet, plastic, 1-mL
- Graduated cylinder, 100-mL
- Beaker (2), 25-mL
- Beaker, 100-mL
- Beaker (2), 400-mL
- Beaker, 250-mL
- Beaker, 1-L
- Ring stand
- Clamps (2), utility
- Hot plate
- 15% Sulfuric acid (H_2SO_4), 800 mL[1]
- Silver nitrate ($AgNO_3$), 15%,10 mL[2]
- 5.10×10^{-2} M Potassium dichromate ($K_2Cr_2O_7$), 30 mL[3]
- Ethanol solution, unknown concentration, 5 mL[4]
- Marking pen
- Wash bottle with distilled water

[1-4] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Stoichiometry
- Oxidation-reduction reactions
- Beer's Law

Related Labs in This Guide

Labs conceptually related to this one include:

- Determine the Equilibrium Constant for a Chemical Reaction
- Absorption Spectra
- Colorimetric Analysis
- Order of Reactions

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting sensors to the data collection system �(2.1)
- Calibrating the colorimeter �(3.2)
- Putting the data collection system into manual sampling mode with manually entered data �(5.2.1)
- Monitoring live data without recording �(6.1)
- Starting a manually sampled new data set �(6.3.1)
- Recording a manually sampled data point �(6.3.2)
- Stopping a manually sampled data set �(6.3.3)
- Applying a curve fit �(6.3)
- Printing �(11.2)

Background

Modern breath analyzers rely on infrared spectroscopy or fuel cell technology (electrochemical oxidation) to measure alcohol content in exhaled air. This was not always the case. The first commercial instrument for estimating a person's blood alcohol content (BAC) by analyzing a breath sample was introduced in 1954 by Dr. Robert Borkenstein. Named the "Breathalyzer," its operation was based on oxidation-reduction (redox) chemistry and absorption photometry. This experiment explores the chemical reaction used in the original breathalyzer.

Ethanol (ethyl alcohol) can be oxidized to acetic acid by dichromate as shown in the following equation:

$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H_3O^+ \rightarrow 4Cr^{3+} + 3CH_3COOH + 27H_2O$$

Because the reaction is fairly slow, silver nitrate is added as a catalyst to reduce reaction time.

As ethanol is oxidized, the yellow-orange dichromate ion is reduced to the chromium(III) ion, which is green. Beer's law can be applied to find the concentration of dichromate. We will be using a colorimeter to measure the light absorbance of the solution. To calculate the quantity of ethanol in the unknown, the concentration of dichromate remaining in a solution with a known initial quantity of dichromate reacted with an unknown quantity of ethanol can be used.

Pre-Lab Experiment

Setting the stage for the experiment

In this experiment, you will prepare five solutions with known $Cr_2O_7^{2-}$ concentrations. Using a colorimeter, you will obtain a calibration curve for the five solutions. You will then prepare two solutions with unknown ethanol concentrations and allow the $Cr_2O_7^{2-}$ ions to react with the ethanol in a hot water bath. The concentration of the remaining $Cr_2O_7^{2-}$ ions will be determined with the colorimeter based on the calibration curve.

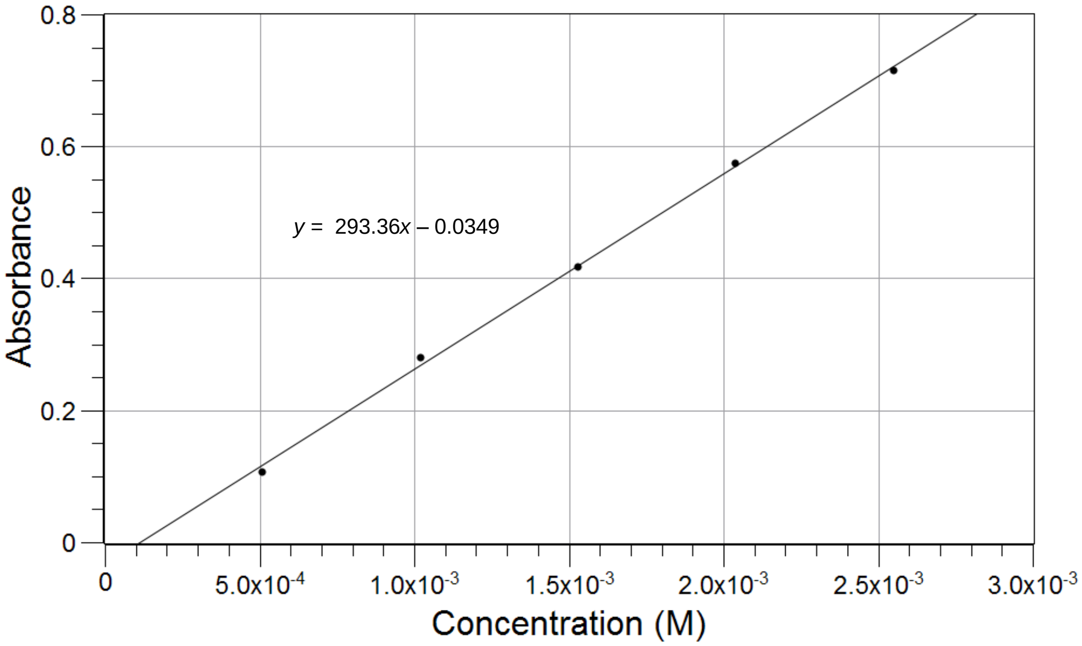
Example calculation to try

In an experiment, the alcohol content of cognac, an alcohol-containing beverage, was determined. 12.00 mL of the cognac sample was diluted to 1 liter as a stock solution. From this stock solution, two unknown solutions were prepared in two 100-mL volumetric flasks as follows:

About 50 mL of 15% H_2SO_4 solution were added to both flasks followed by 5.00 mL of 5.10×10^{-2} M $Cr_2O_7^{2-}$ and then 1.00 mL of 150 g/L $AgNO_3$ solution. There was some light precipitation that disappeared as the solution was mixed.

To the first unknown solution ("Unknown A"), 1.00 mL of the alcohol stock solution was added. To the second unknown solution ("Unknown B"), 2.00 mL of the alcohol stock solution was added. Both flasks were filled to the mark with 15% H_2SO_4. Both solutions were transferred into 125-mL Erlenmeyer flasks and placed in a 75 °C water bath for 45 min.

While the unknowns were in the water bath, five calibrating solutions were made. Each solution was made in a volumetric flask the same way as the unknowns, except there was no alcohol stock added and the amount of $Cr_2O_7^{2-}$ solution varied: 1.00 mL, 2.00 mL, 3.00 mL, 4.00 mL, and 5.00 mL. The following calibration curve was obtained using a colorimeter:



The unknowns were removed from the bath, cooled, and their absorbance measured and recorded in Table 1.

Table 1: Absorbance of the unknown solutions

Solution	**A**
Unknown A	0.577
Unknown B	0.407

Based on the calibrating equation derived from the slope and y-intercept of the graph, the concentration of the remaining $Cr_2O_7^{2-}$ ions is calculated for Unknown A:

$$y = 296.36x - 0.0349$$

$$x = \frac{y + 0.0349}{296.36}$$

$$\frac{(0.577 + 0.0349)}{296.36\ \text{M}^{-1}} = 2.06 \times 10^{-3}\ \text{M}$$

For Unknown B, 1.49×10^{-3} M was obtained the same way.

The original concentration of $Cr_2O_7^{2-}$ ions in both solutions was:

$$\left(\frac{5.00\ \text{mL}}{100.00\ \text{mL}}\right)\left(5.10 \times 10^{-2}\ \text{M}\right) = 2.55 \times 10^{-3}\ \text{M}$$

The concentration of the $Cr_2O_7^{2-}$ ions that reacted with the ethanol in Unknown A is:

$$\left(2.55 \times 10^{-3}\ \text{M}\right) - \left(2.06 \times 10^{-3}\ \text{M}\right) = \left(4.90 \times 10^{-4}\ \text{M}\right)$$

Using the same calculation, Unknown B was 1.06×10^{-3} M. Knowing the amount of $Cr_2O_7^{2-}$ ions used, based on the stoichiometry, the concentration of the alcohol can be calculated:

$$\left(4.90 \times 10^{-4}\ \text{M}\ Cr_2O_7^{2-}\right)\left(\frac{3\ \text{mol}\ C_2H_5OH}{2\ \text{mol}\ Cr_2O_7^{2-}}\right) = 7.35 \times 10^{-4}\ \text{M}\ C_2H_5OH$$

Using the same calculation for Unknown B, 1.59×10^{-3} M ethanol was obtained. Since the concentrations are 7.35×10^{-4} M and 1.59×10^{-3} M, there is 7.35×10^{-3} mol and 1.59×10^{-2} mol of ethanol, respectively in the 100 mL stock solutions. The amount of ethanol in grams can be calculated from its concentration and its formula weight, 46. g/mol:

$$\left(7.35 \times 10^{-3}\ \text{mol}\ C_2H_5OH\right)\left(\frac{46\ \text{g}\ C_2H_5OH}{1\ \text{mol}\ C_2H_5OH}\right) = 3.38 \times 10^{-3}\ \text{g}\ C_2H_5OH$$

This means there was 3.38×10^{-3} g of ethanol in the 100-mL solution. Considering that this amount of ethanol was in the 1.00 mL of stock solution that was used to make the 100-mL solution, the original 1-liter stock solution had 3.38 g of ethanol. That amount of ethanol was in the 12.00 mL original alcohol. The density of ethanol is 0.800 g/mL, the ethanol concentration of the original alcohol is:

$$\frac{3.38\ \text{g}}{\left(12.00\ \text{mL}\right)\left(0.800\ \frac{\text{g}}{\text{mL}}\right)} \times 100 = 35.2\%$$

Using the same type of calculation for Unknown B, 38.1% ethanol was obtained.

1. Which color do you think has to be used with the colorimeter if we know that the color of the $Cr_2O_7^{2-}$ solution is yellow?

According to the color chart, the yellow color comes from the mix of red and green. This means mostly blue is absorbed from the light. Monitoring the "blue" trace seems to be the most appropriate.

2. The remaining $Cr_2O_7^{2-}$ concentration, after the reaction, was appropriate because it fell approximately in the middle of the calibration curve. However, if you had a sample which had ten times less ethanol, the concentration of $Cr_2O_7^{2-}$ ions would have been outside of the calibration curve. How would you change the experiment to account for such a change in the ethanol concentration?

Ten times more of the original alcohol solution (120.0 mL instead of 12.00 mL) or ten times more stock solution (10.00 mL instead of 1.00 mL) would have had to be used.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***15% H_2SO_4:*** Dissolve 150 mL of concentrated H_2SO_4 in some water in a 1-L volumetric flask and fill it to the mark. Please note each group needs about 800 mL. Scale accordingly.
2. ***15% $AgNO_3$:*** Dissolve 15.0 g of $AgNO_3$ in 100 mL water.
3. ***5.10×10^{-2} M K_2CrO_7:*** Dissolve 15.0 g of K_2CrO_7 in about 300 mL of water in a 1-L Erlenmeyer flask. Slowly add 300 mL of concentrated H_2SO_4. Allow the solution to cool to room temperature.

   Transfer the solution into a 1-L volumetric flask and fill it to the mark with water. Mix the solution well.

   DANGER: Wear a NIOSH-approved respirator with proper cartridges when obtaining the mass of dry $K_2Cr_2O_7$. $K_2Cr_2O_7$ is a known carcinogen and can be fatal if absorbed through the skin. Use gloves to handle this chemical.

4. ***Ethanol, unknown concentration:*** Combine 5.0 mL of ethanol with some water in a 1-L volumetric flask and fill it to the mark.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Obtain about 30 mL of 5.10×10^{-2} M standard potassium dichromate stock solution in a 100-mL beaker. Record the exact concentration of the dichromate solution in Table 3.

2. Put 5 mL of the ethanol solution of unknown concentration in a 25-mL beaker. Obtain about 800 mL of 15% sulfuric acid solution in a 1-L beaker and 6 mL of silver nitrate solution in a 25-mL beaker.

Note: The use of gloves is recommended. If you get silver nitrate on your skin, wash it off immediately with plenty of water as it leaves black stain on the skin.

3. Label five 125-mL Erlenmeyer flasks from “1 mL” to “5 mL”.

4. Label the other two flasks “Unknown A” and “Unknown B”.

5. Fill the two 400-mL beakers 3/4 full of water.

6. Place the beakers on the hot plate and turn it on to maintain the temperature of the water baths between 75 °C and 80 °C.

Prepare the ethanol test solutions

7. Using a 10-mL graduated pipet, transfer 5.0 mL of the potassium dichromate solution to a 100-mL volumetric flask.

8. Fill the flask about half full with 15% H_2SO_4.

9. Mix the solution by swirling.

10. Using a plastic pipet, add about 1 mL of silver nitrate solution to the flask and mix the solution again.

Note: If any white precipitate is visible, stopper the flask and shake the solution until the precipitate dissolves.

11. Using a 5-mL graduated pipet, transfer 1.0 mL of the ethanol solution to the volumetric flask with the solution prepared in the previous step and swirl it to mix.

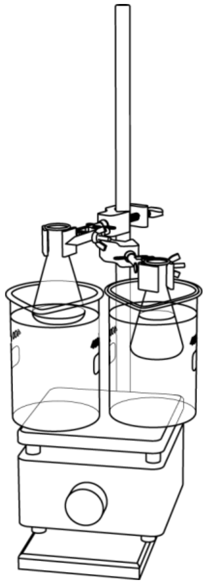
12. Fill the flask to the calibration mark with 15% H_2SO_4.

13. Stopper the flask and mix the solution by inverting the flask several times.

14. Transfer this solution to the flask marked "Unknown A".

15. Using the ring stand and one of the clamps, place the flask containing the unknown into a water bath, being careful to avoid getting water from the bath in the flask.

16. Rinse the volumetric flask thoroughly with distilled water and repeat the procedure using 2.0 mL of the same ethanol solution.



17. Transfer the resulting solution to the flask marked "Unknown B" and use the clamp to place it in the second hot-water bath.

18. Why do you prepare two unknown solutions?

In order to reduce experimental error, multiple measurements are taken.

