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Preface

The person responsible for the administration of a general chemistry laboratory program is often the hardest-working member of his or her department. There is an endless number of details associated with this job: scheduling laboratory experiments, scheduling lab instructors, ordering supplies, preparing reagents, grading lab reports, and so on, ad infinitum. The reader perhaps can tell that this is the author’s own occupation!

This Instructor’s Resource Guide is intended to make the job as painless and as rewarding as possible. The notes for each experiment are divided into four parts, described below. In particular, detailed recipes are provided for the preparation of the many reagents required, which in itself will save the instructor much time and effort.

Part A of each set of notes is a general introduction to each experiment from the instructor’s point of view, illustrating what students are expected to learn from the experiment, and oftentimes pointing out pitfalls in the experiment. Specific suggestions for specialized equipment, or possible modification of the experiment, are given for many experiments.

The materials required for each experiment are given as Part B of the notes. In particular, instructions are given for the preparation of the many solutions required for the laboratory experiments. Since a school may be running several sections of laboratory in different rooms at the same time, instructions are most commonly given in terms of preparing one liter of a particular solution, even though the experiment may call for more or less than this as actually performed. One liter was chosen as a standard amount, since it should be relatively easy from this to calculate the actual amounts of solute/solvent needed for your particular situation. For some special reagents, requiring more complicated preparation, instructions are given for the specific amount required for the experiment as performed. The instructor should also take into account that in some instances a given substance may be available in both a hydrated and an anhydrous form: It is always specified in the notes which form the amounts given refer to.

Part C of these notes contains answers to the Pre-Laboratory Questions, whereas Part D has the answers to the Post-Laboratory Questions. Questions requiring students to look up a definition or explanation are keyed as far as possible to sections of the Zumdahl text. Questions involving the looking up of data are generally keyed to the CRC Handbook of Chemistry and Physics.

Comments, criticism, and suggestions are always welcome from users of Experimental Chemistry and this Instructor’s Resource Guide. Over the years I have heard from users as close as the next town, and from as far away as the other side of the world. I always appreciate your help in improving these materials for your students.

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EXPERIMENT 1 The Laboratory Balance: Mass Determinations

A. General Notes

The correct measurement of mass is essential to students’ future performance in the general chemistry laboratory, and this experiment will give the instructor a chance to determine what students may have difficulties in the future. In particular, students need much help in learning to read measuring scales correctly. In everyday life, altogether too many devices have digital displays, and students may have learned to trust such devices absolutely and may not be able easily to read an analog scale correctly.

It is especially difficult for students to appreciate the concept of estimating between the smallest scale divisions of an analog device to obtain the last figure of the measurement. This experiment is a good place to discuss with them the concept that some numbers in a measurement are “certain” and some are “uncertain”. On a triple beam balance, for example, the students see how having to estimate the position of the pointer between scale divisions makes the last significant figure “uncertain”.

As this experiment progresses, it is wise for the instructor to examine student data as they are being recorded by circulating in the lab. In this manner, if it is discovered that a student is reading or recording data incorrectly, the student can be corrected before he or she mentally reinforces the incorrect technique.

This experiment is written without specific reference to a particular type of balance, since so many types of balances are available. The instructor should present a short discussion of the particular type of balance present in the laboratory and should demonstrate the use of the balance to small groups of students. It is helpful to post instructions for the balance on the wall above them for student reference after the demonstration.

If more than one type of balance is available for student use, discuss the rationale for which balance is to be used in which circumstances (e.g., why an analytical balance capable of mass determinations to 0.0001 g would not be used when an experiment calls for only an approximate amount). Since modern balances are so expensive, the instructor should explain and enforce rules for balance use (especially cleanliness).

Estimated time to complete: 60–75 minutes

B. Materials Required (given per 25 students)

2–3 unknown objects per student for mass determination. These may be such things as rubber or glass stoppers of different sizes, or items sold commercially for such purposes. The items should be coded or marked somehow for identification (very small items may be dispensed in coded vials). The correct masses of the items should be measured by the instructor or stockroom staff before the laboratory so that students may check their results. Students must be encouraged to turn in these items at the end of the lab period for use by later sections.

C. Answers to Pre-Laboratory Questions

1. Mass is a measure of the amount of matter in a sample, whereas weight is a measure of the force of gravity acting on a sample. In the laboratory, we determine the mass of a sample by comparison (on a balance) to reference masses.

2. This statement means that the overall mass of the sample should be in the neighborhood of 5 grams but that the precise mass of the sample must be known to the third decimal place.
3. The mass (amount of matter in the object) would not change; however, since the force of gravity is less on the moon, the object would have a lower weight.

4. Most balances contain metallic parts. Having liquids spilled could cause corrosion of the metal parts. In addition, if the balance is electronically powered, liquids can destroy the electronic circuits of the balance, and there would be a danger of electrical shock to the user.

5. The “difference” method typically means that the object has its mass determined when contained in a beaker, and then the mass of the empty beaker is subtracted from the combined weight. This is primarily to keep corrosive chemicals away from the pan of the balance. In the case of balances without an electronic tare feature (e.g., triple-beam balances), using the difference method also avoids having to ensure that the instrument balances when there is no load on the pan each time the balance is used.

D. Answers to Post-Laboratory Questions

1. Most mass measurements are made by difference to allow for discrepancies in the tare weight exhibited by the balance. Using the same balance allows many such discrepancies to cancel out.

2. If an object is warm, it heats the air around it. Since warm air rises, an upward-flowing air current is created around the balance pan, which results in an apparent mass that is lower than the true mass.

3. The typical electronic balance costs in excess of $1000. If a reagent were spilled into the mechanism of the balance, it would almost certainly destroy the balance. Even very careful weighings of reagents on the pan of the balance are likely to leave a residue which would invalidate future determinations. Such reagents might also corrode the pan of the balance which would also affect the masses determined on the balance.
EXPERIMENT 2  The Use of Volumetric Glassware

A. General Notes

The correct measurement of volume is essential to students’ future performance in the general chemistry laboratory, and this experiment will give the instructor a chance to determine what students may have difficulties in the future. In particular, students will need a great deal of help in learning to read measuring scales correctly. It is especially difficult for students to appreciate the concept of estimating between the smallest scale divisions of a device to obtain the last figure of the measurement.

As this experiment progresses, it is wise for the instructor to examine student data as they are being recorded by circulating in the lab. In this manner, if it is discovered that a student is reading or recording data incorrectly, the student can be corrected before he or she mentally reinforces the incorrect technique. For example, if the instructor notices that a student is recording buret volumes to only one decimal place, it is possible to explain to the student on the spot, while the buret is in front of him or her, how and why we record such volume readings to a second, estimated decimal place.

This experiment introduces students to volumetric measuring glassware of both low and high precision. In particular, the use of a volumetric transfer pipet is covered since a number of the later experiments make use of such pipets. Because several types of pipet safety bulbs may be available, the instructor should demonstrate the type of bulb the students will actually use.

Estimated time to complete: 75–90 minutes

Since students may not have yet covered the concept of density in their lecture course, it is suggested that the calculations of pipet volumes/mass of water transferred be covered at the chalkboard.

B. Materials Required (given per 25 students)

Set-up of several different-sized graduated cylinders containing different amounts of colored water. The cylinders should be marked with a code letter for students to distinguish them. Either the cylinders should be sealed with a rubber stopper to prevent evaporation, or the instructor should read and record the volume of liquid in the cylinders at the start of the lab period.

25 25-mL pipets
25 pipet safety bulbs
25 50-mL burets and buret stands/clamps
5–6 buret brushes
C. Answers to Pre-Laboratory Questions

1. For the 1-mL pipet: \( \frac{(5)(0.05)/(1.00)}{(100)} = 25\% \text{ error} \)
   For the 5-mL pipet: \( \frac{(5)(0.05)/(5.00)}{(100)} = 5\% \text{ error} \)
   For the 10-mL pipet: \( \frac{(5)(0.05)/(10.00)}{(100)} = 2.5\% \text{ error} \)

2. For the 10-mL sample: \( \frac{(0.5)/(10)}{(100)} = 5\% \text{ error} \)
   For the 20-mL sample: \( \frac{(0.5)/(20)}{(100)} = 2.5\% \text{ error} \)
   For the 40-mL sample: \( \frac{(0.5)/(40)}{(100)} = 1.25\% \text{ error} \)

3. A rubber safety bulb is always used to prevent aspiration of toxic or corrosive substances into the mouth.

4. When water is confined to a narrow glass tube, the interaction between water molecules in contact with the molecules of the glass is different than the interaction among water molecules far away from the glass. This results in the curving of the surface of the water, and this curved surface is referred to as a meniscus. By convention, we read across the bottom of a meniscus.

5. “TC” indicates that the device is intended “to contain” the marked volume; “TD” means the device is intended “to deliver” the indicated volume. The temperature is usually specified since the volume changes with temperature. So, for example, a 250-mL volumetric flask marked “TC-20” would contain 250.0 mL at 20°C. A 5-mL pipet marked “TD-20” would deliver 5.00 mL at 20°C.

D. Answer to Post-Laboratory Question

It is likely that students will conclude that the buret and the pipet permit similar precision, whereas the graduated cylinder permits less precision. Typically, a graduated cylinder is used when only an approximate volume is needed. A volumetric transfer pipet is used when a precise, specific volume is needed, and a buret may be used when a precise, nonspecific volume is required.
A. General Notes

Density is a useful property of matter and one that is often misunderstood by students. It might be helpful to have set out in the laboratory, for students to compare, several samples that have the same mass, but have very different densities (e.g., a pound of plastic foam packing “peanuts” and a pound of lead pellets). The age-old question, “Which weighs more, a pound of feathers or a pound of lead?”, can be a real problem for students. It may be necessary to review the geometry involved in the calculation of the volume of the regularly shaped solid.

Estimated time to perform: 120–150 minutes

B. Materials Required (given per 25 students)

25 regularly shaped solids, coded with identification numbers. The densities of these solids should be measured by the techniques discussed in Part A of the experiment for grading purposes. Such solids are sold commercially from science education vendors.

2–3 500-g bottles of metal pellets (e.g., copper or lead shot). A container should be provided for collecting these pellets. The pellets may be spread out on a large evaporating dish or tray and dried in a 110°C oven for 1–2 hours for reuse.

unknown liquid samples (25 mL per student)

If desired, individual samples may be dispensed in coded 25×200-mm test tubes. Otherwise, the instructor should be provided with several coded 8-ounce bottles of the different liquids for dispensing to students. Possible unknown liquids include

- 95% ethanol
- cottonseed oil
- corn syrup
- 5–30% sodium chloride solutions (see Part C)

1–2 kg sodium chloride

Salt sold at the super market for pickling or as Kosher salt is more than adequate, and much less expensive
C. **Answers to Pre-Laboratory Questions**

1. Volume of metal = 26.8 – 21.7 = 5.1 mL  
   Density of metal = 18.45 g/5.1 mL = 3.6 g/mL

2. Mass of liquid = 40.1825 – 32.4257 = 7.7568 g  
   Density of liquid = 7.7568 g/10.00 mL = 0.7757 g/mL

3. \[50.0 \text{ g} \times \left( \frac{1 \text{ mL}}{0.785 \text{ g}} \right) = 63.7 \text{ mL} \]  
   \[50.0 \text{ mL} \times \frac{0.785 \text{ g}}{1 \text{ mL}} = 39.3 \text{ mL} \]

4. Specific gravity is the *ratio* of the density of a sample to the density of some reference substance (usually water) at the same temperature. Since specific gravity is a ratio of two densities, it has no units.

D. **Answers to Post-Laboratory Questions**

1. If the solid were hollow, the volume measured would be larger than the actual volume of the matter in the solid. If the volume measured is too large, the density determined will be too low.

2. If air bubbles adhered to the metal pellets, the volume determined would be larger than the actual volume of the metal pellets. If the volume determined were too large, the density determined from it would be too low.

3. Using a pipet would give greater precision in the determination of volume than does the graduated cylinder. It was primarily to save time that the pipet method was not used.