19. What is the advantage of making the concentration of the unknowns different?

Since we do not know the actual concentration of ethanol, having two samples with significantly different concentrations help in the situation when one concentration turns out to be way off, for example, too much ethanol and not enough $Cr_2O_7^{2-}$.

20. Leave the unknown solutions in the water baths for 45 minutes, then remove the flasks from the water baths and allow them to cool to room temperature.

Prepare the standardized solutions

21. While the unknown solutions are in the water baths, prepare a set of standard solutions:

- **a.** Using a 10-mL graduated pipet, transfer 1.0 mL of the dichromate solution to a rinsed, 100-mL volumetric flask.
- **b.** Using a plastic pipet, add about 1 mL of silver nitrate solution to the flask and mix.
- **c.** Fill the flask about half full with 15% H_2SO_4 solution and mix well, being sure that any white precipitate is dissolved.
- **d.** Fill the volumetric flask to the calibration mark with additional 15% H_2SO_4 solution.
- **e.** Mix well and transfer the solution from the volumetric flask to the flask labeled "1 mL".
- **f.** Rinse the volumetric flask thoroughly with distilled water and prepare a new solution following the same steps but this time adding 2.0 mL of dichromate solution.
- **g.** Follow the same procedure to prepare solutions containing 3.0 mL, 4.0 mL and 5.0 mL of dichromate solution.

22. Based on the concentration of the stock dichromate solution, calculate the concentration of the five standard solutions and record the values in Table 2.

For the solution that was made with the 1.0 mL standard:

$$\left(\frac{1.0\ \text{mL}}{100.00\ \text{mL}}\right)\left(5.1 \times 10^{-2}\ \text{M}\right) = 5.1 \times 10^{-4}\ \text{M}$$

Table 2: Potassium dichromate concentration in 100 mL of standardized solutions

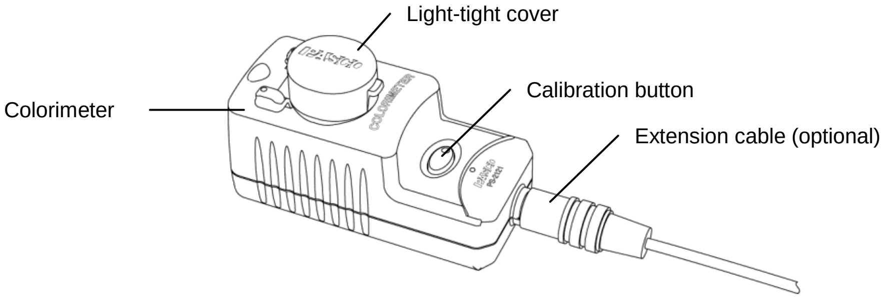
Volume of $Cr_2O_7^{2-}$ Standard (mL)	Final Concentration (M)
1.0	5.1×10^{-4} M
2.0	1.0×10^{-3} M
3.0	1.5×10^{-3} M
4.0	2.0×10^{-3} M
5.0	2.5×10^{-3} M

23. Start a new experiment on the data collection system. �(1.2)

24. Connect the colorimeter to the data collection system using a sensor extension cable. �(2.1)

25. Configure the data collection system to manually collect absorbance of blue (468 nm) light and the concentration of dichromate in a table. Define the concentration as a manually entered data set with units of units of mol/L. �(5.2.1)

26. Calibrate the colorimeter using 15% sulfuric acid as a blank. �(3.2)



Important: Always make sure that the cuvette is clean and dry on the outside before placing it into the colorimeter.

27. Start a new, manually sampled data set. �(6.3.1)

Collect Data

Obtain the calibration curve

28. Measure the absorbance of the five standardized solutions, starting with the one labeled "1 mL" and ending with the one labeled "5 mL", following the steps below.

a. Rinse the cuvette twice with a small portion of the first solution and then fill the cuvette two-thirds full. Wipe the cuvette clean and dry and place it into the colorimeter.

b. Why do you have to rinse the cell with some of the solution?

If there is any residual water in the cuvette, it will dilute the concentration of the solution and falsify the data.

c. After the reading stabilizes, record a data point. �(6.3.2)

d. Dispose of the solution appropriately and rinse the cell thoroughly with water.

e. Why do you think it is important to rinse the cell thoroughly between measurements?

You need to rinse the cell to avoid contamination of the solutions.

f. Stop the data set. �(6.3.3)

29. Why did you have to prepare multiple calibrating solutions?

Calibration is usually done to measure the response of an instrument to the variation of an experimental parameter over a range of that parameter. In this case, you measure the response of the colorimeter over a concentration range of the $Cr_2O_7^{2-}$. Also, having multiple points that reflect the relationship between the signal and the varied parameter helps minimize the experimental error.

30. Create a graph to display Concentration on the x-axis and Absorbance on the y-axis. �(7.1.1)

31. Adjust the scale of the graph to show all data. �(7.1.2)

32. Find the slope of the best-fit line. �(9.6)

33. Print the graph. �(11.2)

34. Set the data collection system to monitor live data without recording. �(6.1)

Measure the absorbance of the unknowns

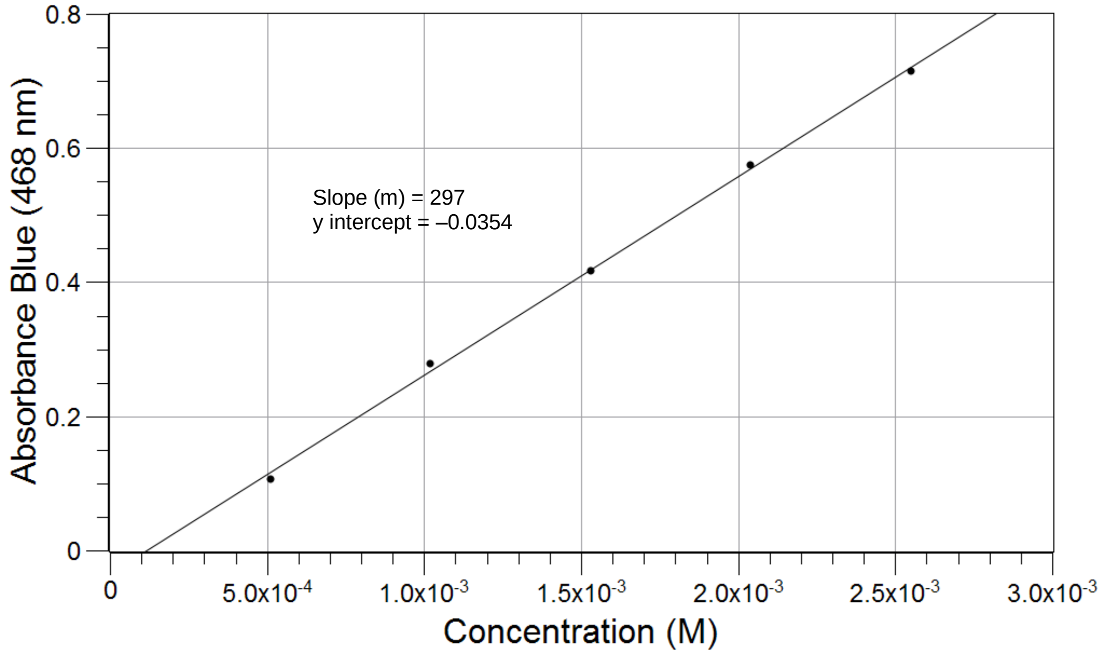
35. Obtain the absorbance of Unknown A and then Unknown B as follows:

- **a.** Clean the cuvette and then rinse it with the cooled solution, then fill the cuvette with the solution.
- **b.** Place the cell into the colorimeter and record the value in Table 3.

36. Save your experiment �(11.1) and clean up according to your instructor's instructions.

Data Analysis

1. Sketch or paste the calibration curve below and record the slope and y-intercept on the graph.



2. Calculate the initial concentration of $Cr_2O_7^{2-}$ in the reaction flask. Record this value in Table 3.

$$\left(\frac{5.00\text{ mL}}{100.00\text{ mL}}\right)\left(5.10 \times 10^{-2}\text{ M}\right) = 2.55 \times 10^{-3}\text{ M}$$

3. What is the calibrating equation for this calibration curve?

The calibrating equation is: $y = 297x - 0.0354$

4. Based on the calibrating equation, calculate the concentration of the remaining $Cr_2O_7^{2-}$ ions for Unknown A and Unknown B. Record these values in Table 3.

For Unknown A, y = 0.567, so solving for the $Cr_2O_7^{2-}$ ion concentration x results in

$$\frac{(0.567 + 0.0354)}{297\text{ M}^{-1}} = 2.03 \times 10^{-3}\text{ M}$$

5. Calculate the concentration of the $Cr_2O_7^{2-}$ ions that reacted with the ethanol for Unknown A and Unknown B. Record these values in Table 3.

For Unknown A:

$$\left(2.55 \times 10^{-3}\text{ M}\right) - \left(2.03 \times 10^{-3}\text{ M}\right) = 5.2 \times 10^{-4}\text{ M}$$

6. Knowing how much of the $Cr_2O_7^{2-}$ ions was used, based on the stoichiometry calculate the concentration o f the alcohol solutions labeled “Unknown A” and “Unknown B”.

Also determine the amount of ethanol in the 100-mL solution. Record these values in Table 3.

For Unknown A:

$$\left(5.20 \times 10^{-4}\text{ M }Cr_2O_7^{2-}\right)\left(\frac{3\text{ mol }C_2H_5OH}{2\text{ mol }Cr_2O_7^{2-}}\right) = 7.80 \times 10^{-4}\text{ M }C_2H_5OH$$

$$\left(7.80 \times 10^{-4}\,\frac{\text{mol}}{\text{L}}\;C_2H_5OH\right) \times \left(0.100\text{ L}\right) = 7.80 \times 10^{-5}\text{ mol }C_2H_5OH$$

7. Determine the mass of ethanol added to the unknown solutions, the mass of ethanol in the 100-mL stock solution, and calculate the average of the mass of ethanol in the 100-mL stock solution for the two unknown solutions. Record your data in Table 3.

For Unknown A. the mass of ethanol that had been added to the unknown solution is

$$\left(7.80 \times 10^{-5}\text{ mol }C_2H_5OH\right)\left(\frac{46.1\text{ g }C_2H_5OH}{1\text{ mol }C_2H_5OH}\right) = 3.60 \times 10^{-3}\text{ g }C_2H_5OH$$

This was the amount in 1 mL of the stock solution, so the mass of ethanol in the 1-L stock solution is $(3.60 \times 10^{-3}\text{ g/mL}) \times (1000\text{ mL/L}) = 3.60\text{ g }C_2H_5OH$. The average is (3.60 g + 3.36 g)/2 = 3.48 g.

Table 3: Determination of the amount of ethanol in the two solutions

Parameters	Unknown A	Unknown B
Initial concentration of $Cr_2O_7^{2-}$ (M) in the 1-L stock solution	5.10×10^{-2}	
Initial concentration of $Cr_2O_7^{2-}$in the reaction flask (M)	2.55×10^{-3}	
Absorbance	0.567	0.435
Remaining concentration of $Cr_2O_7^{2-}$ (M)	2.03×10^{-3}	1.58×10^{-3}
Amount of $Cr_2O_7^{2-}$ reacted with ethanol (M)	5.20×10^{-4}	9.70×10^{-4}
Equivalent ethanol concentration (M)	7.80×10^{-4}	1.46×10^{-3}
Amount of ethanol in the 100-mL solution (mol)	7.80×10^{-5}	1.46×10^{-4}
Mass of ethanol in the 100-mL "Unknown" solution (g)	3.60×10^{-3}	6.73×10^{-3}
Mass of ethanol in the 1-L stock solution (g)	3.60	3.36
Average mass of ethanol in 1-L stock solution (g)	3.48	

Analysis Questions

1. How would significant evaporation of water during the heating of the unknowns influence your results?

Less solvent would yield a higher $Cr_2O_7^{2-}$ concentration (indicated by the absorbance). This would imply a lower amount of $Cr_2O_7^{2-}$ was consumed, which would result in calculating less ethanol than there really was.

2. If the result demonstrated a lower ethanol concentration than the outcome should have been, how would you improve your results?

Reducing evaporation during the heating would increase the amount of ethanol that was detected. Also, the reaction may not have gone to completion, being a slow reaction. Extending the reaction time of the solutions in the hot water bath could improve the results.

3. How many milliliters of 100% ethanol were used to make your unknown, if the density of ethanol is 0.800 g/mL?

$$\frac{0.348\text{ g}}{0.800\ \frac{\text{g}}{\text{mL}}} = 0.435\text{ mL}$$

Synthesis Questions

Use available resources to help you answer the following questions.

1. Can you think of any other way to follow the reaction with the colorimeter? (Hint: Consider what other species present in the reaction mixture would absorb in the visible range.)

The Cr(III) ions are green and would be suitable to follow the reaction.

2. How would you have to change the experiment to utilize the option above?

The calibrating solutions would have to be Cr(III) solutions and we would have to measure the Cr(III) concentration, which is proportional to the amount of alcohol present in the solution, rather than the amount of unreacted reactant.

3. For this change, which trace would you utilize to make your measurements? (Hint: Remember the color of the species in question.)

Since the Cr(III) is green, there should be significant absorption in the red and in the blue range. Considering that the remaining $Cr_2O_7^{2-}$ ions also absorb in the blue range, it would interfere with the detection of Cr(III). So the red trace is a better choice.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. Which statement is *not* correct?

- **A.** Ethanol reacts with $Cr_2O_7^{2-}$ in a redox reaction.
- **B.** One of the products of the reaction is Cr(III).
- **C.** The amount of the remaining $Cr_2O_7^{2-}$ ions is measured.
- **D.** **$AgNO_3$ is used to oxidize the ethanol.**

2. The blue trace is used to detect the $Cr_2O_7^{2-}$ ions because:

- **A.** $Cr_2O_7^{2-}$ is blue.
- **B.** **$Cr_2O_7^{2-}$ absorbs in the blue range.**
- **C.** $Cr_2O_7^{2-}$ is yellow.
- **D.** $Cr_2O_7^{2-}$ absorbs in the yellow range.

3. Which statement is correct regarding the $Cr_2O_7^{2-}$ ion?

- **A.** It is used to catalyze the reaction.
- **B.** It is employed in the stoichiometric ratio with ethanol.
- **C.** **It is added in a known quantity from which some reacts with the ethanol present and the rest is detected with the colorimeter.**
- **D.** It is added in a known quantity from which it is detected with the colorimeter after which some is used up by the ethanol.

4. Why were the unknowns kept in a 75 to 80 °C water bath?

- **A.** To catalyze the reaction.
- **B.** **To accelerate the reaction**.
- **C.** To help the dissolution of the reagents.
- **D.** To help get more accurate colorimetric measurements.

Extended Inquiry Suggestions

This method can be utilized or adapted to measure the ethanol content of a regular alcoholic beverage. In the example below, the ethanol content of cognac is determined. The bottle shows a 43% ethanol content. The same analysis was performed as before, except based on the predicted ethanol content, 12.00 mL of the beverage was used:

	Unknown A	Unknown B
Initial concentration of $Cr_2O_7^{2-}$ in the reaction flask (M)	2.55×10^{-3}	
Absorbance	0.577	0.407
Remaining concentration of $Cr_2O_7^{2-}$ (M)	2.06×10^{-3}	1.49×10^{-3}
Amount of $Cr_2O_7^{2-}$ reacted with ethanol (M)	4.90×10^{-4}	1.05×10^{-3}
Equivalent ethanol concentration (M)	7.35×10^{-4}	1.59×10^{-3}
Amount of ethanol in the 100-mL solution (mol)	7.35×10^{-4}	1.59×10^{-3}
Mass of ethanol in the 100-mL solution (g)	3.35×10^{-3}	7.30×10^{-3}
Volume taken from the 1-L stock solution (mL)	1	2
Mass of ethanol in the 1-L solution (g)	3.35	3.65
Average mass of ethanol in the 1-L stock solution (g)	3.50	

The solution therefore had 3.50 g/L of ethanol. The concentration of the original beverage was:

$$\frac{3.50\ \text{g}}{(12.00\ \text{mL})(0.800\ \frac{\text{g}}{\text{mL}})} \times 100 = 36.5\%$$

The error of the measurement:

$$\text{Percent Error} = \left|\frac{43.00 - 36.46}{43.00}\right| \times 100 = 15.2\%$$

Organic Chemistry

35. Organic Synthesis I—Preparation

Objectives

Organic Synthesis I: Students synthesize an organic compound (aspirin).

Organic Synthesis II: Students analyze the purity of the aspirin they synthesized.

Procedural Overview

Students gain experience conducting the following procedures:

- Organizing and conducting the steps of a chemical reaction (Organic Synthesis I)
- Performing separation processes to isolate the product (Organic Synthesis I)
- Determining the percent yield of the reaction (Organic Synthesis I)
- Performing qualitative and quantitative analytical methods (Organic Synthesis II)

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	120 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- Ring stand
- Clamp (2)
- Erlenmeyer flask, 125-mL
- Graduated cylinder, 10-mL
- Beaker, 100-mL
- Beaker, 400-mL
- Hot plate
- Filter flask
- Büchner funnel
- Filter paper
- Salicylic acid ($C_7H_6O_3$), 2 g
- Acetic anhydride ($C_4H_60_3$), 4 mL
- Concentrated phosphoric acid (H_3PO_4), 1 mL
- Wash bottle with distilled water
- Eye dropper
- Rubber policeman
- Ice-cold distilled water, 50 mL[1]
- Ice for ice bath, 300 mL[2]
- Forceps

[1, 2] To prepare these items, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Stoichiometry
- Titration
- Acid-base reactions

Related Labs in This Guide

Labs conceptually related to this one include:

- Standardizing a Solution of Sodium Hydroxide*
- Acid–Base Titration*
- Synthesis of a Coordination Compound*
- Organic Synthesis II—Analysis*

Using Your Data Collection System

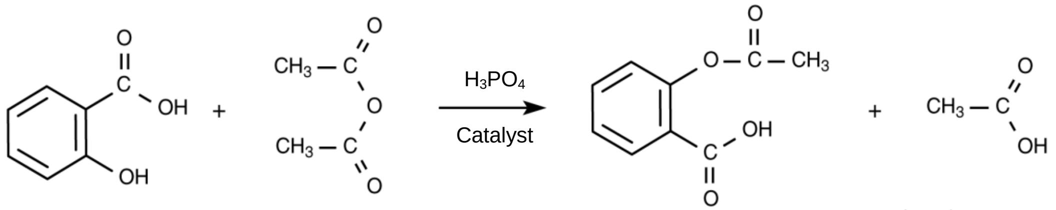
Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system �(2.1)
- Monitoring live data �(6.1)

Background

Aspirin is a widely used analgesic (pain killer), antipyretic (fever reducer), anti-inflammatory (inflammation fighter) and blood thinner. It was the first synthetic drug to be manufactured. Aspirin is the patented trade name for acetylsalicylic acid. It was synthesized from salicylic acid by Felix Hoffman in 1897 and patented by Friedrich Bayer & Co. in Germany in 1899. Bayer named its new product "aspirin"; the name originated from "a" for acetyl, and the root "-spir", from the Latin name Spiraea Ulmaria, the meadow sweet flower, from which salicylic acid had been isolated.

The synthesis of aspirin from salicylic acid can be accomplished by reacting it with acetic anhydride (also called "acetic acid anhydride") in the presence of a catalyst, phosphoric acid:



$C_7H_6O_3$
Salicylic acid

$C_4H_4O_3$
Acetic anhydride

$C_9H_8O_4$
Acetyl salicylic acid
(Aspirin)

$C_2H_4O_2$
Acetic acid

Pre-Lab Experiment

Setting the stage for the experiment

The synthesis of aspirin involves the reaction of salicylic acid and acetic anhydride in the presence of a catalyst, phosphoric acid, H_3PO_4. Once the aspirin is synthesized it has to be separated from the unreacted salicylic acid and purified. Aspirin is insoluble in cold water, and can be isolated by filtering the chilled reaction solution. Purification is necessary to remove any unreacted salicylic acid and acetic anhydride, as well as the acetic acid product and the phosphoric acid which is used as the catalyst. Acetic anhydride will decompose with the addition of water once the formation of aspirin is complete:

$$C_4H_6O_3 + H_2O \rightarrow 2C_2H_4O_2$$

Acetic anhydride Water Acetic acid

Example calculation to try

In a test experiment, 2.5 g of salicylic acid was measured and transferred into a 125-mL Erlenmeyer flask. 5 mL of acetic anhydride and 5 drops of 85% H_3PO_4 was added drop wise under a hood. The flask was mounted in a water bath and kept at 60 °C for 20 min. 10 mL of ice-cold water was added to the reaction mixture drop wise and the flask was set in an ice bath.

Once the mixture cooled, 25 mL of ice-cold distilled water was added; after which the crystals started to precipitate. The precipitate was filtered out using a Büchner funnel and washed with 15 mL of ice-cold distilled water. The filter paper was set aside, allowing the crystals to dry. The mass of the product was measured and found to be 2.8 g. Considering that the formula weight of salicylic acid (SA) is 138.12 g/mol, and180.15 g/mol for aspirin (A) the theoretical yield was:

$$\left(2.5\text{ g SA}\right)\left(\frac{180.157\text{ g A}}{138.120\text{ g SA}}\right) = 3.3\text{ g A}$$

The experimental yield was:

$$\left(\frac{2.8\text{ g}}{3.3\text{ g}}\right) \times 100 = 85\%$$

1. Can you provide some explanation for the yield being less than 100%?

The reaction may not have been 100% complete. Also, aspirin is somewhat soluble in cold water and some of the product could have remained in solution.

2. What do you think the purpose of adding the ice-cold 10 mL water drop wise was?

The purpose of adding the 10 mL ice-cold water drop wise was to remove the unreacted acetic anhydride and decrease the solubility of the product.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. Place 2000 mL of deionized water on ice in a bucket or pail.
2. Place a pound of shaved ice for the class in a bucket or pail.

Safety

Add this important safety precaution to your normal laboratory procedures:

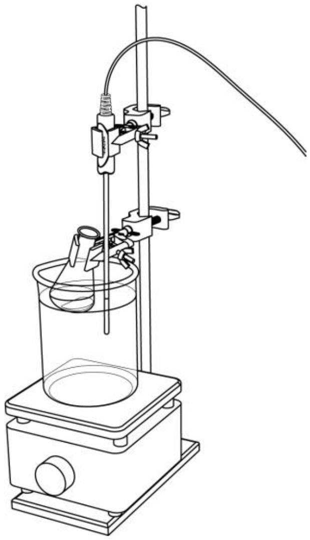
- Acetic anhydride and phosphoric acid are extremely caustic and must be handled under a hood. Handle them with care.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Set Up

1. Measure about 2.0 g of salicylic acid and place it into a 125-mL Erlenmeyer flask. Record in Table 1 the actual mass of salicylic acid used, to the precision of the balance.



2. In the hood:

- **a.** Add 4 mL of acetic anhydride, by drops, to the Erlenmeyer flask containing the salicylic acid.
- **b.** Add 5 drops of 85% phosphoric acid to the Erlenmeyer flask.

CAUTION: Both acetic anhydride and phosphoric acid can cause burns. Handle them carefully.

3. Clamp the Erlenmeyer flask in the water bath so that the reaction mixture is below the level of the water. Tilt the flask to minimize the chance of the mixture boiling over.

4. Start a new experiment on the data collection system. �(1.2)

5. Connect the stainless steel temperature sensor to the data collection system. �(2.1)

6. Clamp a stainless steel temperature sensor to the ring stand and immerse the tip of the sensor in the water.

Note: Do not allow the temperature sensor to touch the sides or bottom of the flask.

7. Monitor live data without recording. �(6.1)

8. Use the temperature sensor to maintain the temperature of the water bath around 90 °C.

Collect Data

9. Heat the mixture in the water bath for 20 minutes. Check that all solids have dissolved.

10. Remove the reaction flask from the water bath.

11. Obtain 50 mL of ice-cold distilled water. Measure 10 mL of cold distilled water into a 10 mL graduated cylinder. Allow the flask to cool down to room temperature. Add the 10 mL of cold distilled water to the reaction flask 3 to 5 drops at a time.

CAUTION: The decomposition of excess acetic anhydride is exothermic. Beware of vapors and spattering.

12. Why do you think you have to add water to the reaction mixture?

Water is added to remove unreacted acetic anhydride.

13. Prepare the ice bath in the 400-mL beaker. Chill the reaction mixture in the ice bath for about 30 minutes.

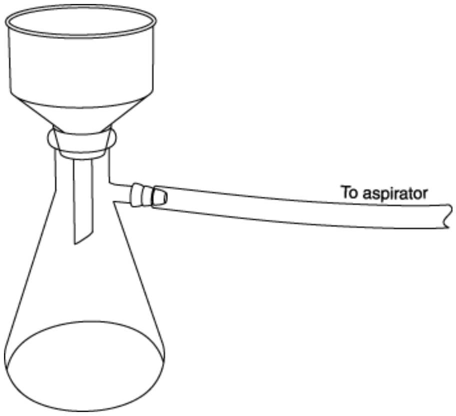
14. Add 25 mL of cold, distilled water to the reaction mixture. Aspirin crystals should begin to precipitate.

15. Why do the crystals precipitate?

The crystals precipitate because the product has little solubility in cold water.

16. While the flask is cooling in the ice bath, prepare a filter setup as illustrated.

17. Obtain the mass of a piece of filter paper and place it in the Büchner filter. Using a wash bottle, moisten the filter paper with a small amount of distilled water in order to seal it to the surface of the funnel.



18. Turn on the aspirator. Swirl the contents of the flask and pour them into the center of the filter paper. Use a rubber policeman to make sure all of the contents of the flask have been transferred to the filter paper.

19. When all of the liquid has been drawn through the filter, wash the precipitate with a measured amount of ice-cold distilled water while the suction is still being applied. Do not exceed 15 mL.

20. Break the vacuum and shut off the aspirator. Carefully remove the filter paper from the Büchner filter with the forceps and set it aside to dry.

21. Obtain the mass of the filter and product after they have dried and enter this measurement in Table 1.

22. Save your product (aspirin crystals) for analysis (refer to the Organic Synthesis II experiment).

23. Clean up according to the instructor's instructions.

Data Analysis

1. Calculate the theoretical amount of aspirin to be produced in this reaction.

$$2.000\text{ g Salicylic Acid} \times \frac{180.157\text{ g Aspirin}}{138.120\text{ g Salicylic Acid}} = 2.608\text{ g Aspirin}$$

2. Calculate the percent yield of the synthesis and enter it in Table 1.

$$\frac{2.149\text{ g Aspirin (experimental)}}{2.608\text{ g Aspirin (theoretical)}} \times 100 = 82.40\%\text{ yield}$$

Table 1: Determine the efficiency of the reaction

Parameter	Data and Calculated Results
Mass of salicylic acid (g):	2.000
Mass of theoretical amount of aspirin (g):	2.608
Mass of experimental aspirin (g):	2.149
Yield of the synthesis (%):	82.40

Analysis Questions

1. What compound or compounds do you think your product contains?

The product could contain unreacted salicylic acid and aspirin.

2. What compounds from the reaction mixture would you not find in your product?

The product cannot have acetic anhydride. The excess acetic anhydride was removed by adding water. Also, being volatile compounds, both acetic anhydride and acetic acid (the product of the hydrolysis of acetic anhydride) are liquid at room temperature but drying removes them.

3. Propose ways of improving the yield.

Longer reaction time would probably improve the yield. Also, lowering the temperature of the ice bath may help remove more products.