4. Assuming that a linear relationship between density and concentration holds true, one could measure the density of a solution of unknown concentration and then use the graph to read off the concentration corresponding to that density.

5. The volume of a liquid varies with temperature. Since the calculation of density involves the volume of the liquid, the density of the liquid would also vary with temperature.
EXPERIMENT 4 The Determination of Boiling Point

A. General Notes

Temperature measurements are an important part of this and several later experiments. Characteristic temperatures (such as the boiling and melting points of pure substances) are an important part of many experiments, whereas in other experiments, a change in temperature is used as an index of reaction.

The experiment is written in terms of the use of “red-liquid” thermometers. Although such thermometers tend to be somewhat less accurate, the avoidance of the problems associated with the traditional mercury thermometer makes them desirable. If mercury thermometers are still in use at your institution, some means should be provided for the collection and legal disposal of mercury if any thermometers are broken. If possible, you should consider switching immediately to red-liquid thermometers to avoid the hazard of mercury vapor being released into the laboratory.

The experiment calls for Thiele tube oil baths for the heating of melting- and boiling-point samples. Although Thiele tubes are relatively expensive, their use makes it unnecessary for students to stir the oil baths and avoids possible burns. If it is not possible to obtain Thiele tubes, 250-mL beakers half full of oil may be provided, and students should be advised to stir such oil baths vigorously during heating.

A common hazard exists whenever oil is used in such heating baths. If any moisture is introduced into the oil, such moisture will superheat when the oil bath is subsequently used by students, and the heated oil will splatter badly. The instructor should examine the oil baths before the beginning of each laboratory period and should replace any oil that appears cloudy due to the presence of moisture. It is best to use plain paraffin oil in the heating baths, since it does not begin to smoke at as low a temperature as other common oils. In the calibration of the thermometer, make certain that students have arranged the thermometer so that the bulb is squarely in the middle of the ice- or boiling-water baths and is not resting on the bottom of the beaker.

Estimated time to perform: 150–180 minutes

B. Materials Required (given per 25 students)

ice
25 Thiele tubes (or other) paraffin-oil-filled baths
2–3 vials (100 count) melting-point capillaries
rubber bands (size 8) or short lengths of rubber tubing
barometer
triangular files or glass scorers
boiling chips
boiling-point samples

If desired, individual small samples may be prepared and dispensed in coded 2-dram polyseal vials. Otherwise, 2–3 250-mL coded polyseal bottles of liquid may be provided to the instructor, who will dispense small amounts of a liquid to the students. Suitable unknowns include

<table>
<thead>
<tr>
<th>Substance</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>b.p. 56°C</td>
</tr>
<tr>
<td>methanol</td>
<td>b.p. 65°C</td>
</tr>
<tr>
<td>95% ethanol</td>
<td>b.p. 78.2°C</td>
</tr>
<tr>
<td>2-propanol</td>
<td>b.p. 82.4°C</td>
</tr>
</tbody>
</table>
C. Pre-Laboratory Questions

1. A mixture of ice and water at 1 atm represents an equilibrium system whose temperature is accurately known. Ice alone could be at virtually any temperature below 0°C as prepared and stored in the ice machine.

2. Boiling represents the point at which the pressure of vapor escaping from the surface of a liquid is equal to the magnitude of the pressure above the liquid. In a container open to the atmosphere, the pressure above the liquid is the day’s barometric pressure. At lower barometric pressures, the temperature required to reach the point where the pressure of the liquid equals the barometric pressure will be lower.

3. acetone, 56°C; methyl ethyl ketone, 79.6°C; methanol, 65°C; ethanol (pure), 78.6°C (CRC Handbook)

4. A characteristic property of a substance is one that does not change under given conditions, regardless of the source of the substance. For example, both water on earth and water from Mars (if it exists) would boil at 100°C at 1 atm.

D. Post-Laboratory Questions

1. The normal boiling point is the boiling point when the external pressure is exactly 1 atm.

2. In high-altitude areas, the barometric pressure is lower than at sea level. A food will take longer to cook to the point of “doneness” at high altitude, particularly if heated in water or if the food contains a high percentage of water, because the water is boiling at a lower temperature.

3. As long as both ice and water are present, the mixture is assumed to represent the equilibrium between solid and liquid phases. Addition or removal of heat will shift the equilibrium in either direction.

4. Solids and liquids are virtually incompressible and are not nearly as affected by changes in pressure as would be the gaseous state (boiling).

5. A rough surface at the broken end of the capillary was designed to provide a rough, irregular surface upon which the bubbles of vapor produced by boiling could nucleate. The rough edge on the capillary serves the same purpose as the boiling stones in the water bath.
EXPERIMENT 5 The Determination of Melting Point

A. General Notes

Temperature measurements are an important part of this and several later experiments. Characteristic temperatures (such as the melting points of pure substances) are an important part of many experiments, whereas in other experiments, a change in temperature is used as an index of reaction.

The experiment is written in terms of the use of “red-liquid” thermometers. Although such thermometers tend to be somewhat less accurate, the avoidance of the problems associated with the traditional mercury thermometer makes them desirable. If mercury thermometers are still in use at your institution, some means should be provided for the collection and legal disposal of mercury if any thermometers are broken. If possible, you should consider switching immediately to red-liquid thermometers to avoid the hazard of mercury vapor being released into the laboratory.

The experiment calls for Thiele tube oil baths for the heating of melting- and boiling-point samples. Although Thiele tubes are relatively expensive, their use makes it unnecessary for students to stir the oil baths and avoids possible burns. If it is not possible to obtain Thiele tubes, 250-mL beakers half full of oil may be provided, and students should be advised to stir such oil baths vigorously during heating.

A common hazard exists whenever oil is used in such heating baths. If any moisture is introduced into the oil, such moisture will superheat when the oil bath is subsequently used by students, and the heated oil will splatter badly. The instructor should examine the oil baths before the beginning of each laboratory period and should replace any oil that appears cloudy due to the presence of moisture. It is best to use plain paraffin oil in the heating baths, since it does not begin to smoke at as low a temperature as other common oils. It is assumed that students’ thermometers have been checked for accuracy (see Experiment 4). If not, such a check would be appropriate before this experiment.

Estimated time to perform: 150–180 minutes

B. Materials Required (given per 25 students)

25 Thiele tubes (or other) paraffin oil-filled baths
2–3 vials (100 count) melting-point capillaries
rubber bands (size 8) or short lengths of rubber tubing
melting-point samples

If desired, individual small samples may be prepared and dispensed in coded, heat-sealed polyethylene bags. Otherwise, 2–3 coded 8-ounce bottles of solid may be provided to the instructor, who will dispense small amounts of a solid to the students. Suitable unknowns include

- acetanilide m.p. 114°C
- benzoic acid m.p. 122.5°C
- p-toluenesulfonamide m.p. 138°C

triangular files or glass scorers
C. Pre-Laboratory Questions

1. A characteristic property is one that is always the same for a given substance when measured under the same conditions.

2. An impurity will lower and broaden the melting range of the pure substance.

3. In a mixed melting point determination, a mixture is made of an unknown and an authentic sample of the substance the unknown is believed to be. If the mixture melts at the same temperature as the unknown itself, then the unknown may be assumed to be the same substance as the authentic sample.

4. If the oil is cloudy, it may mean moisture has gotten into the oil (oil and water do not mix, resulting in the cloudiness). If the oil is heated, the water will boil suddenly and spatter the oil. Students are told to report cloudy oil to the instructor for replacement.

D. Post-Laboratory Questions

1. Samples A and B are the same substance; Sample C is a different substance.

2. NaCl, 801°C
   biphenyl, 71°C
   naphthalene, 80.5°C
   benzene, 5.5°C
   2-methyl-2-propanol, 26°C

3. The Thiele tube is designed to be “self-stirring”. As the oil in the side arm is heated, the heated oil rises in the top of the side arm, and mixes with the bulk of the oil in the main chamber, thereby heating it. Cooler oil from the main chamber is then drawn into the side arm for further heating. Because of its shape, the Thiele tube must be clamped to a ring stand for use, and so is less likely to spill hot oil than an open, unclamped beaker of oil.
EXPERIMENT 6  The Solubility of a Salt

A.  General Notes

The word “solubility” may differ in meaning depending on the context in which it is used. In this experiment, solubility is introduced as the mass of a substance that will dissolve in 100 g of a solvent.

Students must pay very careful attention in this experiment to recording volumes of water used precisely. Students must also pay very close attention to their test tubes during cooling to detect the first appearance of crystals of solute. The first few crystals typically begin to appear in the bottom curvature of the test tube, which makes them more difficult to see. If students are not sure whether crystals have appeared, they might try tapping the test tube with their fingers to see if they can detect any motion by the crystals.

Estimated time to perform: 120–150 minutes

B.  Materials Required (given per 25 students)

25 8-inch test tubes (if not locker equipment) with slotted stoppers to fit

25 10-inch lengths of heavy-gauge copper wire (if desired, these can be bent in advance into the correct shape for stirring and can be reused by later sections)

25 50-mL burets

salt samples for solubility determination

The most commonly used salt for this determination is potassium nitrate, but other very soluble salts may be tried. KNO₃ works well because it shows a relatively large change in solubility with temperature. Each student will use approximately 5 g of salt.

C.  Answers to Pre-Laboratory Questions

1. Student examples

2. A saturated solution is one that is in equilibrium with undissolved solute: a saturated solution contains as much solute as is ordinarily possible at a given temperature. The solubility of a substance represents the maximum mass of the substance that will dissolve in a given amount of solvent at a particular temperature.

3. Stirring overcomes localized saturation of a solution in the region of remaining undissolved solute, removing any concentration gradients that exist. The ultimate amount of solute that will eventually dissolve, however, is a fixed amount for a given amount of solute at a particular temperature.

4. In a saturated solution of an ionic salt, equilibrium exists between the ions of the salt dissolved in the solution and the remaining undissolved salt. Ions leave the solution and enter the solid. Ions leave the solid and enter the solution. When these two processes are occurring at the same speed, equilibrium has been reached and the solution is saturated.
D. Answers to Post-Laboratory Questions

1. In a saturated solution, an equilibrium exists between the dissolving of further solute molecules from the remaining solid, and the reentry into the solid state by molecules already in solution.

2. The temperature is caused to rise by applying heat, whereas the temperature is allowed to drop spontaneously. The heating of the solution may be uneven (i.e., the bottom of the test tube is nearer the source of heat and may be warmer), whereas after the heat is removed and the solution is stirred, the temperature throughout the test tube should be uniform.

3. The solution had to be almost saturated at 100°C to ensure that the solution would become truly saturated as the temperature dropped to temperatures below 100°C.

4. The test tube should be kept in the boiling-water bath for as short a time as possible to prevent evaporation of the solvent. (The vapor pressure of the solution is larger at the elevated temperature.) If some of the solvent were to have evaporated from the test tube then the volume of solvent would not be known. If some of the solvent had evaporated, then the actual volume would be less than the expected volume: less solute would dissolve in a smaller volume of water, and the measured solubility would be lower than expected.
EXPERIMENT 7 Identification of a Substance

A. General Notes

This experiment ties together techniques learned in several earlier experiments and introduces new material on solubility. Although students are asked to reread the material in these earlier experiments, it is worthwhile for the instructor to review the techniques and precautions involved (especially in regard to the Thiele tube oil baths).

The instructor should be aware that it may not be possible, using only the methods covered in this experiment, to distinguish among some of the unknown substances given in Table 7-1. For example, the differences between the densities, solubilities, and boiling points of 2-propanol and 2-methyl-2-propanol are within the limits of experimental error expected from students at this level. It may be worthwhile for the instructor to hold a discussion of what other methods of identification may be necessary in such a situation.

Estimated time to perform: 150–180 minutes

B. Materials Required (given per 25 students)

unknowns

These may be dispensed in stoppered, coded 18×150-mm test tubes, giving students 10–15 mL of liquid unknowns and at least 10 g of solid unknowns.

100 mL 95% ethanol
100 mL cyclohexane
20 g sodium chloride
20 g naphthalene
20 g copper(II) sulfate pentahydrate
25 mL pentane
25 mL oleic acid
25 Thiele tubes, oil-filled, for melting-point and boiling-point determination
2–3 vials melting-point capillaries
rubber bands (size 8) or short lengths of rubber tubing
C. Answers to Pre-Laboratory Questions

1. These temperatures represent the same equilibrium, approached from opposite directions.

2. **Solubility:** the maximum quantity of solute that will dissolve in a given amount (usually 100 g) of solvent.

   *Normal boiling point:* the temperature at which the liquid boils at a pressure of 1 atm

   *Physical properties:* properties of a substance (such as boiling point, melting point, color, density, smell, etc.) that do not involve a chemical change or reaction of the substance.

3. The interaction between a solute and a saturated solution represents a dynamic physical state of equilibrium. This state of equilibrium is affected only by temperature. Factors affecting the rate of dissolution include particle size, whether the mixture is stirred, etc.; these factors do not, however, affect the ultimate amount of solute which dissolves.

4. Students summarize the tests (solubility, density, boiling/melting point) they will be performing.

D. Answers to Post-Laboratory Questions

1. These phase changes represent *characteristic equilibria* for a given substance, which at a particular pressure will always occur at the same temperature.

2. Conceivably, one could prepare a saturated solution by adding an excess of solute to a quantity of solvent. The solution could then be decanted from the undissolved solute, the solvent evaporated, and the mass of solute in the saturated solution determined.
EXPERIMENT 8 Resolution of Mixtures I: Filtration and Distillation

A. General Notes

This experiment provides good demonstrations of classical separation methods for mixtures of solids and liquids, which are then expanded with the more modern methods of chromatography in Experiment 9.

It is strongly recommended that the instructor perform the distillation as a demonstration because of the danger involved in distilling volatile flammable mixtures. It is further recommended that electrical heating mantles be used, rather than a direct flame, so that the speed of the distillation may be controlled more precisely. Students must be cautioned about the dangers of distillation to dryness.

Estimated time to perform: 120–150 minutes

B. Materials Required (given per 25 students)

- benzoic acid
- charcoal
- 5–10 Thiele tubes, oil-filled, for melting-point determination
- 1 vial melting-point capillaries
- small rubber bands (size 8) or short lengths of rubber tubing
- 11-cm-diameter “fast” filter paper
- 250-mL 1% sodium chloride solution (10 g NaCl diluted to 1 L)
- 100-mL 0.1 M silver nitrate solution (17 g AgNO3 diluted to 1 L)
- unknown mixtures for fractional distillation

Individual coded 50-mL unknowns may be prepared, or several 500-mL bottles of general unknown may be provided. Simple mixtures of water with one of the lower-molecular-weight alcohols make inexpensive unknowns, although such mixtures form azeotropes.

- simple distillation apparatus

A diagram of such an apparatus is given in the experiment. Individual set-ups will depend on the equipment available in your laboratory.

- fractional distillation apparatus

A diagram of such an apparatus is given in the experiment. Although individual set-ups will depend on the equipment available in your laboratory, the set-up used should contain a fractionating column that is either packed with glass rings or constructed with internal indentations to provide the needed surface area for the distillation.
C. **Answers to Pre-Laboratory Questions**

1. Answers depend on student choices.

2. The column packing provides for a greatly increased surface area, providing effectively thousands of individual equilibrations in the column.

3. An azeotrope is a mixture of two (or more) liquids that boils at a constant composition: the composition of the vapor phase produced is the same as that of the liquid phase. The most common example of an azeotrope is the 95% ethanol used in the laboratory.

4. The flask may overheat and break if all the liquid is boiled from it. In addition, many organic liquids may also form explosive peroxides, which might detonate if the flask is heated to dryness: however, at this point, students are unlikely to know that.

5. \( \text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl(s)} + \text{NaNO}_3(aq) \)

D. **Answers to Post-Laboratory Questions**

1. Simple distillation and fractional distillation are essentially the same process. The two methods differ primarily in terms of the greater surface area available in fractional distillation for the equilibration of the components of the mixture. Fractional distillation is better able to separate components whose boiling points are relatively close together.

2. Although some minor use of the distillation of sea water has been made in desert nations, the process is very expensive in terms of the amount of energy needed, and also in terms of the physical plant necessary to provide useful amounts of water. Sodium chloride in the presence of moisture tends to be very corrosive to many of the materials of which such a distillation apparatus might be constructed.
A. General Notes

This experiment provides demonstrations of two related techniques of chromatography. Choice I is especially simple, and parts of it could even be done as an “armchair” experiment in the classroom, or perhaps as a homework assignment. Choice II allows students to investigate the effect of the solvent system used on a chromatographic separation. Choice I is to be preferred if time is a constraint for the experiment.

In Choice I, students determine whether the inks used in felt-tip pens consist of a single colored dye or are a mixture of dyes. Students test both water-soluble and “permanent” inks.

In Choice II, commercially available alumina TLC slides are most convenient, although to reduce expense, the slides may be cut from a larger sheet of TLC medium. No fluorescent dye is needed on the TLC medium for this separation. Several of the solvent mixtures in this choice will lead to a decent separation; it might be worthwhile to discuss with students the nature of the solvents that did or did not effect a separation.

For both choices, students should be encouraged to keep the spots they apply as small as possible: more is definitely not better in this sort of chromatography. The idea of applying the spots is to build up a small but concentrated spot of solute. Encourage students not to hurry when drying the spots with the heat source: if the filter paper or TLC slide is still wet from the first application, the second spot applied will spread over too great an area.

Estimated time to perform:

Choice I: 45–60 minutes
Choice II: 120–150 minutes

B. Materials Required (given per 25 students)

Choice I

- a selection of felt-tip pens, laboratory markers, overhead projector pens, etc.
- filter paper (Whatman #1, cut into 5\(\times\)10-cm strips)
- 25 pairs latex surgical gloves
- 2–3 heat guns
- 1 L acetone/water mixture (50% v/v)
- plastic food wrap
Choice II
500-mL bottles of the following solvents
acetone       hexane (mixed isomers may be used)
ethyl acetate absolute ethanol (200 proof)

25 pairs latex surgical gloves
150 Bakerflex® TLC slides (no fluorescent dye needed)
2–3 packs (100 count) of 10 μL micropipets
5–6 heat guns or IR lamps
plastic food wrap

25-mL samples of 1% solutions of the following indicator dyes (prepared by dissolving 1 g of the dye in 100 mL of 95% ethanol):

- methyl red
- xylenol orange
- bromocresol green

C. Answers to Pre-Laboratory Questions

Choice I

1. There may be many possible definitions, specific to the type of chromatography involved. In general, chromatography involves separating a mixture into its components by exploiting the fact that the components of the mixture differ in their affinity for a solid material, and in their solubility and flow rate through a solvent system.

2. Paper chromatography has been widely applied to plant extracts.

3. \( R_f = \frac{5.2 \text{ cm}}{8.9 \text{ cm}} = 0.58 \)

Choice II

1. Most inks are mixtures of colored dyes. The ink would be likely to undergo the same chromatographic process as the indicators under study. The graphite used in pencils is not soluble in water or in the other solvents used.

2. \( \begin{align*}
\text{Indicator} & \quad \text{Low pH (acidic)} & \quad \text{High pH (basic)} \\
methyl red & \quad \text{red} & \quad \text{yellow} \\
xylenol orange & \quad \text{yellow} & \quad \text{red} \\
bromocresol green & \quad \text{yellow} & \quad \text{blue}
\end{align*} \)

3. Alumina: various forms and hydrates of \( \text{Al}_2\text{O}_3 \).
   Silicagel: silicic acid, precipitated by acidification of sodium silicate, from which the water has been driven out by heating.
D. Answers to Post-Laboratory Questions

Choice I

1. A mixture of solvents is used, because the components of the solvent mixture also move at different speeds through the filter paper, producing an ever-changing solvent composition, which helps effect the separation. Since the second set of inks are soluble in acetone but are not soluble in water, this provides for a better separation than would acetone alone.

2. The skin of the fingers contains water-insoluble oils. If such oils were transferred to the paper to be used for chromatography, the presence of such oils would serve as a barrier to the rising of the solvent front.

3 and 4 Dependent on student results

Choice II

1. The idea is for the spot to be swept along easily by the solvent front. If the spot is too large, this cannot be done easily. Also, if spots are too large, different spots on the same paper may run into one another.

2. The atmosphere in the beaker must be saturated with the solvent mixture vapor for capillary action to be able to draw the solvent to the top of the paper. Otherwise, the solvent will begin to dry out as it rises away from the layer of solvent in the bottom of the beaker.

3. As always, “like dissolves like.” If the dye is very polar, it will tend to dissolve in and be swept along by the polar solvents.
EXPERIMENT 10 Counting by Weighing

A. General Notes

Although this experiment is very simple, it introduces two important concepts: (1) how chemists are able to relate a macroscopic, measurable amount of substance to the number of atoms or molecules the sample contains, and (2) the concept of a weighted average as it applies to the average atomic mass of an element.

Although the idea of every student in a class determining data for 25 pennies may seem like a lot of work (for a class of 24 this is 600 pennies!), it is important that the sample be large enough. Although students are asked to write their results on the chalkboard, the instructor may wish to organize these data for students into tables drawn on the chalkboard.

B. Materials Required (given per 25 students)

Students should ideally bring their own pennies to lab; the instructor should have additional pennies available for students who forget to bring their own.

felt-tip pens (lab marker pens)

C. Answers to Pre-Laboratory Questions

1. Atoms and molecules are too small to have their masses directly determined. Chemists have developed a method for relating the mass of a sample (which is an easily determined, macroscopic property) to the number of atoms or molecules the sample contains. By this method, the molar mass of a substance, in grams, contains \(6.02 \times 10^{23}\) (Avogadro’s number) atoms or molecules.

2. Counting by weighing can be used whenever many small, identical items must be counted out. The mass of one such item is determined, and then the mass of a bulk sample of the items is determined, with the number of items present in the bulk sample determined by dividing the mass of the bulk sample by the mass of a single item.

3. Students may come up with many sorts of examples, some of which may bear a tenuous relationship to reality! Try to assess whether their answers are possible, rather than probable or actually able to be done experimentally.

4. \(6.368/5 = 1.274\)

5. (a) \((152 \text{ bolts})(0.26 \text{ g/bolt}) = 40 \text{ g}\)

(b) \((500. \text{ g})(1 \text{ bolt/0.26 g}) = 1923 \text{ bolts (}1.92 \times 10^3\text{ bolts)}\)
D. Answers to Post-Laboratory Questions

1. The individual average mass reported by a given student will probably be close to, but not exactly the same as, the overall average mass calculated for the whole class. Since students are bringing their own pennies, and since those pennies are randomly distributed between pre- and post-1982 pennies, the average mass reported by a given student will depend on the particular number of each type of penny the student has in his or her sample.

2. The two chief isotopes of boron (with their associated percentage abundances) are

   B-10 (mass 10.0129, 19.9%) and B-11 (mass 11.0093, 80.1%).

   The average atomic mass of boron would be calculated from the masses and relative abundances as

   \[(0.199)(10.0129) + (0.801)(11.0093) = 10.81 \ (10.8)\]
A. General Notes

Stoichiometry is perhaps the most important topic in general chemistry: Not only are the usual sort of mass/mass problems first encountered important in themselves, but stoichiometric considerations come up again and again in the later discussions of the gas laws, solutions, electrochemistry, etc. In spite of this importance, there have been developed very few simple yet meaningful stoichiometric experiments—experiments that clearly illustrate the concept of limiting reagent and theoretical yield at a level that students can appreciate. The three choices of this experiment will help your students appreciate these concepts more fully.

Choice I makes use of Job’s method to determine the stoichiometry of some simple strong acid/strong base reactions. Students measure temperature changes associated with the reactions and plot these to visualize the stoichiometric ratio. Note that for the sulfuric acid/sodium hydroxide reactions, the actual 1:2 stoichiometry is not one of the data sets listed in the manual: students will have to be guided in locating the maximum of the graph between two measured points. The method of continuous variations used in Choice I has been widely applied in the study of transition metal complexation reactions, in which the reactions performed contain systematically varied concentrations of metal ion and ligand, making it possible to determine the formula of the resulting complex.