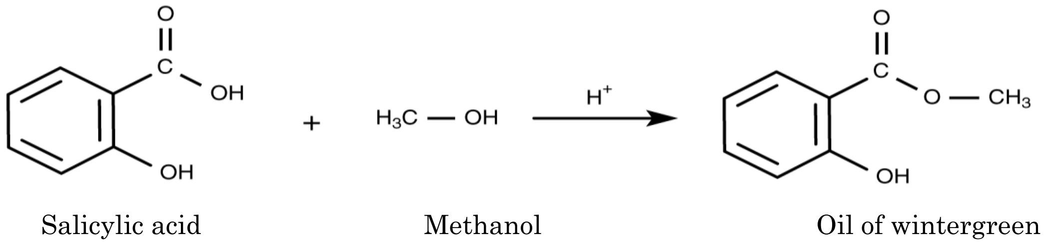
4. Explain in your own words what is happening during the chemical reaction that produces aspirin.

Acetic anhydride breaks up into CH_3CO^+ and acetate ions (CH_3COO^-). The CH_3CO^+ ion replaces the hydrogen on the OH group in the salicylic acid. The displaced hydrogen forms an acetic acid molecule with the acetate ion.

Synthesis Questions

Use available resources to help you answer the following questions.

1. A similar reaction can produce "oil of wintergreen." Based on the procedure used to synthesize aspirin, propose a method to synthesize oil of wintergreen.



Instead of acetic anhydride one would use methanol as a solvent and as the second reactant. The rest of the procedure should be the same.

2. Propose a method to purify your product.

Recrystallization from ice-cold water would improve the purity of the product.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. What happens to the excess acetic anhydride in the reaction mixture?

- **A.** There is no excess acetic anhydride.
- **B.** The excess acetic anhydride is removed by cooling the reaction mixture in an ice-cold water bath.
- **C. The excess acetic anhydride is removed by reacting the reaction mixture with ice-cold water.**
- **D.** The excess acetic anhydride is removed by filtering the reaction mixture.

2. The dry product will have:

- **A.** Salicylic acid only
- **B.** Aspirin only
- **C. Aspirin and salicylic acid**
- **D.** Acetic anhydride only

3. The yield can be improved by:

- **A.** Using more salicylic acid
- **B.** Using more acetic anhydride
- **C. Allowing a longer reaction time**
- **D.** Using a different kind of acid catalyst

4. The filtration process will introduce an error if:

- **A. Not all of the product is collected from the filter paper**
- **B.** Not all acetic anhydride is removed

C. Not all salicylic acid is reacted

D. Too much acid catalyst is used

Extended Inquiry Suggestions

If time allows, have students synthesize oil of wintergreen in the same way as aspirin. Isolation of the product from the reaction mixture however, is not necessary. The product can be identified by its pungent aroma.

36. Organic Synthesis II—Analysis

Objectives

Organic Synthesis I: Students synthesize an organic compound (aspirin).

Organic Synthesis II: Students analyze the purity of the aspirin they synthesized.

Procedural Overview

Students gain experience conducting the following procedures:

- Performing qualitative and quantitative analytical methods to determine the composition of their synthesized product, including melting point determination and titration

Time Requirement

♦ Preparation time	15 minutes
♦ Pre-lab discussion and experiment	15 minutes
♦ Lab experiment	120 minutes

Materials and Equipment

For each student or group:

- Data collection system
- Stainless steel temperature sensor
- pH sensor
- Drop counter with micro stir bar
- Ring stand
- Clamp, utility
- Clamp, right-angle
- Clamp, buret
- Beaker (2), 150-mL
- Beaker, 100-mL
- Beaker (2), 25-mL
- Test tubes (3), 15-mL
- Melting point capillary tube
- Buret, 50-mL
- Graduated cylinder, 100-mL
- Magnetic stirrer and stir bar
- Hot plate with magnetic stirrer and stir bar
- Mortar and pestle
- Product from Organic Synthesis I experiment
- Aspirin tablet
- Ethanol, 15 mL
- 0.1 M Sodium hydroxide ($NaOH$), 75 mL[1]
- 1% Iron chloride ($FeCl_3$), 2 mL[1]
- Mineral oil, 150 mL
- Buffers, pH 4 and pH 10, 10 mL
- Water, distilled, 100 mL
- Rubber band, small
- Wash bottle with deionized water

[1] To prepare the solutions, refer to the Lab Preparation section.

Concepts Students Should Already Know

Students should be familiar with the following concepts:

- Stoichiometry
- Titration
- Acid-base reactions

Related Labs in This Guide

Labs conceptually related to this one include:

- Standardizing a Solution of Sodium Hydroxide
- Acid–Base Titration
- Organic Synthesis I—Preparation

Using Your Data Collection System

Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

- Starting a new experiment on the data collection system �(1.2)
- Connecting a sensor to the data collection system �(2.1)
- Connecting multiple sensors to your data collection system �(2.2)
- Calibrating a drop counter �(3.4)
- Calibrating a pH sensor �(3.6)
- Starting and stopping data recording �(6.2)
- Displaying data in a graph �(7.1.1)
- Changing the variable on the x-axis and y-axis of a graph �(7.1.9)
- Finding the coordinates of a point in a graph �(9.1)

Background

The aspirin synthesis reaction may not have been 100% complete. Therefore, it is likely that there will be some unreacted salicylic acid (SA) left in the product. In this experiment, students perform a qualitative and a quantitative test to determine how much of the SA has remained unreacted.

Pre-Lab Experiment

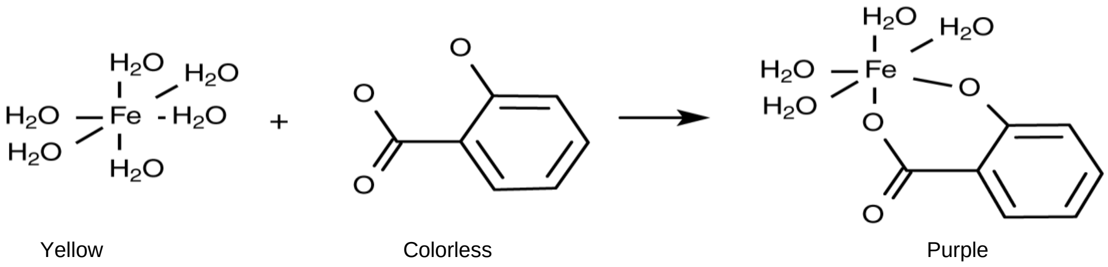
Setting the stage for the experiment

Three types of tests for unreacted salicylic acid impurities will be performed: a qualitative color test, a melting point test, and a titration test.

Students will test both their product and factory-made aspirin for the presence of salicylic acid.

Iron(III) chloride test

Salicylic acid forms a purple complex with the $Fe(H_2O)_6^{3+}$ ion (which is the common form of Fe^{3+} in water):



Melting point test

Students will measure the melting point of their product. Salicylic acid and aspirin have distinctly different melting points (see table below). If there is salicylic acid in the product, the melting point will be between the melting points of the two chemicals.

Titration test

Both salicylic acid and aspirin are acids. They do, however, have distinctly different acidity constants (K_a) and therefore can be identified in a mixture by performing a titration with a base such as sodium hydroxide.

Properties of salicylic acid and acetylsalicylic acid

Parameter	Salicylic Acid (SA)	Acetylsalicylic Acid (ASA)
Formula	$C_7H_6O_3$	$C_9H_8O_4$
Molar mass (g/mol)	138.12	180.15
K_a	1.10×10^{-2}	3.27×10^{-4}
pK_a	1.96	3.48
Solubility (g/100 mL)	0.18	0.25
Melting point (°C)	159	138–140

Example calculation to try

The product of an aspirin synthesis was analyzed for salicylic acid impurities. The iron(III) chloride test showed a purple coloration, indicating a significant amount of salicylic acid impurity. The melting point was found to be 145 °C, which is slightly higher than the melting point of aspirin. This result also confirms the presence of salicylic acid.

The titration of 0.200 g of the product with 0.1000 M NaOH showed a jump in the pH at 5.80 mL and a second jump at 12.45 mL (the jumps in pH represent equivalence points). The first jump corresponds to salicylic acid, since it has the lower pK_a value. The amount of titrant used to reach the equivalence point of SA (which is the same as the number of moles of the salicylic acid due to the 1:1 ratio between NaOH and salicylic acid) is

$$(5.80\text{ mL})\left(\frac{0.1000\text{ mol}}{1000\text{ mL}}\right) = 5.80 \times 10^{-4}\text{ mol NaOH}$$

The mass of salicylic acid in the sample then is

$$\left(5.80 \times 10^{-4}\text{ mol NaOH}\right)\left(\frac{1\text{mol SA}}{1\text{mol NaOH}}\right)\left(\frac{138.12\text{ g SA}}{1\text{ mol SA}}\right) = 0.0766\text{ g SA}$$

The amount of titrant consumed to reach the equivalence of aspirin was: 12.45 mL – 5.80 mL = 6.65 mL, which would account for

$$(6.65\text{ mL NaOH})\left(\frac{0.1000\text{ mol NaOH}}{1000\text{ mL}}\right) = 6.65 \times 10^{-4}\text{ mol NaOH}$$

The amount of titrant is equivalent to the amount of aspirin due to the 1:1 ratio between NaOH and aspirin. The amount of aspirin (A) in the sample is

$$\left(6.65 \times 10^{-4}\text{ mol NaOH}\right)\left(\frac{1\text{mol A}}{1\text{mol NaOH}}\right)\left(\frac{180.15\text{ g A}}{1\text{ mol A}}\right) = 0.120\text{ g A}$$

The percent aspirin the product contains is, therefore

$$\left(\frac{0.120\ \text{g}}{0.200\ \text{g}}\right) \times 100 \ = \ 60.0\%$$

1. Can you provide some explanation for the less than 100% yield?

The reaction may not have been 100 % completed. Also, aspirin is somewhat soluble in cold water and some of the product remained in solution.

Lab Preparation

These are the materials and equipment to set up prior to the lab:

1. ***0.1 M NaOH:*** Dissolve 8.00 g of NaOH in distilled water in a 2-L volumetric flask and then fill it to the mark.
2. ***1% $FeCl_3$:*** Dissolve 1.67 g of $FeCl_3 \cdot 6H_2O$ in distilled water in a 100-mL volumetric flask and then fill it to the mark.

Safety

Follow all standard laboratory procedures.

Procedure with Inquiry

Note: Students use the following technical procedures in this experiment. The instructions for them (identified by the number following the symbol: "�") are on the storage device that accompanies this manual. Choose the file that corresponds to your PASCO data collection system. Please make copies of these instructions available for your students.

Part 1 – $FeCl_3$ test

Set Up

1. Put 1 mL ethanol in three clean test tubes.

2. Put 1 to 2 drops of 1% $FeCl_3$ in each test tube.

Collect Data

3. Add a few crystals of factory-made aspirin to the first test tube and a few crystals of your product into the second test tube. The third test tube is your control. Label the test tubes appropriately.

4. Record your observations in Table 2.

Part 2 – Melting point test

Set Up

5. Start a new experiment on the data collection system. �(1.2)

6. Connect the stainless steel temperature sensor to the data collection system. �(2.1)

7. Display temperature in a digits display. �(7.3.1)

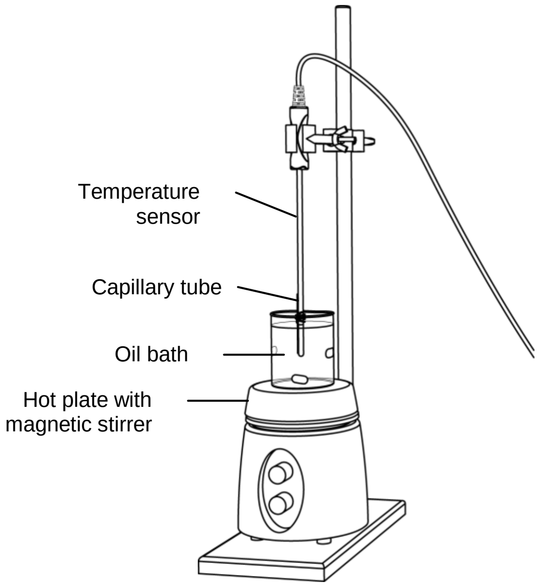
8. Begin setting up the melting point detection apparatus: put the stir bar in the 100-mL beaker and fill it with mineral oil almost to the top. Put the beaker on the hot plate on the support stand.

9. Use a mortar and pestle to crush about 20 mg of the product into a fine powder. Collect the powered material in a pile in the center of the mortar.

10. Push the open end of a capillary tube into the pile of crushed product. Pack it into the capillary tube by inverting the tube and tapping it lightly on the bench top. Pack about 1 cm of powder into the capillary tube.

11. Use a small rubber band to fasten the capillary tube to the end of the stainless steel temperature sensor.

12. Clamp the assembly to the support stand so that the end of the temperature sensor and capillary tube are immersed in the mineral oil bath without letting any oil get into the capillary tube.



Collect Data

13. Start data recording. �(6.2)

14. Turn on the hot plate to slowly heat the oil bath. Turn on the magnetic stirrer.

15. Observe the material in the capillary tube until it has melted. Record the melting point in Part 2 of the Data Analysis section.

CAUTION: The oil bath will be extremely hot; exercise caution. Let it cool before cleaning up.

Part 3 – Titration test

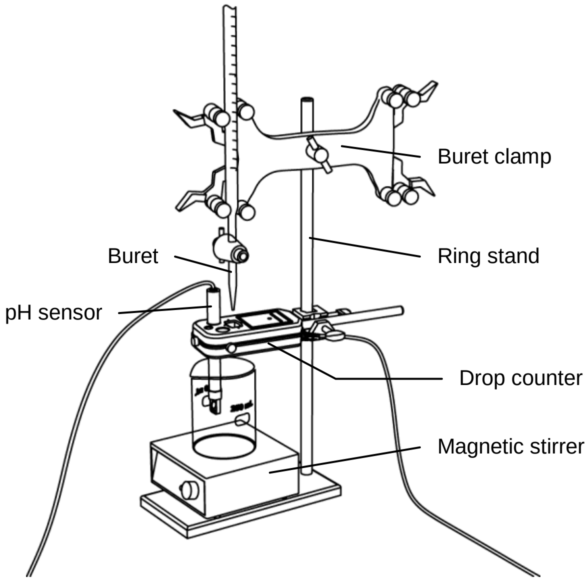
Set Up

16. Start a new experiment on the data collection system. �(1.2)

17. Connect a pH sensor to the data collection system. �(2.1)

18. Connect the drop counter to the data collection system. �(2.2)

19. Display pH versus Drop Count (drops) on a graph. �(7.1.1)



20. Calibrate the pH sensor. �(3.6)

21. Assemble the titration apparatus, using the steps below and the illustration as a guide.

- **a.** Position the magnetic stirrer on the base of the ring stand.
- **b.** Place a waste container on the magnetic stirrer.
- **c.** Use the buret clamp to attach the buret to the ring stand.
- **d.** Position the drop counter over the waste container and attach it to the ring stand using the right-angle clamp.
- **e.** Place the pH sensor through one of the slots in the drop counter.