Choice II also makes use of Job’s method to determine the stoichiometry of the reaction between iron(III) and a phenol. Since iron(III)-phenol complexes are brightly colored, a spectrophotometric method is used.

Choice III is a classic experiment, which can work reasonably well only if no MgO is lost during the heating. Many students have trouble with this experiment, however, and it has often proved to be very frustrating to them, both in the experimental skill needed at an early point in their laboratory experience, and also in the poor results they obtain if anything goes wrong.

Estimated time to perform:

Choice I: 120–150 minutes
Choice II: 120–150 minutes
Choice III: 120–150 minutes

B. Materials Required (given per 25 students)

Choice I

10 L 3.0 $M$ NaOH (1200 g NaOH diluted to 10 L; Caution!)

5 L 3.0 $M$ HCl (1.25 L conc. HCl diluted to 5 L; Caution!)

5 L 3.0 $M$ H$_2$SO$_4$ (830 mL conc. H$_2$SO$_4$ diluted to 5 L; Caution!)

The sulfuric acid generates a tremendous quantity of heat when diluted. The container to be use should be packed in ice during the dilution. The sulfuric acid should be added to the water to prevent spattering from the heat evolved.
25 plastic foam coffee cups

thermometers

**Choice II**

10 L $1.7 \times 10^{-3} M$ iron(III) nitrate [Add 6.87 g iron(III) nitrate nonahydrate to a 10-L volumetric flask. Half fill the flask with distilled water; then add 50 mL conc. nitric acid (*Caution!*). Mix to dissolve. Finally dilute to the calibration mark with distilled water, mix and transfer to 1-L bottles for dispensing.]

10 L $1.7 \times 10^{-3} M$ 5-sulfosalicylic acid [Add 3.71 g 5-sulfosalicylic acid to a 10-L volumetric flask. Half fill the flask with distilled water; then add 50 mL conc. nitric acid (*Caution!*). Mix to dissolve. Finally dilute to the calibration mark with distilled water, mix, and transfer to 1-L bottles for dispensing.]

marking pens

visible spectrophotometers (Spectronic 20 or similar)

18 × 150 mm test tubes (20 per student)

10-mL Mohr pipets and bulbs

**Choice III**

25 crucibles and covers (allow extras for breakage)

25 crucible tongs

25 clay triangles

500 g magnesium turnings (sold for Grignard reagent synthesis)

1 vial pH paper

1 L 6 $M$ hydrochloric acid solution (500 mL conc. HCl diluted to 1 L; *Caution!*)

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**C. Answers to Pre-Laboratory Questions**

**Choice I**

1. a. $Mg + Cl_2 \rightarrow MgCl_2$

   b. $(5.00 \text{ g Mg})(1 \text{ mol}/24.3 \text{ g}) = 0.206 \text{ mol}$

   $(10.0 \text{ g Cl}_2)(1 \text{ mol}/71.0 \text{ g}) = 0.141 \text{ mol}$; therefore $Cl_2$ is the limiting reactant.

   $(0.141 \text{ mol MgCl}_2)(95.3 \text{ g/1 mol}) = 13.4 \text{ g MgCl}_2$

2. $(500. \text{ mL})(1.0 \text{ M})/(3.0 \text{ M}) = 167 \text{ mL required}$

3. The graph has a maximum at the equimolar ratio.
Choice II
1. 1.50 mL = 0.00150 L

\[(0.00150 \text{ L})(1.7 \times 10^{-3} \text{ mol/L}) = 2.55 \times 10^{-6} \text{ mol}\]

2. 15.2% \((A = 0.818)\); 34.1% \((A = 0.467)\); 52.9% \((A = 0.277)\); 79.5% \((A = 0.0996)\)

Choice III
1. Molar mass MgO = 24.31 + 16.00 = 40.31
%Mg = \((24.31/40.31)(100) = 60.31\% \text{ Mg}\)
%O = \((16.00/40.31)(100) = 39.69\% \text{ O}\)

2. \((2.033 \text{ g Mg})(40.31 \text{ g MgO/24.31 g Mg}) = 3.371 \text{ g MgO}\)

D. Answers to Post-Laboratory Questions

Choice I
1. A plastic coffee cup is fairly well insulated. The heat of the reaction therefore would not be lost to the outside world before it could be measured.

2. Since phosphoric acid is triprotic, with a strong base like NaOH students will expect the stoichiometric ratio to be at the ratio in which phosphoric acid and NaOH are in a 1:3 ratio.

Choice II
1. The transmittance is the fraction of the incident light that passes through a colored solution without being absorbed. The percent transmittance represents this fraction multiplied by 100. The absorbance of a colored solution represents the portion of incident light that is absorbed by colored species in the solution. Since many spectrophotometers measure the percent transmittance, most commonly the working definition of absorbance is used: \(A = 2 – \log\%T\)

Choice III
1. Molar mass of \(\text{Mg}_3\text{N}_2\) = \(3(24.3) + 2(14) = 100.9\)
% Mg = \((72.9 \text{ g Mg/100.9 g Mg}_3\text{N}_2)(100) = 72.2\% \text{ Mg}\)

The apparent %Mg would be higher than expected for MgO.

2. Molar mass CaO = 40.08 + 16.00 = 56.08 g
%Ca = \((40.08 \text{ g Ca}/56.08 \text{ g CaO})(100) = 71.47\% \text{ Ca}\)

\((1.358 \text{ g Ca})(56.08 \text{ g CaO/40.08 g Ca}) = 1.900 \text{ g CaO}\)
A. General Notes

Although the hydration of inorganic salts is a fairly simple concept, generally students encounter such compounds before they know enough about structure and bonding to appreciate how water molecules may be tied up with metal ions in crystals in fixed proportions. In particular, students are usually concerned about the “dot” notation used to indicate the water molecules and are confused about whether the water molecules are to be considered in calculating a compound’s molar mass. This experiment is an attempt to present hydrates in such a way that students will understand their properties, structures, and uses more clearly.

This experiment vividly demonstrates the difference between the hydrated and the anhydrous forms of several salts, by monitoring the color changes that take place on dehydration by heat. It also examines the concept that the water molecules in a hydrated salt occur in a fixed, definite proportion by mass, and implies that the water molecules must actually be chemically bonded to the metal ions involved.

The hydrated salts used are for the most part environmentally unsafe and should be disposed of properly. Separate waste beakers should be provided for each salt (the salts may be rehydrated by the instructor and used at a future time, if desired).

Estimated time to complete: 120–150 minutes

B. Materials Required (given per 25 students)

25 casseroles or evaporating dishes

10–15-g samples of the following hydrated crystalline salts

- copper(II) sulfate pentahydrate
- nickel(II) chloride hexahydrate
- cobalt(II) chloride hexahydrate
- chromium(III) chloride hexahydrate
- barium chloride dihydrate
- anhydrous calcium chloride (pellets)

25 clay triangles

25 crucible tongs
C. Pre-Laboratory Questions

1. Strontium chloride forms the dihydrate, SrCl$_2$·2H$_2$O
   
   Sodium chromate forms the decahydrate, Na$_2$CrO$_4$·10H$_2$O
   
   Nickel(II) nitrate forms the hexahydrate, Ni(NO$_3$)$_2$·6H$_2$O
   
   Iron(II) ammonium sulfate forms the hexahydrate, FeSO$_4$·(NH$_4$)$_2$SO$_4$·6H$_2$O

2. Expect only the most rudimentary answer to this question from students at this point: transition metal salts show color because of electronic transitions between the d-orbitals of the metal; water molecules (and other ligands) that are coordinately bonded to the transition metal ion provide the electrons for these transitions.

3. Molar mass of CuSO$_4$·5H$_2$O = 249.6
   
   Molar mass of CuSO$_4$ = 159.6
   
   Mass of anhydrous salt remaining = 2.3754 g (159.6/249.6) = 1.5189 g

4. The water molecule is bonded to the sulfate by hydrogen bonding.

D. Post-Laboratory Questions

1. A desiccant is a material that either chemically or physically absorbs or adsorbs water. A hygroscopic material is one that chemically absorbs water (usually forming a hydrate). A hydrated material that loses or gains waters of hydration (frequently because the hydrated material is in equilibrium with moisture in the atmosphere) is said to be deliquescent.

2. Carbohydrates are long-chain compounds consisting of a carbon backbone, typically an aldehyde or ketone function, and a large number of hydroxyl groups attached to the carbon chain. It is pretty much just a coincidence that the empirical formula is (CH$_2$O)$_n$. When a new compound is isolated, however, the first determinations made are that of percentage composition and empirical formula, so it is not unreasonable that chemists working at the time came up with the name “carbohydrate”.
EXPERIMENT 13 Preparation and Properties of Some Common Gases

A. General Notes

If it is desired to perform all three choices of this experiment during one 3-hour laboratory period, then it is strongly suggested that the gas-generating apparatus be assembled in advance for student use. Assembling the apparatus in advance also minimizes the likelihood of students cutting themselves while inserting the thistle tube and glass tubing through the rubber stopper of the generating flask.

The experiment is written in terms of using a thistle tube to introduce the liquid needed. It is suggested that unbreakable plastic thistle tubes be used. Alternatively, a long-stemmed filter funnel can be substituted. If a glass thistle tube or funnel is used, make certain that glycerine is available as a lubricant and that the instructor discusses the correct method for inserting such tubing through a rubber stopper.

Estimated time to complete: approximately 60 minutes each choice.

B. Materials Required (given per 25 students)

**All choices**

25 gas-generating/collection apparatuses: 250-mL Erlenmeyer with tightly fitting two-hole stopper, glass tubing (two 90° bends), thistle tube or long-stem funnel, water trough, 8-ounce gas collection bottles (with stoppers or glass plates to fit), rubber tubing

**Choice I**

500 g mossy zinc
2 L 3 M hydrochloric acid (250 mL conc. HCl diluted to 1 L; *Caution!*)
wooden splints

**Choice II**

50 g manganese(IV) oxide, brown MnO₂
2 L 3% hydrogen peroxide (commercially sold, or diluted 100 mL of 30% H₂O₂ to 1 L)
wooden splints
50 g sulfur
25 deflagrating spoons
pH test paper
25 iron nails (not steel)
1 L 1 M hydrochloric acid (83 mL of conc. HCl diluted to 1 L; *Caution!*)
Choice III

300 g calcium carbonate
2 L 3 M hydrochloric acid (250 mL conc. HCl diluted to 1 L; Caution!)
wooden splints
pH test paper
2 L limewater [saturated Ca(OH)$_2$, 2–3 g Ca(OH)$_2$ diluted to 1 L, stirred 1 hour and filtered before dispensing]
100 g crushed dry ice

C.  Pre-Laboratory Questions

1. Hydrogen is prepared commercially primarily from the electrolysis of water. Oxygen is prepared primarily from the distillation of liquid air. Carbon dioxide is generated commercially by the heating of carbonate and bicarbonate ores.

2. \[ d = \frac{PM}{RT} \]
   
   for hydrogen, \[ d = \frac{(1)(2.0)}{(0.082)(298)} = 0.082 \text{ g/L} \]
   
   for oxygen, \[ d = \frac{(1)(32)}{(0.082)(9298)} = 1.31 \text{ g/L} \]
   
   for nitrogen, \[ d = \frac{(1)(28)}{(0.082)(298)} = 1.15 \text{ g/L} \]
   
   for carbon dioxide, \[ d = \frac{(1)(44)}{(0.082)(298)} = 1.80 \text{ g/L} \]
   
   apparent molar mass for air = \( (0.80)(28) + (0.20)(32) = 28.8 \text{ g/mol} \)
   
   density of air, \[ d = \frac{(1)(28.8)}{(0.082)(298)} = 1.18 \text{ g/L} \]

3. \[ \text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g) \]
   
   \[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O(l)} \]
   
   \[ 2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O(l)} + \text{O}_2(g) \]
   
   \[ \text{S(s)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) \]
   
   \[ 2\text{Fe(s)} + \text{O}_2(g) \rightarrow 2\text{FeO(s)} \]
   
   \[ \text{Ca(OH)}_2(aq) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O(l)} \]
   
   \[ \text{CaCO}_3(s) + \text{HCl(aq)} \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O(l)} + \text{CO}_2(g) \]

D.  Post-Laboratory Questions

1. The net ionic reaction is between Zn and H$^+$ ion and was not specific for HCl: other acids might have been substituted.

2. The decomposition of hydrogen peroxide is a spontaneous process. Manganese(IV) oxide served as a catalyst for the reaction. Many other substances (e.g., many iron salts) could have been used equally well.

3. The gases are bubbled through liquid water before collection. Water vapor could be removed by using a chemical desiccant—a substance that absorbs moisture. For example, gases are frequently dried by passing them through a tube containing anhydrous calcium chloride.
A. General Notes

Study of the gas laws constitutes a major portion of the general chemistry curriculum; Yet for many students, these gas laws represent merely a set of formulas and equations that are difficult to remember, and even more difficult to use. This experiment should enable students to see for themselves that the gas laws tell us very simple, predictable things about the effect of environmental changes on a sample of gas.

Since one of the important gas variables is pressure, experiments demonstrating the gas laws invariably make use of apparatuses containing elemental mercury. The instructor must be prepared to deal with mercury spills and clean-up. Choice I (Boyle’s law) in particular makes use of a mercury-filled manometer and leveling bulb: it is most strongly urged that students not manipulate the apparatus for Choice I themselves (students forget that if they lower the leveling bulb too far, the mercury will run out of the system). It is recommended further that the apparatus for Choice I be set up in a large plastic tray or basin to catch the mercury if it is spilled. The instructor can assist small groups of students with the measurements required, while the remaining students work on one of the other choices. Choice II (Charles’s law) makes use of only a droplet of mercury, but the instructor should nonetheless make sure that mercury is cleaned up if an apparatus is broken; the instructor should also take special care that students return the capillary tubes, to avoid spillage in their lockers.

Estimated time to complete:

<table>
<thead>
<tr>
<th>Choice</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choice I</td>
<td>45–60 minutes</td>
</tr>
<tr>
<td>Choice II</td>
<td>120–150 minutes</td>
</tr>
<tr>
<td>Choice III</td>
<td>60–75 minutes</td>
</tr>
</tbody>
</table>

B. Materials Required (given per 25 students)

Choice I

Pressure/volume measuring apparatus (see Figure 14-2) consisting of: a buret, rubber tubing, leveling bulb, meter stick, barometer, and mercury to fill the system. If a true manometer is available, it may be substituted for the buret assembly. The buret should be attached to the meter stick with rubber bands, and the entire assembly should be clamped above a plastic tray or basin to catch any mercury spills.

Choice II

25 capillary volume/temperature tubes, made from 2-mm-inside-diameter capillary tubing (6–8 inches in length, sealed at one end) into which a single droplet of mercury is inserted with a Pasteur pipet (the droplet should be positioned about one-third of the way down from the open end of the capillary tube). These tubes are easily broken, and the mercury droplet is easily split by rough handling of the tubes. Make sure the tubes have cooled completely to room temperature after glass-working before adding the mercury droplet.

small rubber bands (size 8) or short lengths of rubber tubing

25 wooden rulers (plastic rulers will melt in the boiling-water bath)
Choice III

lengths (3–4 feet) of 1-cm-diameter glass tubing, fire-polished solid rubber stoppers to fit the above tubing latex surgical gloves meter sticks china markers

500 mL concentrated ammonia solution; Caution!

500 mL concentrated hydrochloric acid solution; Caution!

plastic food wrap forceps cotton balls

C. Answers to Pre-Laboratory Questions

Choice I

1. The data are prepared so as to give perfect graphs: mention to students that, in real practice, data obtained might not produce such good graphs. Graph (a) is a hyperbola; Graph (b) is a straight line.

2. Ideal gases assume that molecules of a gas do not have any intrinsic volume of their own (are just points in space) and do not exert any attractive or repulsive forces on each other under any conditions. Real gases approximate ideal behavior under conditions of high temperature and low pressure.

Choice II

1. Charles's law indicates that the volume of an ideal gas sample should decrease in proportion to a decrease in temperature. In particular, Charles’s law implies that the volume of a gas sample should decrease by 1/273 of its volume for each degree the temperature is lowered. However, as the volume of a gas sample becomes smaller, the molecules in the sample get closer and closer together. A real gas would eventually liquefy as its molecules became compressed into smaller and smaller volumes.

2. a. The data gives a straight line.
   b. Slope = 0.275 mL/°C
   c. Intercept = –273°C

Choice III

1. \[ r_{\text{helium}} = \left(\frac{39.95}{4.003}\right)^{1/2}, r_{\text{argon}} = \left(9.980\right)^{1/2}, r_{\text{argon}} = 3.159 \]

2. The uranium isotopes (U-235, U-238) were separated as the hexafluorides, UF₆. The separation was effected by the different rates of diffusion of the two forms of UF₆ through many miles of tubing.
D. Post-Laboratory Questions

Choice I

1. Boyle’s law predicts that if the pressure on an ideal gas sample were increased, the volume of the gas would continue to get smaller. If the pressure were made “infinitely large,” the volume would be predicted to approach zero. This would not actually happen for a real gas: as the volume of a real gas gets smaller, eventually the molecules begin attracting each other, and the gas liquefies.

2. The buret used is a regular cylinder. The volume of a regular cylinder is the area of the cross section of the cylinder times the height of the cylinder. The volume is directly proportional to the height.

3. \[(21.2 \text{ mL})(1.02 \text{ atm}/1.62 \text{ atm}) = 13.3 \text{ mL}\]

\[75 \text{ mm Hg} = 0.0987 \text{ atm}; (21.2 \text{ mL})(1.62 \text{ atm}/0.0987 \text{ atm}) = 348 \text{ mL}\]

\[78.9 \text{ kPa} = 0.779 \text{ atm}; (21.2 \text{ mL})(1.62 \text{ atm}/0.779 \text{ atm}) = 44.1 \text{ mL}\]

Choice II

1. Absolute zero is a “theoretical” temperature predicted by our models and theories. Absolute zero itself has never been reached—but we are coming closer. If liquid helium is evaporated by pumping with a vacuum pump, temperatures of about 1 K can be reached. If the isotope of helium of mass number 3 is used, temperatures of around 0.3 K can be reached.

2. The capillary used is basically a regular cylinder. The volume of a regular cylinder is the area of the cross section of the cylinder times the height of the cylinder. The volume is directly proportional to the height.

3. The fact that the sample produces a straight line at and slightly above room temperature is no guarantee that a linear relationship exists over all possible temperatures. Students may realize from their calculus course that any mathematical function may be approximated by a straight line (i.e., tangent) if the interval under study is very small. The volume of a real gas would never reach zero because the gas would liquefy before this point.

Choice III

1. Methylamine has a larger molar mass than ammonia, and so its molecules, on average, do not move as fast. Therefore, the methylamine molecules would not move as far through the tube as would the ammonia molecules, and the white ring would form farther away from the HCl end of the tube.

2. Since we are using the distance traveled as a measurement of the speed of the molecules involved, obviously giving one molecule a “head start” invalidates the measurement.

3. If both gases were at the same higher temperature, they would both diffuse at a higher speed. They would meet each other in the tube sooner, but they would meet at the same location.

4. \[r_{\text{He}}/r_X = 4 = (M_X/M_{\text{He}})^{1/2}\]

\[M_X \text{ is approximately } 64 \text{ g}.\]
EXPERIMENT 15 Molar Mass of a Volatile Liquid

A. General Notes

This experiment clearly demonstrates the vapor density method of molar mass determination. Although the results obtained are not quite as accurate as when a specialized vapor density bulb is used, the savings in cost is appreciable.

The traditional unknowns for this experiment were typically chlorinated hydrocarbons. With concern over the possible carcinogenicity/toxicity of such compounds, the experiment has been redefined to use less toxic liquids. It is still imperative that students work in the exhaust hood when dealing with the unknown liquids, however, since the unknown liquids suggested for use are volatile and highly flammable. Although the instructor might wish to substitute a smaller Erlenmeyer flask for the experiment, to decrease the amount of unknown liquid required, it has been found that the loss in precision and accuracy is very large with smaller flasks.

To get reliable results, students must be cautioned about the need to dry the outside of the flask after the heating period before the weight of condensed vapor is determined. In particular, steam from the boiling-water bath may condense under the edges of the aluminum foil cover: to minimize this, the foil cover should be trimmed to fit the opening of the flask as closely as possible, without a large excess of foil hanging over the rim of the flask.

Students should be cautioned about splashing from the boiling water bath once the flask is inserted. As small a flame as possible should be used to keep the water bath at barely a simmer.

It is sometimes difficult for students to see the unknown liquid inside the flask once the flask is in the boiling-water bath; this makes it hard for them to determine when the unknown has completely vaporized. If desired, a single crystal of iodine may be added per liter of unknown liquid before dispensing. Iodine dissolves in the liquids used, imparting a slight pink or orange color. The amount of iodine used is not enough to affect appreciably the molecular weight determined.

Estimated time to complete: 120–150 minutes

B. Materials Required (given per 25 students)

1 roll heavy-weight aluminum foil (freezer wrap)
5–6 sewing needles, which have been inserted into corks for handling
small rubber bands (size 8) or short lengths of rubber tubing
2-dram coded polyseal vials of unknown liquids. The following liquids are among those suggested. It may be desired to add a single crystal of elemental iodine per liter of liquid to provide additional visibility.

- anhydrous ethanol, molar mass 46 g
- anhydrous methanol, molar mass 32 g
- acetone, molar mass 58 g

balance capable of weighing at least 1 kg
drying oven (110°C), or heat lamps
C. Answers to Pre-Laboratory Questions

1. density = mass/volume = g/V = PM/RT

2. \[ M = gRT/PV \]
   
   \[ V = 408 \text{ mL} = 0.408 \text{ L} \]
   
   \[ T = 100.4^\circ\text{C} = 373.4\text{K} \]
   
   \[ P = 765 \text{ mm Hg} = 1.01 \text{ atm} \]
   
   \[ M = (1.91)(0.0821)(373.4)/(1.01)(0.408) = 142 \text{ g/mol} \]
   
   \[ d = g/V = PM/RT \]
   
   \[ d = (1.01)(142)/(0.0821)(373.4) = 4.68 \text{ g/L} \]

3. An ideal gas is one that obeys the ideal gas laws; real gases approach ideal behavior at low pressures and high temperatures. In order for a vapor to be near its liquefaction point, the vapor must be at a relatively high pressure or at a relatively low temperature. Under these conditions, the intrinsic volume of the molecules themselves and the forces that exist between those molecules result in deviations from the ideal gas law.

4. The two methods are to fill the flask that contained the vapor with water, and then to either weigh the water on a balance (and then use the density of water to convert to volume), or determine its volume by pouring the water into a graduated cylinder. Mass determinations are generally more precise.

D. Answers to Post-Laboratory Questions

1. 0.05 mL = 0.05 g water if the density is 1.0 g/mL
   
   \[ (0.05 \text{ g})(1 \text{ mol}/18 \text{ g}) = 0.0028 \text{ mol} \]
   
   When 0.0028 mol of water is vaporized at 100°C (373 K) and 1 atm pressure, it would occupy a volume of
   
   \[ V = nRT/P = (0.0027)(0.0821)(373)/(1) = 83 \text{ mL} \]
   
   This volume of water vapor would lead to a significant error.

2. The pinhole opened the vapor to the pressure of the atmosphere.
A. General Notes

It is difficult and expensive, at the beginning level, to measure vapor pressure quantitatively. Yet the concept of vapor pressure is an important one, and one that is frequently misunderstood by students. After an initial demonstration of vapor pressure using the colored vapor of bromine, this experiment uses a simple technique to demonstrate the existence of a vapor pressure above a volatile liquid and allows students to rank-order the vapor pressures of several liquids and to discuss the relationship between vapor pressure and intermolecular forces.