22. Rinse the buret with several milliliters of the 0.1 M NaOH solution:

- **a.** Ensure that the stopcock is closed and rinse the inside of the buret with several milliliters of the standardized NaOH solution.
- **b.** Open the stopcock on the buret and drain the rinse NaOH into the waste container.
- **c.** Repeat this process two more times.

23. Why is it necessary to rinse the buret with the NaOH solution?

If there is any residual water or contaminant in the buret, it will dilute the NaOH and change its concentration. Rinsing eliminates any such contamination.

24. Make sure the stopcock on the buret is in the “off” position and then use a funnel to fill the buret with about 50 mL of the 0.1 M NaOH solution (titrant).

25. Drain a small amount of the titrant through the drop counter into the waste beaker to remove any air in the tip of the buret.

26. Why is it important to remove air from the tip of the buret?

Any air trapped in the buret tip is counted as volume of NaOH. If this happens, the amount of titrant used will be inaccurate.

27. Practice adjusting the stopcock on the buret so that the titrant goes through the drop counter in distinguishable drops that fall at about 1 to 2 drops per second.

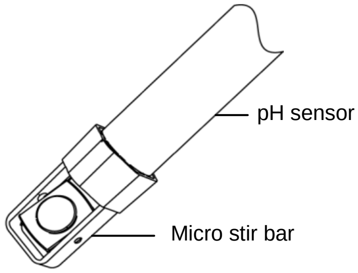
Note: Good control of the stopcock is important. If you accidentally open the stopcock too far and the NaOH streams out (as opposed to coming out in drops), you will have to start over.

28. Why will it be necessary to start your titration over again if you accidentally allow the titrant to stream out of the stopcock instead of emerging by drops?

The drop counter counts distinct drops. If the drops are not sufficiently distinct from one another, the drop counter will not function properly and the fluid volume will not be accurate.

29. Remove the waste container.

30. Add the micro stir bar to the end of the pH sensor.



31. Add additional 0.1 M NaOH to the buret so the solution is above the zero mark. Allow some of the NaOH solution to drip into the waste container until the bottom of the meniscus is lined up with or just below the zero mark and record the initial reading in Table 1.

32. Measure about 0.2 g of your product to the nearest mg. Record the mass in Table 3.

33. Transfer the sample into a 150-mL beaker.

34. Dissolve the sample in 10 mL of ethanol.

35. Add 100 mL of water to the solution.

36. Place the solution on the magnetic stirrer.

37. Turn on the magnetic stirrer at a gentle rate.

Collect Data

38. Clean the lens of the drop counter inside the opening through which the drops are going with water and a cotton swab or tissue.

39. Start recording data. �(6.2)

40. Turn the buret stopcock carefully, allowing the titrant to drip slowly (1 to 2 drops per second) into the solution.

41. Add the titrant drop by drop until the second jump occurs and levels off. If you do not get a second jump after 20 mL of the titrant was added, stop the titration.

42. Why is it important to go past the equivalence point?

It is necessary to go past the equivalence point in order to find the point where the slope is the steepest. The curve needs to continue past the steepest point to ensure you can tell when the slope begins to flatten.

43. Stop recording data. �(6.2)

44. In Table 1, record the final drop count and the final reading of the titrant in the buret to a precision of 0.01 mL.

45. Calculate the volume of titrant (final reading minus initial reading) and record this value in Table 1.

Table 1: Titration data

Titration Information	**Measurement or Calculation**
Initial reading of NaOH in the buret (to 0.01 mL)	0.00
Final reading of NaOH in the buret (to 0.01 mL)	17.00
Volume of titrant (to 0.01 mL)	17.00
Final drop count	333

46. Calibrate the drop counter. �(3.4)

47. Set the horizontal axis to the calculated volume. �(7.1.9)

48. Find the volumes of titrant corresponding to the first and second jumps on the graph and record them in Table 3. �(9.1)

Data Analysis

Part 1 – FeCl$_3$ test

1. Complete the tables below with your data.

Table 2: Iron(III) chloride test

Parameter	**Observations**
Aspirin	Clear with yellow tint
Product	Clear with purple tint
Control	Clear with yellow tint

Part 2 – Melting point test

2. Enter the melting point of the product (°C): 137.7

Part 3 – Titration test

Table 3: Determination of product composition. Show calculations below.

Parameter	Salicylic Acid	Aspirin
Mass of product being titrated (g)	0.200	
Volume corresponding to the first equivalence point (mL)	1.58	▨
Volume corresponding to the second equivalence point (mL) **Note:** Subtract the volume that was necessary for the first equivalence point.	▨	9.80
Amount of titrant added (mol)	1.58×10^{-4}	9.80×10^{-4}
Amount of titrated substance (mol)	1.58×10^{-4}	9.80×10^{-4}
Formula weight (g/mol)	138.12	180.15
Mass of titrated substance (g)	2.18×10^{-2}	0.177
Composition of product (%)	10.9	88.3

3. Calculate the number of moles of titrant added and enter these values in Table 3.

a. Salicylic acid

$$(1.58\text{ mL NaOH})\left(\frac{1\text{mol SA}}{1\text{mol NaOH}}\right)\left(\frac{0.1000\text{ mol NaOH}}{1000\text{ mL}}\right) = 1.58 \times 10^{-4}\text{ mol SA}$$

b. Aspirin

$$(9.8\text{ mL NaOH})\left(\frac{1\text{mol A}}{1\text{mol NaOH}}\right)\left(\frac{0.1000\text{ mol NaOH}}{1000\text{ mL}}\right) = 9.8 \times 10^{-4}\text{ mol A}$$

4. Calculate the number of moles of titrated substance added and enter these in Table 3.

a. Salicylic acid

1.58×10^{-4} moles

b. Aspirin

9.80×10^{-4} moles

The amount of titrated substance is equivalent to the amount of titrant due to the 1:1 ratio between NaOH and salicylic acid or aspirin.

5. Calculate the mass of the titrated substances and enter these in Table 3.

a. Salicylic acid

$$\left(1.58 \times 10^{-4}\ \text{mol SA}\right)\left(\frac{138.12\ \text{g SA}}{1\ \text{mol SA}}\right) = 0.0218\ \text{g SA}$$

b. Aspirin

$$\left(9.80 \times 10^{-4}\ \text{mol A}\right)\left(\frac{180.15\ \text{g A}}{1\ \text{mol A}}\right) = 0.176\ \text{g A}$$

6. Determine the percentage of the components in the product and enter these in Table 3.

a. Salicylic acid

$$\left(\frac{0.0218\ \text{g}}{0.200\ \text{g}}\right) \times 100 = 10.9\%$$

b. Aspirin

$$\left(\frac{0.177\ \text{g}}{0.200\ \text{g}}\right) \times 100 = 88.3\%$$

Analysis Questions

1. What conclusion have you drawn from the iron(III) chloride test?

Most likely students will find the test positive with their product while the blank and the industrial aspirin show negative results since the blank and the industrial aspirin will not have salicylic acid residue.

2. What conclusion can be drawn from the melting point test?

The melting point should be near the melting point of pure aspirin. The extent of deviation is related to the amount of unreacted salicylic acid.

3. What conclusion can you draw from the titration test?

The titration test may not show a reliable "jump" for salicylic acid on the titration curve, which indicates that the amount of salicylic acid in the product is small.

4. Combine the results of the tests and argue about the purity of your product. Consider the accuracy of the individual tests when you answer this question.

Student should primarily rely on the fact that the titration is the most quantitative test, the melting point test is reliable, and the iron(III) chloride test is qualitative.

Synthesis Questions

Use available resources to help you answer the following questions.

1. How do you think the purity of the product can be improved?

Recrystallization would improve the purity of the product.

2. What is the trade-off with increasing the purity of the product?

Any purifying process will result in losing some of the product. Therefore, the overall yield of the synthesis will decrease.

Multiple Choice Questions

Select the best answer or completion to each of the questions or incomplete statements below.

1. The melting point of the product should be:

- **A.** Higher than the melting point of salicylic acid
- **B.** Higher than the melting point of aspirin
- **C. Between the melting points of aspirin and salicylic acid**
- **D.** Higher than salicylic acid but lower than aspirin

2. The lack of the first jump (around pH 4 to 5) and the presence of the second jump (around pH 6 to 7) on the titration curve indicate:

- **A.** An error in the procedure
- **B. The lack of salicylic acid in the product**
- **C.** The lack of aspirin in the product
- **D.** Poorly calibrated pH sensor

3. The purple color after adding iron(III) chloride to the product indicates:

- **A. The presence of salicylic acid**
- **B.** The presence of the product, aspirin
- **C.** The lack of salicylic acid in the product
- **D.** The lack of aspirin in the product

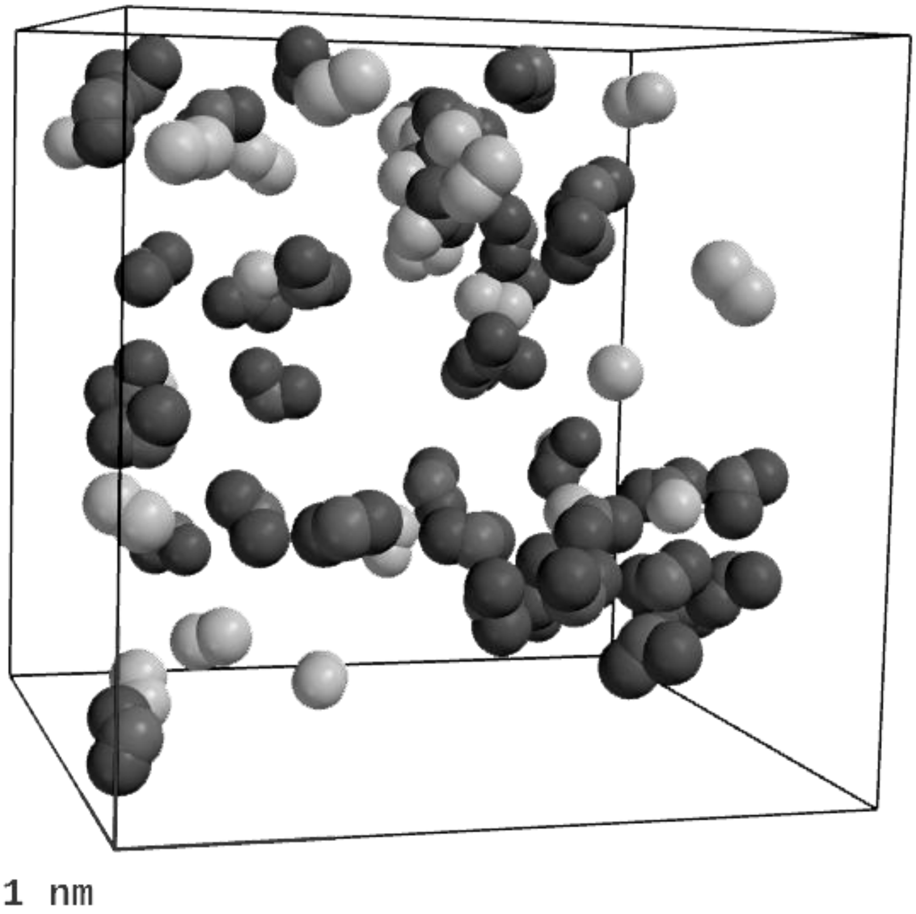
4. The titration test will

- **A. Show the presence of both salicylic acid and aspirin**
- **B.** Show the presence of only salicylic acid
- **C.** Show the presence of aspirin
- **D.** The presence of any organic acids

Extended Inquiry Suggestions

Have students recrystallize the product from ice-cold water to improve purity. Then have them repeat these tests to determine if there is any affect on the purity and yield due to the recrystallization.

ODYSSEY Molecular Labs



ODYSSEY Molecular Labs

This section contains the student worksheets that accompany the Molecular Lab simulations. The simulations and the answer key can be found on the *ODYSSEY* storage device that came with this manual.

Introduction

Using ODYSSEY Molecular Labs

Wavefunction's *ODYSSEY* is a unique software program for use in chemistry classes. Maker of *Spartan* molecular modeling software, Wavefunction created *ODYSSEY* so students could use scientifically-based simulations to experiment with core chemistry topics from a molecular perspective. The additional perspective provided by the *ODYSSEY* software enhances and complements the hands-on, experiential PASCO activities in this manual.

ODYSSEY includes a collection of ready-to-use chemistry experiments (called "Molecular Labs") and student worksheets. A number of the Molecular Labs applicable to the PASCO activities are identified under selected topic areas in the table of contents. The student worksheets for these labs are provided in the *ODYSSEY* Molecular Labs section of this manual and the answer key can be found on the accompanying storage device. A fully functional 60-day licensed version of the *ODYSSEY* Instructor Edition, containing the complete set of *ODYSSEY's* Molecular Labs, is included with this manual.

In addition to the Molecular Labs, *ODYSSEY* provides:

- Prelabs (Tutorials) – ideal for learning about how to use the program
- Applied Chemistry – a collection of chemistry samples commonly encountered in modern society
- Molecular Stockroom – the electronic equivalent of your chemistry stockroom with more than a thousand pre-constructed samples spanning the periodic table

To successfully get started with *ODYSSEY,* check the system requirements and install the software that is on the accompanying *ODYSSEY* storage device; use the activation code provided to access the software for 60 days. Contact PASCO (www.pasco.com) for information on instructor and student licensing.

Thermochemistry and Thermodynamics

The Reaction Energetics of Nitroglycerin

Objectives

In this experiment, you will calculate the energy of reaction associated with the explosive decomposition of a well-known substance:

⊙ **1,2,3-Propanetriol Trinitrate** (Nitroglycerin) $C_3H_5N_3O_9$

The reaction energy will be obtained from calculated energy values for all the individual species that participate in the reaction.