The procedure described in the manual makes use of ordinary titration burets. If gas (Bunsen) burets are available, they may be used, in which case the buret should be filled with water to within 4–5 inches of the rim. This allows that, when the buret is inverted, there will be space into which the volatile liquid can evaporate, and any uncalibrated volume on the barrel of the buret will be bypassed.

The liquids chosen for the demonstration must meet several criteria for the experiment to work: the liquids must be very volatile, must be less dense than water so that they will rise to the top of the buret when inverted, and must not be appreciably soluble in water. Some suggestions for suitable liquids are given in Part B below. Since most of the liquids having the properties required are highly flammable, no flames are permitted in the lab, and it should be ensured that the lab is well ventilated.

Estimated time to complete: 120 minutes

B. Materials Required (given per 25 students)

25 burets (titration or gas burets, see Part A above)

25 basins

A plastic dishwashing tub provides students with more room. Check your local “dollar store”.

25 65-mm funnels

Pasteur pipets and rubber bulbs

several volatile liquid samples, 500 mL each. Caution: highly flammable! Suitable liquids include

hexane (mixed isomers may be used)

n-pentane

diethyl ether

ice

bromine sample:

It is best to have 0.5-1 mL of liquid bromine in a sealed tube approximately 1/2 inch in diameter and about 12 inches long. In a pinch, a 1-L volumetric flask can be substituted: a small amount of bromine is introduced into the flask, and it is quickly stoppered and the stopper wired to keep it from being displaced. Because of its corrosivity, the bromine should be handled only by qualified personnel. If the sample is heated with an infrared lamp, the lamp should be introduced only for a brief period of time so as to not build up the pressure to too high a level in the tube or flask. All operations involving the bromine should be conducted in the exhaust hood by the instructor.
C. Answers to Pre-Laboratory Questions

1. The vapor pressure of a liquid is the equilibrium pressure above the liquid when it is in a closed container at a particular temperature. Evaporation represents molecules leaving the liquid state and entering the vapor state, whereas condensation is the exact reverse.

2. The vapor pressure of a liquid increases with increased temperature, as more and more molecules come to have sufficient kinetic energy to escape from the liquid.

3. Addition of a solute will lower the vapor pressure of the solvent. Fewer solvent molecules are able to escape from the surface of the liquid at a particular temperature.

4. The development of a vapor pressure above a liquid is due to the balancing of two opposite processes (evaporation and condensation) going on at the same time at the same speed once equilibrium is reached. The fact that the vapor pressure of a liquid does not increase with time is one indication of the existence of the equilibrium.

D. Answers to Post-Laboratory Questions

1. Since the total pressure of vapor in the inverted tube can only equal the barometric pressure (the other end of the system is open to the atmosphere), the presence of water vapor implies that the vapor pressure of the volatile liquid is less than if the liquid had evaporated into a vacuum.

2. The amount of volatile liquid called for in the experiment is only a few milliliters. If a small amount of a very soluble volatile liquid like ethanol were used, it is unlikely that any change in the water level would be detectable.

3. If the samples were cooled, the vapor pressure of the volatile liquids would be lower, and the water level should rise.

4. The direct phase transition from solid to vapor is called sublimation. Experiment 17 demonstrates the sublimation of elemental iodine. Dry ice, iodine, and “moth balls” are examples of substances that undergo sublimation at or near room temperature.
EXPERIMENT 17 Calorimetry

A. General Notes

Choice I (Determination of a Calorimeter Constant) should be performed before any of the later choices, and the same calorimeter assembly should be used in each case.

In Choice II (Specific Heats of Metals and Glass), be certain that students do not spill the metal or glass samples on the floor of the laboratory. (If spills occur, they must be cleaned up immediately.)

Realize that the thermodynamic data obtained from experiments employing such a crude, nonadiabatic calorimeter will almost certainly not provide particularly great accuracy relative to the “true” values in the literature. The experiment does, however, provide a “real world” opportunity for students to apply the thermochemical information provided in the text/lectures. Although lack of accuracy should not be penalized, students should be encouraged to make their measurements to the precision permitted by the equipment used for the experiment.

It is unlikely that all four choices can be completed in a 3-hour lab period. It is suggested that students be assigned Choice I and then only one of the other choices.

Estimated time to complete:

Choice I: 45–60 minutes
Choice II: 60–75 minutes
Choice III: 75–90 minutes
Choice IV: 75–90 minutes
Choice V: 75–90 minutes

It is strongly recommended that calculations of heat flows \(Q\) and enthalpy changes \(\Delta H\) be reviewed at the chalkboard before students begin the experiment. This is the sort of experiment in which students can adequately perform the manipulations required without ever truly understanding what it is they are measuring.

B. Materials Required (given per 25 students)

Several of the choices require diluted acid solutions. Exercise suitable caution in handling the commercial concentrated acid solutions. In each case, the concentrated acid should be added slowly to a quantity of water. For sulfuric acid, ice should be used to cool the mixture as it is diluted.

All choices

50 8-fluid-ounce plastic foam cups with lids
25 8–10-inch lengths of heavy gauge wire (for stirring)
one-hole paper punch (several per laboratory)
Choice II

unknown metal pellet samples

If individual unknown samples are desired, they can be conveniently dispensed (50–60 grams per student) in coded plastic weighing “boats” or small beakers. Alternatively, all students can determine the same general unknown in a given lab section: 2–3 500-g bottles should be provided in this case. Metal pellets should be collected, dried, and reused by other lab sections.

glass beads or rings (2–3 500-g bottles)

Although spherical glass beads are more readily available, it is strongly recommended that glass rings be used instead because of the hazard of spillage. Such rings (“raschig rings”) are sold as packings for fractional distillation columns.

Choice III

12.5 L 2.0 M HCl (165 mL conc. HCl diluted to 1 liter; Caution!)
12.5 L 2.0 M NaOH (80 g NaOH diluted to 1 liter; Caution!)
12.5 L 2.0 M HNO₃ (126 mL conc. HNO₃ diluted to 1 liter; Caution!)
12.5 L 2.0 M KOH (112 g KOH diluted to 1 liter; Caution!)

Choice IV

25 L 1.0 M HCl (83 mL conc. HCl diluted to 1 liter; Caution!)
25 L 1.0 M HNO₃ (63 mL conc. HNO₃ diluted to 1 liter; Caution!)
25 L 1.0 M H₂SO₄ (69 mL conc. HCl diluted to 1 liter; Caution!)

Choice V

The salts may be provided as 15–20-g coded unknown samples in vials. Or several 500-g bottles of suitable salts may be placed in the lab for the students to choose from. Suitable nontoxic salts include calcium chloride, potassium bromide, ammonium chloride, etc. Each student will need two samples.

C. Answers to Pre-Laboratory Questions

Choice I

1. 1 joule = 1 kg m²/s²

2. \[(51.203 \text{ g})(4.18 \text{ J/g}°\text{C})(55.2 - 37.6°\text{C}) = \]
\[(49.783 \text{ g})(4.18 \text{ J/g}°\text{C})(37.6 - 23.5°\text{C}) + (C_{\text{calorimeter}})(37.6 - 23.5°\text{C})\]
\[
(51.203)(4.18)(17.6) = (49.783)(4.18)(14.1) + (C_{\text{calorimeter}})(14.1)
\]

\[
3766.9 = 2934.1 + (C_{\text{calorimeter}})(14.1)
\]

\[
832.8 = (C_{\text{calorimeter}})(14.1)
\]

\[
C_{\text{calorimeter}} = 59.1 \text{ J/}^\circ\text{C}
\]

**Choice II**

1. Specific heats in J/g\(^\circ\)C: Al (0.902); S (0.706); Fe (0.449); ice (2.03); Pb(0.128). Note that different references may vary slightly in the numbers reported.

2. J/g\(^\circ\)C

**Choice III**

1. A strong acid or base is one that ionizes completely when dissolved in water. Students usually think “strong” means “dangerous,” and although the strong acids and bases are dangerous, this does not imply that “weak” acids and bases are necessarily safe.

2. Neutralization, in aqueous solution, is the combination of a proton (from an acid) with a hydroxide ion (from a base) to make a water molecule. More commonly, students will describe neutralization as representing the point when enough base has been added to an acid sample to react exactly with the acid present.

**Choice IV**

1. \[
Q = (150 \text{ g})(4.18 \text{ J/g}\(^\circ\)\text{C})(8.43\^\circ\text{C}) = -5286\text{ J} = -5.29 \text{ kJ}
\]

2. \[
0.673 \text{ g/113 g/mol} = 5.96 \times 10^{-3} \text{ mol}
\]

\[
\Delta H = -5.29 \text{ kJ}/5.96 \times 10^{-3} \text{ mole} = -888 \text{ kJ/mol}
\]

**Choice V**

1. A salt is an ionic compound. Salts are most commonly thought of by students as the product of an acid–base neutralization reaction.

2. When an ionic solid dissolves in water, there typically is an interaction between the ions and the water molecules. Ions typically attract several polar water molecules to form a hydration sphere. It is the energy of formation of these hydration spheres that students measure in this choice.
D. Answers to Post-Laboratory Questions

Choice I

1. The calorimeter constant would be larger if the material of which the calorimeter is constructed were a good absorber of heat energy. Plastic foam is a good insulator and does not absorb much heat energy.

2. The "heat sink" is the material used in the calorimeter as the primary absorber (or source) of the heat energy. Water is used for several reasons. Most importantly it is easily available and can be easily handled, and it has a relatively large heat capacity.

3. The minus sign indicates that heat lost from one source has the opposite sense when gained by another part of the universe.

4. The calorie is the amount of heat energy required to warm 1.0 g of water by 1.0 Celsius degree: 1 cal = 4.18 joule

Choice II

1. The specific heat of ice is smaller, because if energy is applied to the molecules in a solid, all that can really happen is for the molecules to vibrate faster (until the melting point is reached); the specific heat of steam is larger than either the specific heat of the liquid state or that of the solid state; in the gaseous state, it is easy for the molecules to absorb additional energy since they are freely moving.

2. The glass has a larger specific heat; metal is the better conductor of heat; glass is a better insulator.

Choice III

1. When a proton (or hydroxide ion) is hydrated, it is surrounded by a layer of water molecules. Energy is transferred in the formation of the hydration sphere. Thus students determined the heat of reaction for

   \[ \text{H}^+(\text{H}_2\text{O})_n + \text{OH}^-(\text{H}_2\text{O})_m \rightarrow \text{H}^+ + \text{OH}^- \]

   rather than for

2. A weak acid (or base) is one that does not ionize completely to \( \text{H}^+ \) or \( \text{OH}^- \) when dissolved.

Choice IV

1. The net reaction in each case is the reaction of the metal with the (hydrated) proton. All strong acids are good sources of hydrated protons, so the identity of the acid should not matter.

2. Magnesium evolves more heat on both a gram and a molar basis.

Choice V

2. The overall enthalpy of solution of an ionic substance depends on the enthalpy of hydration of both the positive and the negative ions. With different positive and negative ions, it may turn out that the overall enthalpy of solution is either positive or negative.
A. General Notes

Historically, observance of line spectra was a major incentive in the development of modern theories of atomic structure: here was an easily observable phenomenon, that would have to be explainable by any such theory. Atomic structure is a very abstract topic for most beginning students, and all too often, students approach the study of energy levels and orbitals as just something else that has to be memorized, without really having any appreciation for what such information means. Observing of a few line spectra will not make them into quantum mechanicians, but it should help them to appreciate the atomic mysteries faced by physicists and chemists during the early part of this century, and how far we have come since that time.

The sort of spectroscope called for in the experiment is available commercially from many sources. One spectroscope for each five or six students should be sufficient, since the actual spectral measurements are not very time-consuming. If the cost of the commercial spectrosopes is too high, an inexpensive alternative can be constructed by joining two meter sticks at right angles into a T-shape. A diffraction grating is mounted on the long arm of the T, and the gas-discharge tube is positioned at the intersection of the two meter sticks (students view the discharge tube through the grating, noting the position of spectral lines along the second meter stick). This homemade spectroscope must be used in as dark a room as possible.

Students should be cautioned that the power supply used to excite the gas-discharge tubes is a source of very high voltage and that the tubes are very hot and must be handled with care. Students should be warned not to touch the glass of the discharge tubes when mounting them in the power supply. (Oils from the fingers considerably shorten the life of the discharge tubes.)

In Choice III, the spray method works considerably better, since students can spray the metal ion solution into the flame almost continuously: such sprayers can be found in garden centers as “plant misters,” or empty window cleaner bottles work fine. Some of the salts used are toxic, and the bench where the spraying has been undertaken should be washed down thoroughly.

Students should wear eye protection during this experiment to filter out ultraviolet wavelengths; students should not be allowed to work with the discharge tubes for extended periods to avoid reflected UV light.

Estimated time to complete:

Choice I: 45 minutes
Choice II: 45 minutes
Choice III: 60–75 minutes

B. Materials Required (given per 25 students)

All choices

5–6 spectrosopes

5–6 high-voltage power packs with lamp holders
Choice I

6–7 mercury gas-discharge tubes (to fit power packs above)

Choice II

6–7 hydrogen gas-discharge tubes (to fit power packs above)
6–7 nitrogen gas-discharge tubes (to fit power packs above)

Choice III

Spray Method

5–6 sets of 6 spray bottles (30–36 bottles total), containing 0.1 M solutions of:

- lithium chloride (4.2 g LiCl diluted to 1 L)
- sodium chloride (5.9 g NaCl diluted to 1 L)
- potassium chloride (7.5 g KCl diluted to 1 L)
- calcium chloride (11 g anh. CaCl$_2$ diluted to 1 L)
- strontium chloride (16 g SrCl$_2$ diluted to 1 L)
- barium chloride (21 g anh. BaCl$_2$ diluted to 1 L)

combination solutions:

mixtures of approximately equal amounts of two of the solutions above

- lithium chloride/sodium chloride
- potassium chloride/sodium chloride
- calcium chloride/potassium chloride

Wire Method

roll of light-gauge nichrome wire (for flame test wires): if time allows, the wire can be precut into 6-inch lengths

2 L 6 M hydrochloric acid (500 mL conc. HCl diluted to 1 L; Caution!)

500 mL each of the six solutions listed above for the spray method

unknown samples

Rather than individual student unknowns, it is most convenient to provide the instructor with coded 8-ounce dropper bottles of the six solutions above for him or her to dispense directly to the students. Also, 2–3 similar bottles should be prepared for the instructor, each containing 50/50 mixtures of two of the solutions.
C. Answers to Pre-Laboratory Questions

Choice I

1. The graph should bear some relationship to the mercury line spectrum, in terms of the location of the lines on the wavelength scale. Students, of course, do not know anything about the relative intensity or broadness of the lines at this point.

2. Wavelengths given are only approximate, as the colors indicated occur over a range of wavelengths:
   - red 650 nm
   - yellow 550 nm
   - green 510 nm
   - blue 470 nm

3. The frequencies will depend on the wavelength values listed by students in Question 2. For the wavelengths given above, the frequencies are
   - red $4.62 \times 10^{16}$ Hz
   - yellow $5.45 \times 10^{16}$ Hz
   - green $5.88 \times 10^{16}$ Hz
   - blue $6.38 \times 10^{16}$ Hz

Choice II

1. This represents the Balmer Series for hydrogen:
   - $n = 6$ to $n = 2$: 410.1 nm
   - $n = 5$ to $n = 2$: 434.1 nm
   - $n = 4$ to $n = 2$: 486.1 nm
   - $n = 3$ to $n = 2$: 656.3 nm

2. For a multielectron atom, the various subshells of the principal energy levels do not have the same energy (e.g., the 2s and 2p subshells are of different energy). For an atom like nitrogen, with many electrons undergoing excitation and relaxation, and with many levels of different energy for the electrons to move among, a very complicated spectrum results.

Choice III

1. A discussion of these methods is given as an appendix in the Zumdahl text. Emission spectroscopy studies the energy emitted by excited atoms. Absorption spectroscopy studies the energy absorbed by atoms from an external source.

2. The spectrum of a mixture represents the spectra of the constituent elements superimposed on one another. The elements in the mixture still absorb and emit radiation at their characteristic wavelengths.
D. **Answers to Post-Laboratory Questions**

**Choice I**

1. The slit limits the amount of light that can be viewed and provides a sharper image for observation. If the slit were not used, the lines of the spectrum would be much broader and more diffuse.

2. Mercury is used because its spectrum contains several lines that are both intense and sharply-defined, which makes their position on the spectroscope scale easier to measure.

3. In addition to light in the visible region, gas-discharge tubes also produce ultraviolet radiation, which is damaging to the eyes.

**Choice II**

1. Ultraviolet emissions result from transitions to the $n = 1$ level; infrared emissions result from transitions to the $n = 3$ level.

2. The continuous portion of the spectrum arises from a series of emissions by the atoms at closely spaced wavelengths, corresponding to similar energies for the transitions. A continuous spectrum may also result if the gas pressure in the tube is too high or if contaminants are present.

**Choice III**

1. Generally, the gross color imparted to the flame will correspond to the brightest emission lines in the spectrum.

2. If a gross observation is made of a flame into which sodium ions and other ions have been introduced, the intense yellow-orange emission of sodium tends to overwhelm any emissions from the other atoms: the overall observed color of the flame will be yellow-orange because of the sodium. On a gross scale, cobalt blue filters are used to absorb the sodium emission so that other colors in the flame can be observed. Viewing through a spectroscope, however, it should be possible to observe the individual lines of the other elements, although these may appear more faint than usual because of the brightness of the sodium emission. In qualitative analysis, if a sample contains sodium, flame tests are often viewed through “cobalt blue” glass which filters the orange light from sodium emission and allows emissions from other elements to be seen.
A. General Notes

Choice I of this experiment is potentially one of the most helpful to your students. At the time a typical student is taking general chemistry, it is likely that he or she has studied only plane geometry, with perhaps a little bit of analytic geometry in the calculus class. The typical student at this point has almost certainly not studied the geometry of solids in depth. What may seem to the instructor to be perfectly straightforward molecular geometries are a great mystery to the beginning student with no background in three-dimensional shapes. The problem may be compounded in the lecture, because only two-dimensional projections can be presented on the chalkboard. Students at the author’s university were polled after their first general chemistry course as to which laboratory exercise best helped in understanding the lecture material: students overwhelmingly named the experiment on molecular structures and shapes.

Various sorts of model kits are available commercially, and these are to be preferred to any sort of homemade model-building scheme (e.g., gumdrops and toothpicks): the bond angles in commercial kits are predetermined and prevent students from constructing the two-dimensional projections they have seen in lecture. Ideally, a model kit should be available for each two students. A larger-scale model kit should be available for the instructor’s pre-laboratory discussion: this demonstration model kit should contain parts that are of the same basic type as the individual student kits, only larger.

Students must be encouraged several times during the lab period to return all component parts to the model kits before turning them in. It is imperative that parts not be left on the lab benches or in student lockers. Protractors are needed for students to measure bond angles. These can be the cheapest plastic models available.

The laboratory instructor’s discussion for this experiment should undoubtedly be longer than for most experiments. The instructor should review the writing of Lewis electron dot structures and should discuss the prediction of electron-pair and overall geometry from the VSEPR theory. Numerous examples, ranging from the very simple to the most complex, should be used.

Choice II is fun for students, because invariably it is a bit messy. Make sure students clean the pie pans thoroughly with soap and water and then rinse thoroughly. Any oils from the hand or soap will cause the monolayer to not form a circular disk on the water. The technique of blowing a thin layer of powder on the water may take a couple of attempts: it is best if the powder does not clump up anywhere on the surface of the water. Students are usually impressed with the numbers they generate in this experiment in having measured such a small length.

Estimated time to complete:

Choice I: 120–150 minutes
Choice II: 90–120 minutes
B. Material Required (given per 25 students)

Choice I

student model kits
instructor large-scale model kit
protractors

Choice II

9-inch pie plate or cake pan (disposable) - 1 per student

Pasteur pipets and bulbs

Glass pipets work better than plastic pipets for this: a plastic pipet seems to develop a static electric charge as the drops move through the narrow tip

powder (as fine as possible)

Various types of powders can be used, but it is essential that they be oil-free. Many commercial baby/body powers contain oils. The old standby for this is lycopodium powder which works very well, but is flammable and a bit hard to find. In a pinch, finely powdered sulfur works reasonably well: have students grind it up with mortar and pestle just before use.

rulers (see-through works best)

10-mL graduated cylinders

stearic acid solution in cyclohexane (0.15 g stearic acid diluted to 1 L); labeled “flammable” and kept in the exhaust hood.

C. Answers to Pre-Laboratory Questions

Choice I

1. The valence electron pairs are arranged about the central atom of a molecule so as to be as far away from each other as possible. This leads to a basis shape that will determine the bond angles in the molecule. The overall geometric shape of the molecule is then determined and described in terms of the locations of the atoms that are attached to the central atom.

2. $\text{PCl}_3$ bond angles approximately tetrahedral ($109.5^\circ$), although the influence of the lone pair on P compresses this $\text{SF}_6$ bond angles $90^\circ$ resulting from a perfect octahedron $\text{IF}_5$ bond angles of $90^\circ$ between axial and equatorial Cl atoms, and $120^\circ$ between equatorial Cl atoms (trigonal bipyramid structure) $\text{HI}$ bond angle $180^\circ$ (a molecule with only 2 atoms must be linear) even though the electron pairs on Br are tetrahedral $\text{H}_2\text{S}$ bond angle approximately tetrahedral ($109.5^\circ$), although the influence of the lone pairs on Se compresses this
Choice II

1. Oils consist of nonpolar chains of hydrocarbons that are not attracted by water molecules.

2. approximately 0.077 nm

3. diameter of atom (2)(0.077 nm) = 0.154 nm; straight chain of 18 atoms (18)(0.154) = 2.77 nm

4. Not really; the bond angles around each carbon atom would be expected to be the tetrahedral 109.5°, which would still make the long chain “zig-zag” in space if it were stretched out.

D. Answers to Post-Laboratory Questions

Choice I

1. The bond angles of molecules in which there are lone pairs will be compressed to less than the ideal geometric angle predicted from VSEPR theory. For example, in the ammonia molecule, the H–N–H angle is less than the tetrahedral angle of 109.5° because of the lone pair on nitrogen.

2. A second or third bond between the central atom and another atom must lie in the same general direction from the central atom as the first bond. This effectively reduces the number of “things” around the central atom. For example, in acetylene, C$_2$H$_2$, each carbon atom effectively has two “things” around it: a bond to hydrogen and a triple bond to the other carbon atom. Thus, the prediction for the H–C–C bond angle is 180°.

Choice II

1. Students will most likely find that their “measured” length is less than their calculated value. The calculation does not take into account the bond angles about the carbon atoms or the possibility that the molecules may not line up perfectly.

2. Oils and soaps already present would have prevented the stearic acid monolayer from spreading out; oils and soaps are similar in nature to the oleic acid.
A. General Notes

This experiment illustrates for students some simple properties and reactions of the more common representative elements in an attempt to at least hint at the periodic properties demonstrated by these elements. A full investigation of periodicity is beyond the scope of the introductory laboratory, the cost of the less common elements and their compounds alone being prohibitive.

Portions of this experiment are intended to be performed by the instructor for small groups of students, who will then take the products of the demonstration for individual testing. Under no circumstances should students be permitted to perform these reactions themselves. A large number of reagents is required for this experiment. The amount needed of each reagent is small, but the number of reagents may prove confusing to students. It is best if the reagents are grouped in the laboratory into stations, corresponding to the portions of the experiment. The instructor may assign students to begin with different sections of the experiment to prevent students having to wait to obtain the reagents at any one station.

Students should be warned that although methylene chloride appears to be the least harmful of the chlorinated hydrocarbons, they should still exercise caution in its use, avoiding contact with the skin and using the reagent in the hood.