Procedure

In a chemical reaction, the nuclei and electrons of the reactants reorganize so as to end up in a new arrangement—the product (or products). In the following, you will calculate the energy released if 1 mol of nitroglycerin "droplets", each containing 20 molecules, explodes:

○ **Reactant** ○ **Products**

Note: The computer autoscales the models—being gaseous, the product mixture really takes up a *much* larger volume than the liquid reactant.

The reaction equation is (written so as to correspond to the 20 molecules of the droplet):

$$20\ C_3H_5N_3O_9\ (l) \rightarrow 30\ N_2\ (g) + 60\ CO_2\ (g) + 50\ H_2O\ (g) + 5\ O_2\ (g)$$

You can determine the total chemical energy of the reactant as well as the product mixture using quantum mechanics. The difference between the two values is the source of the energy that is released during the explosion:

Energy of reaction = Difference of the chemical energies of reactants and products.

Here are molecular models of all participants in the reaction (the two surfaces display the calculated electron density for two different density values):

○ **Nitroglycerin** $C_3H_5N_3O_9$

○ **Nitrogen** N_2
○ **Carbon Dioxide** CO_2
○ **Water** H_2O
○ **Oxygen** O_2

- Select one of the molecules in the list.
- From the **View** menu, select **Properties**. From the **Add Property** menu (lower left corner), select **Energy → Energy (Quantum Theory)**. (If the property seems to be missing, you may not yet have selected one of the molecules from the list above.)
- Find the energy value and proceed to the next molecule.

Note: All energies come out as huge negative numbers because of the strong electrostatic attraction between the positively charged nuclei and the negatively charged electrons. Initially, the quantum mechanical calculations assume that all nuclei and electrons are at infinite distance from each other. The particles are then brought together so as to form the final molecule—this is bound to yield very strong electrostatic attraction no matter the details.

Analysis

1. What is the chemical energy of 1 mol of nitroglycerin molecules?

2. What is the chemical energy of 1 mol of each of the product molecules?

3. What is the *total* chemical energy of 1 mol of nitroglycerin "droplets," each containing 20 molecules?

4. Neglecting intermolecular energy terms, what is the *total* chemical energy of 1 mol of product mixtures (each obtained from 20 molecules of nitroglycerin)?

5. What is the calculated energy of reaction for 1 mol of nitroglycerin "droplets"?

6. What is the calculated energy of reaction for 1 mol of nitroglycerin *molecules*?

7. Is this an endothermic or exothermic reaction?

Name **_Lab Section_** **_Date_**

The Entropy of the Phases of Iodine

Objectives

How do we explain that many chemical phenomena will spontaneously proceed in one direction, but not in the opposite direction? It is common to invoke "favorable" energy changes, but these can't really be the explanation, since the Law of Energy Conservation means that every favorable change must be accompanied by an *unfavorable* change somewhere else—it is just that we usually don't pay any attention to it!

The concept really needed to explain the directionality of processes is entropy. In this experiment, you will

- monitor the entropy changes associated with common phase transitions,
- connect the concept of entropy with positional disorder.

Procedure

Iodine is a solid at room temperature. While sublimating easily (going directly from the solid phase to the gas phase), it also undergoes a "regular" melting transition at T = 114 °C, followed by evaporation at T = 184 °C.

Shown are molecular models for the three phases, each containing 48 molecules and at temperatures of 25 °C, 114 °C, and 184 °C, respectively:

Iodine: ● **Solid** ○ **Liquid** ○ **Gas**

Note: To facilitate the subsequent analysis, the three samples have all been "autoscaled", i.e., each sample is shown screen-filling. The gas phase sample is much bigger than the liquid and solid samples, and the molecules in it (shown in a different style for easier visibility) in fact do move faster than the molecules in the liquid and solid samples.

Start simulations of the samples by clicking on the corresponding button at the bottom of the model area:

☐ *When Running, Autostart After Sample Change*

The entropy of the chosen sample is:

$$S = \ldots$$

The value shown is the *molar* entropy, i.e., the value for 1 mol of the shown system (~6×10^{23} molecules). Notice that the unit of the molar entropy (J K^{-1} mol^{-1}) happens to be the same as that of the universal gas constant, R.

Analysis

1. The structure of the solid exhibits a considerable degree of symmetry (despite a certain "blur" that is due to thermal motion). Does this "order" go along with a relatively low or relatively high value of the entropy?

2. In the gas, everything is random—more or less, that is. For example, the particles change their positions regardless of the positions of other particles. Does this "disorder" go along with a relatively low or relatively high value of the entropy?

3. At first glance, the liquid structure also looks random. However, locally there is still structure, as each particle is temporarily confined to the "cage" or "cavity" formed by its neighbors. In other words, the liquid particles are not in completely random positions. What is the entropy of this sample relative to the two other ones?

4. Given your observations, propose a correlation between positional ("visible") order and entropy.

To gain more insight into the phase changes, generate a plot of the entropy as a function of temperature:

- From the **View** menu, select **Plots**. From the **Add Plots** menu (upper left corner), select **XY Plot...**.
- For the "X Axis," select **Temperature**. For the "Y Axis," select **Entropy (Molar)**. Click **Next** and request a **Smoothed Fit**. Click on **Finish**.
- With the simulation running, record a temperature-entropy datapoint by clicking on the **Record** button above the plot.
- Using the shown slider control for temperature, record another 4 datapoints that span the given temperature range.

- Switch to the next sample and record a total of 5 temperature-entropy datapoints along the same lines.
- When done with all three samples, bring up the **Plot Edit** dialog (above the plot, click on the pencil icon).
- In the "Y Axis" section (lower half of panel), set the checkmark for **User Defined Range** and change the number of "Tickmarks" to **9**. In the same section, also request **Grid Lines**. Click **OK**.

---

5. Print out the plot and mark the "Solid → Liquid" and "Liquid → Gas" phase transitions.

6. The *entropy of fusion* describes the "Solid → Liquid" transition. What do you find for the entropy of fusion of iodine?

7. The *entropy of evaporation* describes the "Liquid → Gas" transition. What do you find for the entropy of evaporation of iodine?

8. What is (approximately) the ratio of the entropies of evaporation and fusion?

9. What does the value of the ratio imply for the positional disorder in solids, liquids, and gases—is the liquid closer to the solid or closer to the gas phase?

Atomic and Nuclear Structure

The Structure of an Atom with d-Orbitals

Objectives

To analyze the complete set of occupied atomic orbitals of the lightest noble gas that includes d-orbitals.

Procedure

The shown controls allow you to display any of the occupied orbitals of a *krypton* atom in its electronic ground state. Answer the following questions by inspecting the arrangement of buttons and/or by displaying one (or sometimes several) of the orbitals.

Analysis

1. How many electrons total does a krypton atom have? Explain how you can get the answer to this question simply from the periodic table of the elements (**Tools** → **Periodic Table**).

2. Count the number of occupied orbitals in krypton. Is there a simple relationship with the total number of electrons? What is this relationship?

3. What physical reason or "rule" is behind your answer to the last question?

4. The orbitals of krypton (and of every other atom) differ with regard to three general geometric properties that reflect a certain type of "quantum number". Describe the three geometric properties that are evident by comparing the following orbitals:

   a) $2p_y$, $3p_y$, and $4p_y$

   b) 3s, $3p_x$, and $3d_{z^2}$

   c) $3p_x$, $3p_y$, and $3p_z$

5. How many occupied shells of electrons does the krypton atom have?

6. Some of the shells have "subshells". What are the subshells in krypton for
   a) principal quantum number 2?
   b) principal quantum number 3?
   c) principal quantum number 4?

7. How many electrons does it take to completely fill an s-subshell?

8. Display the 1s orbital. What is the physical reason that it is so "tiny"?

9. How many electrons does it take to completely fill a p-subshell?

10. What are *all* of the individual orbitals of the shell with quantum number 2?

11. One after the other, display the orbitals belonging to the shell of quantum number 2. Why are these orbitals *not* as tiny as the 1s orbital?

12. Is there a difference between two electrons that happen to occupy the same orbital? If yes, spell out the difference.

13. What is the lowest principal quantum number that allows for d-orbitals?

14. While one d-orbital has a distinct "dumbbell+donut" shape, the other d-orbitals have a four-lobed shape. In total, how many orbitals comprise a d-subshell?

15. List the orbitals that are the *valence orbitals* of krypton. What quantum number have all of the valence orbitals of krypton in common?

16. Remove the checkmark for "Show only one orbital at a time", and then display the boundary surfaces for the $4p_x$, $4p_y$, and $4p_z$ orbitals *simultaneously* (but no other surfaces). In terms of the electron density, what is effectively the shape of the atom? (The color [= "phase"] of the orbital lobes doesn't matter once you proceed from the orbitals to the electron density.)

17. Write down the complete electron configuration of krypton.

18. Identify which of the orbitals in the following groups do *not* exist:

    a) 2s, 1p, 3s, 3d

    b) 1s, 3p, 5s, 2d

Chemical Bonding

Name **Lab Section** **Date**

Covalent Bonding in Chlorine and Nitrogen

Objectives

- To examine the formation of a chlorine molecule from its constituent atoms.
- To determine the equilibrium bond length and bond strength from a potential energy diagram.
- To juxtapose the actual electron density of the bonded molecule with symbolic representations of covalent bonds.
- To compare the bond in molecular nitrogen with that in molecular chlorine.

Procedure and Analysis

Molecular chlorine, Cl_2, is a typical example of a covalently bonded molecule. A sequence of calculated electron densities is available that shows two chlorine atoms as they approach each other: E_{relative} = **0 kJ/mol**

The shown energy value is taken relative to the energy of the dissociated atoms. It varies between negative values for favorable ("bonded") distances and positive values for unfavorable distances.

1. Generate a plot of the energy as a function of distance:
    - From the **View** menu, select **Plots**. From the **Add Plots** menu (upper left corner), select **XY Plot...**. For the "X Axis," select **Cl-Cl Distance (pm)**. For the "Y Axis," select **Relative Energy (kJ/mol)**.
    - Click **Next**. Request a **Scatter Plot** and click on **Finish**. (You can make the entire plot bigger by dragging the right-side boundary of the plot area.)

   What do you find for the equilibrium bond length of chlorine?

2. Apart from the fact that it corresponds to a minimum of the energy, is there anything really unique about the equilibrium bond distance? Provided that energy is available, is the molecule "allowed" to be at distances other the equilibrium bond length?

3. The dissociation energy is the difference in energy between the bonded molecule and the completely separated atoms. What is the calculated dissociation energy of chlorine?

4. Usually, we are only interested in the molecule at its normal, minimum energy bond length. We then work with a simplified model (analogous to Lewis structures) that does not show electron distributions, but a symbolic bond:

○ **Abstract Representation** Cl_2

Several model styles are available to depict the molecule in this more cartoonish way:

○ **Ball and Wire**
○ **Ball and Spoke**
○ **Tube**
○ **Space Filling**

What is it that is highlighted by the "Ball and Wire", "Ball and Spoke", and "Tube" model styles?

5. What is it that is highlighted by the "Space Filling" model style?

6. Nitrogen is also known to form a covalently bonded diatomic molecule, N_2, albeit with a rather short bond. Here are some snapshots of the electron density for different distances of the two atoms:

○ **540 pm**
○ **400 pm**
○ **175 pm**
○ **150 pm**
○ **135 pm**
○ **110 pm**
○ **105 pm**
○ **90 pm**
○ **83 pm**

Generate a second plot for the distance-energy relationship of this molecule:

- From the **Add Plots** menu, select **XY Plot...**. For the "X Axis," select **N-N Distance (pm)**. For the "Y Axis," select **Relative Energy (kJ/mol)**.
- Click **Next**. Request a **Scatter Plot** and click on **Finish**.

What do you find for the equilibrium bond length of nitrogen?

7. What is the dissociation energy of nitrogen?

8. Nitrogen has a "triple" bond, while chlorine has a "single" bond. If we ignore the fact that we are comparing molecules whose atoms are different, what is the ratio of the two bond strengths?

9. Do the curves for the energy as a function of distance look fundamentally different for chlorine and nitrogen?

Name ***Lab Section*** ***Date***

Classifying Diatomic Molecules by Bond Polarity

Objectives

The degree of ionic and covalent bonding can often be estimated by simply looking at the difference in electronegativity (EN) between the bonded atoms. In this experiment, you will apply this technique to 18 dimers that show a systematic variation in the electronegativity difference between the atoms.

Procedure and Analysis

The dimers in this experiment are all shown with a connecting "bond"—not only if the bonding is covalent in character (in which case it is "normal" to draw an explicit bond), but also if it is ionic in character (for which we usually do *not* draw explicit bonds).

1. From the **View** menu, select **Properties**. From the **Add Properties** menu (lower left corner), select **Atom → Electronegativity.** Find the electronegativity for both atoms and enter the *difference* in the following table:

	ΔEN	Bonding Type
⊙ **Cl_2**		
○ **BrCl**		
○ **IBr**		
○ **HI**		
○ **ICl**		
○ **HBr**		
○ **HCl**		
○ **BrF**		
○ **LiI**		
○ **NaI**		
○ **KI**		
○ **LiBr**		
○ **NaBr**		
○ **KBr**		
○ **NaCl**		
○ **KCl**		
○ **NaF**		
○ **KF**		

2. Of the elements appearing in these diatomics, which one is the most electronegative and which one is the most electropositive?

3. To which corner of the periodic table would you have to go to find *the* most electropositive element?

4. Display the electrostatic potential maps of the diatomic molecules:

   ○ **Hide** ○ **Mesh** ○ **Transparent** ○ **Solid**

   Blue indicates that the area interacts as if there was *effectively* positive charge and red indicates that the area interacts as if there was *effectively* negative charge; green is the neutral color.

   Using your subjective judgment, classify the bonding type as either "covalent," "polar covalent," or "ionic" in each case (fill in the table above).

5. At what electronegativity difference would you draw the line between ionic and covalent bonding?

6. Do you think that your answers to the last two questions are unique? If yes, explain why. If no, also explain why.

7. Hydrogen fluoride deviates somewhat from "average" behavior with regard to the degree of covalent bonding. Given that hydrogen fluoride is often classified as "polar covalent," is the molecule more ionic or more covalent than one might have expected?

Name ***Lab Section*** ***Date***

Resonance of Carbonate Ion and Ozone

Objectives

- To properly characterize the molecular structures of carbonate ion and ozone.
- To compare the real structure of carbonate to several artificial structures where the geometry is constrained to that of individual Lewis structures.
- To deduce the energy associated with resonance stabilization.

Procedure and Analysis

Shown are a common polyatomic ion and a molecule—both structures have been obtained from good quantum mechanical calculations:

● **Carbonate** $[CO_3]^{2-}$ ○ **Ozone** O_3

1. Both species are of the kind where it is possible to write down more than one Lewis structure. Draw the four plausible Lewis structures for carbonate and the three plausible Lewis structures for ozone.

2. Examine the molecular geometry of the models:
   - From the **View** menu, select **Properties**. From the **Add Property** menu (lower left corner), select **Geometry → Distance**.
   - Measure the bond distances for the ion and for the molecule.

   What are the three bond distances for carbonate and what are they for ozone?

3. Do the measured bond distances for carbonate map onto any of the ion's Lewis structures?

4. Do the measured bond distances for ozone map onto any of the molecule's Lewis structures?

5. Next, examine the partial charges associated with the atoms of the two ions:
   - From the **Add Property** menu (lower left corner), select **Electrostatics → Atomic Charge (Quantum Theory)**.
   - Measure the (calculated) *oxygen* partial charges for carbonate as well as for ozone.

   Is the variation of the measured charges, or the lack of variation, compatible with any of the Lewis structures?

6. Examine the electron clouds of both ion and molecule (they are shown for a relatively high isovalue of the electron density, close to the nuclei):

   Electron Density: ⦿ **Hide** ○ **Mesh** ○ **Transparent**

   Describe the extent to which the electron distributions of the ion and the molecule are "symmetric".

7. On the computer we can do something that we can't do in reality, and that is calculate the energies of structures that resemble individual Lewis structures! What we have do is to "constrain" the molecular geometry to the assumed geometry of the Lewis structure. For carbonate, for example, this can be accomplished if we fix the bond lengths to be that of "standard carbon-oxygen single bonds" and "standard carbon-oxygen double bonds". This has been carried out for the shown models (for reference, the model of the true structure is also included in the list):

   ○ **Artificial I** (Constrained)
   ○ **Artificial II** (Constrained)
   ○ **Artificial III** (Constrained)
   ○ **Artificial IV** (Constrained)
   ⦿ **True Structure** (Unconstrained)

   Now determine the energy of each of these structures:

   - From the **Add Property** menu (lower left corner), select **Energy** → **Energy (Quantum Theory)**.

   As is typical for quantum mechanically calculated molecular energies, you will find a huge negative number for each of the structures, reflecting the strong electrostatic attraction between the positively charged nucleus and the negatively charged electrons. Nevertheless, one of the five structures is *lowest* in energy. Which one?

8. Which of the Lewis structures is energetically "worst" (= has the least negative energy)? What concept can you invoke to rationalize the observation?

9. By how much (in kJ/mol) is the lowest energy structure stabilized relative to the other structures (in other words, what is the "resonance energy" of carbonate)?

10. Measure the bond distances for the four constrained structures and compare them to the bond distances for the true structure. Is the carbon-oxygen bond in real carbonate closer to a single bond or to a double bond or is it right in between?

Gas Laws

Name **Lab Section** **Date**

The Pressure-Temperature Relationship for Gases

Objectives

When a sample of gas is confined to a container of fixed volume, the pressure that the gas exerts varies with the temperature. In this experiment, you will

- examine the pressure-temperature dependence for a sample of gas,
- record multiple "isochores" by also varying the volume of the system.

Procedure

This experiment can be safely ☺ carried out with any of the following very toxic samples of gas:

◉ **Nitric Oxide** NO (*g*)
○ **Boron Trifluoride** BF_3 (*g*)
○ **Carbon Monoxide** CO (*g*)

To investigate the relationship between temperature and pressure, first set up a relevant plot:

- From the **View** menu, select **Plots**. From the **Add Plot** menu (upper left corner), select **XY Plot...**. For the "X Axis," select **Temperature**. For the "Y Axis," select **Pressure**.
- Still in the "Choose Plot Axes" dialog, click on **Advanced...** and select **Allow for multiple curves that differ in the following parameter**. In the menu, select **Volume** and click **OK**.
- Click **Next** and request a **Linear Fit**. Click on **Finish**.
- Start the simulation (below the model, click on the **Start** button). After a while, record a temperature-pressure datapoint by clicking on the Record button above the plot.
- Using the shown slider, record data for at least 5 different settings of the temperature.
- For each new set of conditions, click on the **Record** button (the button only lights up after the simulation data have become available; this may take a little while).

Analysis

1. What are the "controlled variables" in the experiment up to this point? Measure their values by accessing the **Add Property** menu (lower left corner).

2. What is the general dependence of pressure on temperature?

3. Explain how the observed behavior can be explained from the viewpoint of kinetic molecular theory. *Note:* Your explanation should make a connection between the terms "temperature", "molecular speeds", and "collisions".

4. Sketch what a plot of P/T vs. the temperature would look like.

5. Switch to a second volume setting:

   Volume: ○ **Small** ● **Medium** ○ **Large**

   Using the same protocol as before, record datapoints for the new "isochore". When done, repeat the entire procedure for the third volume setting that is available.

   Do the three curves that you obtained have the same functional form?

6. Do the three curves have the same slope?

7. Do the curves intersect and if yes, where?

8. What is the relevance of this computer experiment for the definition of the "absolute zero of temperature"?

9. *Optional:* Repeat the experiment with another one of the samples of gas from above. (You can simply reload the page, but remember to print out all generated plots before reloading—they will be lost during the reload.)

   Do you find any differences and if yes, what are they?

The Effusion of Gas Mixtures

Objectives

Effusion refers to the flow of gas through microscopically small holes—holes so small that for the given gas density only one molecule at a time will pass through. In this experiment, you will

- monitor the effusion of gas mixtures through an opening in an enclosed container,
- determine the rates of effusion for the individual components,
- establish a correlation between the rate of effusion and molar mass,
- assess the applicability of Graham's Law.

Procedure and Analysis

Samples of two gas mixtures are available, each confined to half of its respective simulation cell by an impenetrable barrier:

⦿ **Carbon Monoxide + Hydrogen**
○ **Sulfur Hexafluoride + Nitrogen + Helium**

Select one of the samples—the number of molecules in the (entire) simulation cell is

$N_{\text{Carbon Monoxide}} = 50$
$N_{\text{Hydrogen}} = 50$

1. What is the composition of the gas mixture that you chose (in mole fractions)?

2. Initiate a simulation of the mixture (below the model, click on the **Start** button) and let it run for at least 10×10^{-12} s. The barrier contains a hole that you can alternately open and close:

   Hole: ○ **Closed** ○ **Open**

   Open the hole between the two compartments and watch the simulation for another ~30×10^{-12} s. Do the different kinds of molecules escape at the same rate?

3. What are roughly the rates of escape, in "molecules per 10^{-12} s" for the components? (You may want to refresh the page and carry out multiple runs.)

4. Graham's Law says that the ratio of the effusion rates for two gases is the inverse ratio of the square roots of the molar masses:

$$rate_A / rate_B = (M_B / M_A)^{1/2}$$

Is Graham's Law compatible with the results from the computer experiment?

5. What is the composition (in mole fractions) of the mixture of gas molecules that have escaped after the ~30×10^{-12} s computer experiment?

6. Repeat the experiment with the second gas mixture from above. Which answers to the previous questions remain the same (if any)?

7. Which answers to the previous questions change (if any) and in what way?

8. The molecular explanation of Graham's Law has to do with the *rate* with which the molecules strike the opening. That rate in turn is correlated with the molecular speeds. What is therefore the molecular explanation for the higher effusion rates of light gases?

9. A skeptical student suggested that the sulfur hexafluoride molecules in the second simulation sample only escape more slowly because they "don't fit" that well through the opening. How could this conjecture be disproved?

10. Suppose you had 10 "effusion cells" like the carbon monoxide-hydrogen system that you have been dealing with here. Suppose these cells were chained up such that the effused gas from one cell provides the gas supply for the next. What would be the composition of the gas mixture after passing through the entire chain? (A qualitative answer will suffice.)

Intermolecular Forces and States of Matter

Hydrogen Bonding in Mixtures

Objectives

To investigate hydrogen bonding in mixtures of liquids.

Procedure

Hydrogen bonding is not limited to pure liquids. At least some (or possibly all) of the following mixtures exhibit hydrogen bonding:

I ⦿ **Propanone + Water** (Acetone + Water)
II ○ **Ethanol + Water**
III ○ **DMMA + Propanone** (DMF + Acetone)
IV ○ **DMMA + Water** (DMF + Water)
V ○ **Ethanamide + Methanol** (Acetamide + Methanol)

Initiate short simulations of the samples (below the models, click on the **Start** button):

☐ *When Running, Autostart After Sample Change*

In each case, examine the molecular structure; the analysis is facilitated by using different model styles for the two components.

Analysis

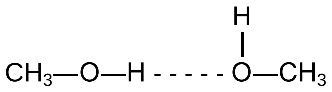
1. Which of the systems show any hydrogen bonding at all? If not, why not?

Hydrogen Bonds: ⦿ **Hide** ○ **Show**

2. If one component is labeled "A" and the other "B," does hydrogen bonding occur
   - between A and A ?
   - between B and B ?
   - between A and B ?

   Analyze each of the systems.

3. Where applicable, draw the hydrogen-bonded dimers, e.g., for methanol-methanol an appropriate drawing would be:



$$CH_3{-}O{-}H \text{ - - - - - } \overset{\overset{H}{|}}{O}{-}CH_3$$

   Is there any case where the same two molecules can be hydrogen-bonded in more than one way?

4. Do you find any "closed rings" of hydrogen-bonded molecules in the simulation cells? If yes, what kind of molecule do they involve in each case? Analyze each of the systems.

5. Hydrogen bonding is among the strongest of intermolecular forces, if not the strongest. Give an example of a physical property of these liquid mixtures that is expected to be prominently affected by the presence of hydrogen bonding.

6. Only a few elements are electronegative enough to occur in compounds with major hydrogen bonding capability. Which strongly hydrogen bond-forming element(s) are *not* represented in any of the examples in this experiment?

7. Water appears in several of the mixtures of this experiment, and it is in fact the most famous hydrogen-bonding pure liquid. Give three examples of the properties of water that are closely related to the presence of hydrogen bonding.

Name ***Lab Section*** ***Date***

Bonding in Crystalline Solids

Objectives

An analysis of the binding forces in crystals suggests to distinguish between four major types of solids: ionic, network-covalent, molecular, and metallic. In this experiment, you will

- examine representative models for the four major types,
- correlate structural features with macroscopic properties.

Concepts

The crystals of *ionic* solids are hard and brittle and melt at high temperatures:

◉ **Cesium Iodide** CsI (*s*)
○ **Calcium Fluoride (Fluorite)** CaF_2 (*s*)
○ **Magnesium Oxide** MgO (*s*)
○ **Ammonium Chloride** NH_4Cl (*s*)

Network-covalent solids are even harder than ionic solids and tend to melt at exceedingly high temperatures:

○ **Diamond** C (*s*)
○ **Silicon Dioxide** (Quartz) SiO_2 (*s*)
○ **Boron** B (*s*)

Molecular solids are the other extreme—they tend to be fairly soft and have moderate melting points:

○ **Iodine** I_2 (*s*)
○ **Solid Water** (Ice) H_2O (*s*)
○ **Glucose** $C_6H_{12}O_6$ (*s*)

Metallic solids are not very uniform in that there is considerable variation with regard to hardness and melting points:

○ **Magnesium** Mg (*s*)
○ **Gold** Au (*s*)
○ **Tungsten** W (*s*)

What sets metallic solids apart from each of the other types of solids is that they exhibit excellent electrical as well as thermal conductivity.

Analysis

1. What group of solids is held together by electrostatic attractions between positive and negative ions?

   Charge Labels: ⊙ **Hide** ○ **Show**

2. What type of solid structure amounts to the presence of "giant molecules"?

3. Which of the four types of solids include examples where there is some covalent bonding?

4. Which of the four types of solids cannot possibly occur as the structure type of an element?

5. The melting points of cesium iodide, fluorite and magnesium oxide are 621 °C, 1,402 °C, and 2,852 °C, respectively:

   ⊙ **CsI** (*s*) ○ **CaF_2** (*s*) ○ **MgO** (*s*)

   What could be a simple physical explanation for the variation of the melting points?

6. The binding forces between the particles of molecular solids are "Van der Waals forces":

   ○ **I_2** (*s*) ○ **H_2O** (*s*) ○ **$C_6H_{12}O_6$** (*s*)

   Two of the molecular solids shown include a particularly *strong* form of Van der Waals force. What force is that and what are the models affected by it?

7. The metallic solids are "densely packed" in that each particle has a large number of immediate neighbors:

   ○ **Mg** (*s*) ○ **Au** (*s*) ○ **W** (*s*)

   - Change the model style of the selected structure to **Style → Ball and Spoke**.
   - *Right-click* on an atom. Select **Set Clipping Center**.
   - Use the scrollwheel to display the clipping sphere screen-filling.
   - Now *select* the clipping sphere by clicking on it → its color changes to golden. Use the scrollwheel to adjust the size of the clipping sphere so that you can see the shell of *nearest* neighbors of the chosen atom. Click on the background to deselect the clipping sphere.

   What is the number of direct (nearest) neighbors for the three metallic structures shown here?

8. Compare the "cohesive energies" of the three metallic substances (those are the energies *relative* to the separated atoms in the gas phase):

   ○ **Mg** (*s*) ○ **Au** (*s*) ○ **W** (*s*)

   - From the **View** menu, select **Properties**.
   - From the **Add Propety** menu (lower left corner), select **Energy → Potential Energy (Molar)**.

   What values do you find and what do you *predict* for the relative melting temperatures of the three metals?

9. The crystal structures of noble gases look very much like that of metals:

   Examples: ○ **Argon** Ar (*s*) ○ **Xenon** Xe (*s*)

   However, the bonding is not metallic, but rather that of weak dispersion forces. Accordingly, noble gas solids melt at very low temperatures (at –189 °C and –112 °C for argon and xenon, respectively). Given these properties, what is the best classification for this type of atomic solid?

10. The solids shown in this experiment already include several substances that we are familiar with from everyday life. For each of the four major categories, give one more example of a "common" substance that represents that category.

Solutions and Solubility

Name ***Lab Section*** ***Date***

Specifying the Concentration of a Dissolved Pesticide

Objectives

The following organic compound is a pesticide that is commonly found in mothballs:

⊙ **1,4-Dichlorobenzene** (p-Dichlorobenzene) $C_6H_4Cl_2$

In this experiment, you will

- compare four different concentration measures—mass percent, molarity, molality, and mole fraction—for solutions of this compound in non-aqueous solvents,
- consider the effect of temperature changes on the various measures of concentration.

Procedure and Analysis

1,4-Dichlorobenzene dissolves much more easily in a nonaqueous solvent such as “ethanenitrile” than in water:

○ **Ethanenitrile** (Acetonitrile) C_2H_3N

A model is available that shows a room temperature solution of 1,4-dichlorobenzene in ethanenitrile:

○ **Solution**

- From the **View** menu, select **Properties.** Determine system properties as needed in order to establish the concentration measures requested below.

Please always make clear what data you used in order to arrive at an answer:

1. What is the concentration of 1,4-dichlorobenzene in this solution in mass percent? Give your answer to two significant figures.

2. What is the molarity of 1,4-dichlorobenzene in this solution? Give your answer to two significant figures and include proper units.

3. What is the molality of 1,4-dichlorobenzene in this solution? Give your answer to two significant figures and include proper units.

4. What is the mole fraction of 1,4-dichlorobenzene in this solution? Give your answer to two significant figures.

5. Suppose the room temperature solution is cooled down to –25 °C. Would you expect the concentration of 1,4-dichlorobenzene in mass percent to be smaller, the same, or larger?

6. What will the effect of the temperature change be on the molarity—will it be smaller, the same, or larger?

7. What will the effect of the temperature change be on the molality—will it be smaller, the same, or larger?

8. What will the effect of the temperature change be on the mole fraction—will it be smaller, the same, or larger?

9. Assume that the solvent is methylbenzene instead of ethanenitrile:

   ○ **Methylbenzene** (Toluene) C_7H_8

   Also assume that the number of solute and solvent molecules is exactly the same as before. Is the concentration in mass percent smaller, the same, or larger, or is it impossible to answer the question without any additional information? (Note that you can determine the molar mass of the new solvent with the **Properties** panel.)

10. Is the mole fraction smaller, the same, or larger, or is it impossible to answer the question without any additional information?

11. Is the molality smaller, the same, or larger, or is it impossible to answer the question without any additional information?

12. Is the molarity smaller, the same, or larger, or is it impossible to answer the question without any additional information?

Acid–Base Chemistry

Name **Lab Section** **Date**

Molecular Structure and Acid Strength

Objectives

- To specify the factors that allow to predict acid strength given a molecular structure.
- To predict the acid strength of several substances from charge interaction maps (electrostatic potential maps).
- To consider acids with resonance stabilization of the conjugate base.

Procedure

If a molecule acts as a Bronsted-Lowry acid, a hydrogen-containing bond is broken and a hydrogen ion is released:

$$X—H \rightarrow X^- + H^+$$

The energetic likelihood of this reaction depends on several factors:

- *Polarity of the X-H bond:* The more of a positive charge the hydrogen carries prior to dissociation, the more easily it will come off as a proton, and the more acidic the molecule.
- *Strength of the X-H bond:* The weaker the bond, the more easily it will break, and the more acidic the molecule.
- *Stability of the conjugate base (X^-):* The more stable the base, the more acidic the molecule.

The first of these three factors can be graphically represented with charge interaction maps ("electrostatic potential maps"). In fact, such maps can be useful for guessing acidity and basicity from molecular structure. This does not mean that one can readily predict the *absolute* acid strength (K_a value) of an arbitrary molecule—this is difficult. What one can do, however, is to

- locate the *most* acidic protons (if a molecule has more than one), and to
- *rank* related molecules by acidity (or basicity).

As an example, here are three potential acids:

◉ **Nitric Acid** HNO_3
○ **Ethanoic Acid** (Acetic Acid) CH_3COOH
○ **Ethanol** C_2H_5OH

Use the shown control to display electrostatic potential maps of the molecules:

○ **Hide** ○ **Mesh** ○ **Transparent** ○ **Solid**

Blue colored regions in these maps act as if they were effectively positively charged. Conversely, *red* colored regions act as if they were effectively negatively charged. Green is the neutral color.

Analysis

1. Here are the measured acid dissociation constants K_a of the three compounds:

    - nitric acid is *strong*: $K_a \rightarrow$ very large
    - ethanoic acid (acetic acid) is *weak*: $K_a = 1.8\times10^{-5}$
    - ethanol is *not* acidic: $K_a = 10^{-16}$

    What is the correlation between acid strength and "blueness" at the hydrogen position?

2. Next, compare the acid-base properties of the following molecules:

    ○ **Phosphoric Acid** H_3PO_4
    ○ **Methanol** CH_3OH
    ○ **Methanoic Acid** (Formic Acid) HCOOH
    ○ **Sulfuric Acid** H_2SO_4
    ○ **Phenol** $_6H_5OH$

    Which acid do you predict to be the most acidic?

3. Which molecule do you predict to the least acidic?

4. For these molecules, retrieve as many experimental acid dissociation constants from your textbook as you can. Is the ranking of the predicted acidities the same as that of the measured ones?

5. Draw the Lewis structure for the *conjugate base* of each of the acids.

6. For each case, compare the structure of the conjugate base with that of the acid. Are there any cases of a “special stability” of the base (i.e., a mechanism of stabilization *not* shown by the acid)?

Kinetics and Equilibrium

Name ***Lab Section*** ***Date***

Examining a Reaction Mechanism

Objectives

Carbonyl difluoride can react to form carbon dioxide and hydrogen fluoride in a gas phase hydrolysis reaction:

$$COF_2\ (g) + H_2O\ (g) \rightarrow CO_2\ (g) + 2\ HF\ (g)$$

● **Reactants** ○ **Products**

In this experiment, you will examine the detailed mechanism by which this reaction takes place.

Procedure

The sequence of models shows the gradual progress of the reaction at the molecular level:

{ **…Reaction Coordinate…** }

You can monitor the progress of the reaction while displaying isosurfaces for the calculated electron density:

Electron Density: ● **Hide** ○ **Solid** ○ **Transparent** ○ **Mesh**

For the purposes of the following analysis, you need to generate a plot of the total system energy as a function of the reaction coordinate:

- From the **View** menu, select **Plots**. From the **Add Pl**ots menu (upper left corner), select **XY Plot…**.
- For the "X Axis," select **Reaction Coordinate**. For the "Y Axis," select **Relative Energy (kJ/mol)**.
- Click **Next** and request a **Smoothed Fit**. Click on **Finish**.
- Note that you can make the plot bigger (or smaller) by dragging the dividing line between plot area and modeling area.

Analysis

1. Compare the energies of the reactants in the very first frame with that of the products in the very last frame. Is this an exothermic or endothermic reaction?

2. The reaction mechanism includes a total of 4 steps, namely 3 elementary reactive steps and 1 step where one of the intermediate molecules changes its geometry ("conformational" change). Write down the chemical equation for the first elementary step.

3. Write down the chemical equation for the second elementary step.

4. Describe in words what is happening during the step where the only event is an internal geometric change.

5. Write down the chemical equation for the last elementary reactive step.

6. Show explicitly that adding up the three elementary reaction steps leads to the total reaction equation.

7. Clearly mark all intermediates in your print-out of the reaction profile.

8. What is the total number of intermediates?

9. Rank the four steps of the reaction mechanism with regard to the ease with which they can take place (from "easiest" to "most difficult"), or point out which steps offer similar levels of difficulty.

10. Which of the reaction steps is rate-determining?

Organic Chemistry

Name ***Lab Section*** ***Date***

Structure and Properties of Straight-Chain Alkanes

Objectives

More than any other element, carbon has the ability to form long and very stable chains. The shortest "chain" has a length of just two carbon atoms:

⦿ **Ethane** C_2H_6

In this experiment, you will

- build and examine models of some of the longer alkanes, up to a chain length of 16,
- establish a correlation between molecular structure and experimentally measured boiling points,
- consider the reactivity of alkanes.

Procedure

From the **Build** menu, select **Add Atoms**. Working with the (default) **Entry-Level** panel and using "tetrahedral carbon" as the atom type, build models of the following linear alkanes:

○ **Chain Length 4** ○ **Chain Length 8**
○ **Chain Length 5** ○ **Chain Length 10**
○ **Chain Length 6** ○ **Chain Length 16**

For each model, go through the following steps:

- If not shown, open the build panel with **Build** → **Add Atoms**.
- Build the model as a linear (unbranched) chain. Finish by finding a good structure with **Build** → **Minimize**.
- Notice that the chain does not have to be built in a stretched-out fashion as the energy minimization will easily relieve "strain" due to coiling.

When done with all models, exit the build panel (in its upper right corner, click on the close button). All models will now be shown with explicit hydrogen atoms rather than free valences.

Analysis

1. Name each of the built molecules.

2. Select **View** → **Properties**, then from the **Add Property** menu (lower left corner), select **Molecule** → **Molar Mass (Standard Value)**. Determine the molar mass of each of the alkanes that you built.

3. Give a formula for *predicting* the molar mass M if only the chain length N (such as "$N = 5$") is known. (Verify that the formula works with your measured molar mass values.)

4. Try to change a carbon-carbon bond length (work with any of your models):
   - *Double*-click on a bond so that it becomes "selected" (as indicated by a red wrap-around arrow).
   - Drag the mouse up and down with the **Space Bar** and the *right* mouse button depressed (this will change the bond length).
   - Select **Build → Minimize**.

   What happens? The energy minimizer of the program takes the bond length back to its normal value. What is this "normal" bond length?

   - If not already shown, display the **View → Properties** panel. From the **Add Property** menu, select **Geometry → Distance**.
   - Click on any two atoms to find the distance.

   What do you find for the approximate carbon-carbon bond length and the approximate carbon-hydrogen bond length in an alkane?

5. The longer alkanes all tend to take on a "zig-zag" structure with regard to their immediate neighbors. Why is that? *Hint*: Think of the local coordination at each carbon atom.

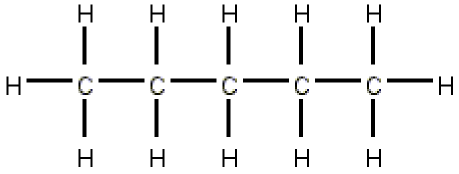
6. Here are the experimental boiling temperatures of the six alkanes that you built:

$$T_A = 287°C \mid T_B = 174°C \mid T_C = 126°C$$
$$T_D = 69°C \mid T_E = 36°C \mid T_F = –0.5°C$$

   How do you expect the temperatures T_A to T_F to correlate with the chain length, i.e., which temperature goes along with which alkane?

7. What is the physical reason for the correlation just stated?

8. Here is a structural formula for one of the molecules:



What aspect of the actual structure is *not* adequately represented by this formula?

9. If not already shown, display the **View → Properties** panel. From the **Add Property** menu, select **Atom → Electronegativity**. Find the *difference* in electronegativity for one of the C–H bonds of one of the molecules. Do you obtain a relatively small (< 0.5) or relatively large (> 1.0) value?

10. Consider how a large difference in electronegativity between the atoms of a molecule contributes to an increase in reactivity. What do you conclude regarding the expected reactivity of alkanes?

Name **Lab Section** **Date**

Structure and Properties of Esters

Objectives

- To identify esters associated with common fruit flavors.
- To build all possible esters of the same molecular formula.
- To consider the synthesis of esters via condensation reactions.
- To predict the products of acid-catalyzed ester hydrolysis.

Procedure and Analysis

Many common fruit flavors can be attributed to the esters of aliphatic carboxylic acids:

- *Apple:* Methyl Butanoate
- *Apricot:* Pentyl Propanoate
- *Banana:* 3-Methylbutyl Ethanoate
- *Orange:* Octyl Ethanoate
- *Pineapple:* Ethyl Butanoate
- *Raspberry:* 2-Methylpropyl Methanoate

1. Assign the right flavors to the following compounds:

A. ____________________

B. ____________________

C. ____________________

D. ____________________

E. ____________________

F. ______________________

2. Switch to an (initially empty) model kit. Select **Build → Add Atoms** and work with the (default) **Entry-Level** panel. Select atom types as appropriate. Determine how many *different* esters you can build with the following molecular formula: $C_4H_8O_2$. Request additional model kits as needed (you may have to reopen the build panel with **Build → Add Atoms**).

3. Name the esters that you built.

4. From the **View** menu, select **Properties**, and from the **Add Property** menu (lower left corner), select **Electrostatics** → **Dipole Moment**. Give the molecular dipole moments of the esters that you built.

5. Give a molecular reason for the similarity or lack of similarity of the dipole moments.

6. The most common synthesis path for esters involves an acid-catalyzed "condensation reaction" between a carboxylic acid and an alcohol. Involving no fewer than half a dozen steps, the actual reaction mechanism is quite complicated, but the essence is the elimination of water from the two reactants. This is highlighted for the reaction of ethanoic acid with ethanol.

   In isotope studies, it has been determined whether the water molecule (or, to be more precise, the water's oxygen) comes from the acid side or alcohol side of the reactant pair. This is illustrated by the models—where does the leaving oxygen come from?

7. By heating esters in acidic solution, the formation reaction can be reversed—this is called *hydrolysis*. Predict the expected hydrolysis products of the listed esters.

   G. ____________________

   H. ____________________

   I. ____________________

   J. ______________________