Estimated time to complete: 150–180 minutes

B. Materials Required (given per 25 students)

5–6 pellets or small chunks of lithium, sodium, and potassium for instructor demonstration. (These should be given to the instructor directly to prevent student use)

1 pack magnesium ribbon
25 g calcium turnings
1 L 6 M hydrochloric acid (500 mL conc. HCl diluted to 1 L; Caution!)
200 mL universal indicator solution
25 6-inch lengths of nichrome wire for flame tests
approximately 25 g each of the following solids:

- lithium chloride
- potassium chloride
- barium chloride
- sodium (per)oxide
- aluminum oxide
- dry ice
- iron(II) sulfide
- sodium chloride
- calcium chloride
- strontium chloride
- calcium oxide
- boric acid
- sulfur
- elemental iodine
500 mL chlorine water (distilled water saturated with Cl\textsubscript{2} gas); 500 mL bromine water (distilled water saturated with Br\textsubscript{2}); 500 mL iodine water (distilled water saturated with I\textsubscript{2}).

Household bleach may be substituted for chlorine water if no tank of the gas is available. Caution should be exercised when preparing bromine water, as elemental bromine is extremely corrosive to the skin and respiratory tract. Iodine is not very readily soluble in water; the solution should be stirred for at least an hour and then decanted from any undissolved iodine.

1 L methylene chloride (dichloromethane)

500 mL 0.1 M NaCl (5.9 g NaCl diluted to 1 L); 500 mL 0.1 M NaBr (10 g NaBr diluted to 1 L); 500 mL 0.1 M NaI (15 g NaI diluted to 1 L)

C. Answers to Pre-Laboratory Questions

1. | Element | Atomic Number | Atomic Mass | Group | Period |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>11</td>
<td>22.99</td>
<td>1A</td>
<td>third</td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
<td>40.08</td>
<td>2A</td>
<td>fourth</td>
</tr>
<tr>
<td>Br</td>
<td>35</td>
<td>79.90</td>
<td>7A</td>
<td>fourth</td>
</tr>
<tr>
<td>He</td>
<td>2</td>
<td>4.003</td>
<td>8A</td>
<td>first</td>
</tr>
<tr>
<td>S</td>
<td>16</td>
<td>32.07</td>
<td>6A</td>
<td>third</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>85.47</td>
<td>1A</td>
<td>fifth</td>
</tr>
<tr>
<td>Ra</td>
<td>88</td>
<td>226</td>
<td>2A</td>
<td>seventh</td>
</tr>
<tr>
<td>Kr</td>
<td>36</td>
<td>83.8</td>
<td>8A</td>
<td>fourth</td>
</tr>
</tbody>
</table>

2. Mendeleev arranged the elements by mass, because the structure of the atom was not yet known. Mendeleev arranged most of the known elements into groups of elements with similar properties, but there were some discrepancies in his tabulation because of errors in atomic masses, “missing” elements, etc. Elements in the same vertical groups have similar valence electron configurations, which far better explains their similar chemical properties.

3. Sublimation is the process by which a solid passes directly into the vapor phase, without first melting to form a liquid phase. Mothballs, snow, solid room, etc. are everyday examples.

4. The halide ions are oxidized first oxidized to the elemental form, and then identified by the characteristic colors of the halogens when extracted into methylene chloride solution.

D. Answers to Post-Laboratory Questions

1. The reactivity increases from lithium to potassium. The single valence electron in the elements is progressively farther from the nucleus and is more easily lost.

2. Metallic oxides are generally basic in aqueous solution, whereas nonmetallic oxides are generally acidic in aqueous solution.

3. Dry ice also sublimed.

4. The colors that appear in a flame test result from emissions from the atoms in the sample. A given element’s atoms have a fixed atomic energy level structure, which results in the same colors (energies) of photons being emitted.
EXPERIMENT 21 Classes of Chemical Reactions

A. General Notes

Students oftentimes have difficulty distinguishing one type of reaction from another on paper. For example, to the student, Cu(s) and Cu^{2+}(aq) don’t seem all that different as written, yet in the laboratory, these two states of copper are easily distinguishable from one another. This experiment will enable students to see clearly for themselves when a reaction has taken place and how the properties of the reactants have changed to the properties of the products. The experiment also emphasizes to the student the observational nature of experimental chemistry: how scientists infer with their senses what has happened.

This experiment requires a large number of reagents. To minimize students having to wait for reagents, it is suggested that the reagents be arranged in the room according to the parts of the experiment. It is also suggested that the instructor assign groups of students to begin the experiment at different points in the procedure.

Portions of the experiment are intended to be performed by the instructor as a demonstration. Under no circumstances should students be allowed to attempt these portions on their own.

Estimated time to complete: 150–180 minutes

B. Materials Required (given per 25 students)

Student experiments:

1 L 0.1 M silver nitrate (17 g AgNO\textsubscript{3} diluted to 1 L)
100 mL 0.1 M sodium chloride (5.9 g NaCl diluted to 1 L)
100 mL 0.1 M lead acetate [33 g Pb(CH\textsubscript{3}COO)\textsubscript{2} diluted to 1 L]
100 mL 0.1 M potassium chromate (19 g K\textsubscript{2}CrO\textsubscript{4} diluted to 1 L)
100 mL 0.1 M barium chloride (21 g BaCl\textsubscript{2} diluted to 1 L)
100 mL 0.1 M sulfuric acid (6 mL conc. H\textsubscript{2}SO\textsubscript{4} diluted to 1 L; Caution!)
500 mL 0.1 M hydrochloric acid (8 mL conc. HCl diluted to 1 L; Caution!)
500 mL 0.1 M acetic acid (6 mL conc. CH\textsubscript{3}COOH diluted to 1 L; Caution!)
500 mL 0.1 M sodium hydroxide (4 g NaOH diluted to 1 L; Caution!)
500 mL 0.1 M ammonia (7 mL conc. NH\textsubscript{3} diluted to 1 L; Caution!)
2–3 vials pH test paper
500 mL universal indicator solution
2 L 0.5 M copper(II) sulfate (125 g CuSO\textsubscript{4}.5H\textsubscript{2}O diluted to 1 L)
500 mL 0.5 M nickel(II) sulfate (140 g NiSO\textsubscript{4}.7H\textsubscript{2}O diluted to 1 L)
1 L concentrated ammonia solution
1 L 1 M ammonium sulfate [132 g (NH$_4$)$_2$SO$_4$ diluted to 1 L]
500 mL 0.5 M iron(III) nitrate (202 g Fe(NO$_3$)$_3$·9H$_2$O diluted with 1 M HNO$_3$ to 1 L; Caution!)
500 mL 1 M sodium chloride (59 g NaCl diluted to 1 L)
500 mL 1 M hydrochloric acid (83 mL conc. HCl diluted to 1 L; Caution!)
100 mL 0.1 M sodium thiocyanate (8 g NaSCN diluted to 1 L)
100 mL 5% 1,10-phenanthroline (50 g PHEN diluted with 50/50 v/v% EtOH/water to 1 L)
100 mL 1% dimethylglyoxime (10 g DMG diluted with 50/50 v/v% EtOH/water to 1 L)
500 mL 0.5 M sodium chloride (29 g NaCl diluted to 1 L)
500 mL 0.5 M sodium bromide (52 g NaBr diluted to 1 L)
500 mL 10% ethylene diamine (100 mL EN diluted to 1 L)
1 pack magnesium ribbon
500 mL 3% hydrogen peroxide (commercial solution)
50 g potassium permanganate solid
wooden splints
50 strips (1 \(\times\) 4 cm) metallic zinc
25 strips (1 \(\times\) 4 cm) metallic copper
1 L 1 M lead acetate [330 g Pb(CH$_3$COO)$_2$ diluted to 1 L]
100 mL 10% potassium iodide (100 g KI diluted to 1 L)
100 mL 10% potassium bromide (100 g KBr diluted to 1 L)
250 mL chlorine water (distilled water saturated with Cl$_2$ gas)
250 mL methylene chloride (dichloromethane)

**Instructor demonstrations:**

light bulb conductivity testers
oxygen gas, set up at a fume hood
steel wool
C. Answers to Pre-Laboratory Questions

1. A precipitation reaction may take place when solutions of two ionic substances are mixed, if one of the new combinations of ions is not soluble in water.

2. The Arrhenius and Brönsted–Lowry definitions of an acid are similar in that both definitions are in terms of the proton. In the Arrhenius definition, an acid is a species capable of producing protons in water. In the Brönsted–Lowry definition, an acid is a species capable of donating a proton to another species and is independent of what the solvent might be. In the Arrhenius definition, a base is a substance that produces hydroxide ions in water. The Brönsted–Lowry definition of a base, however, defines a base as a proton acceptor and (again) does not depend on the identity of the solvent or even on there being a solvent present.

3. A coordination complex is formed when certain neutral or negative species form coordinate covalent bonds to the $d$-orbitals of a metal ion.

4. A “redox” (oxidation–reduction) reaction is an electron transfer reaction. Typically, in order to be able to keep track of the electrons being transferred, we divide the overall redox reaction into two half-reactions, one representing the oxidation, the other the reduction.

D. Answers to Post-Laboratory Questions

1. See manual.

2. A catalyst is a molecule that can speed up a reaction (without being consumed) by providing an alternative pathway for the mechanism of the reaction.

3. (a) precipitation; (b) oxidation–reduction; (c) acid–base
A. General Notes

Students often complain that their laboratory work is not what they feel is “relevant” to the real world and its problems. This experiment, while still demonstrating important redox, complexation, and precipitation reactions and still permitting the evaluation of students, is nonetheless an experiment that students will find ecologically relevant.

Although it might seem that there is a great deal of work to be done in a single laboratory period, with several sets of titrations, each analysis is done only in duplicate, and the titrant and unknown solutions have already been prepared for students.

In Part A, students should not add starch until the solution is pale yellow. (The solution is initially a dark brown because of the level of iodine.) If starch is added too soon, it may adsorb iodine irreversibly. Remind students that they are titrating until the blue-black color of the iodine just barely disappears.

In Part B, the appearance of the indicator color is oftentimes hard to see since only a very tiny amount of silver chromate will have formed at the endpoint. If students are unsure whether they have reached the endpoint, they should take an interim buret reading and then add additional titrant to see if they have in fact reached the endpoint.

The endpoint of Part C may be confusing to students after the first two parts of the experiment. Whereas in Part A they titrate until the solution suddenly turns colorless, and in Part B they titrate until the sudden appearance of the silver chromate color, in Part C the solution is titrated until the red color has disappeared completely, leaving the solution pure blue. The solution passes through a fairly long intermediate stage when blue and red colors are both present (making the solution appear gray). The endpoint is the disappearance of the red color, not the appearance of the first blue color (at the endpoint, when all red is gone, the solution will be pure blue).

The titrant solutions to be prepared are described as “0.0500 M,” indicating that the titration should be good to three significant figures. Since only three figures are expected, the titrant solutions may be made up determinately and need not be standardized by stockroom personnel.

Unknowns for this experiment are best dispensed as individual samples in sealed, coded 4-ounce bottles. A simple scheme for preparing such individual unknowns is given below.

Estimated time to complete: 3 hours

B. Materials Required (given per 25 students)

25 50-mL titration burets
25 25-mL volumetric transfer pipets
25 pipet safety bulbs
1 L 6 M sulfuric acid (330 mL conc. H₂SO₄ diluted to 1 L; dilute with extreme caution)
150 g potassium iodide
4 L 0.0500 M sodium thiosulfate titrant

Exactly 12.4 g of sodium thiosulfate pentahydrate, Na₂S₂O₅·5H₂O, from a freshly opened bottle should be diluted to 1.00 L in a volumetric flask.
1% starch indicator

Boil 250 mL of distilled water; make a slurry of 2–3 g of soluble starch in 5–10 mL of water; add the starch paste to the boiling water and stir to homogenize and clarify; cool and decant into an appropriate bottle. The indicator should not be kept for more than 1 week.

4 L 0.0500 M silver nitrate titrant

Exactly 8.49 g of colorless silver nitrate should be diluted to 1.00 L in a volumetric flask.

0.035 M sodium chromate indicator (5.6 g Na$_2$CrO$_4$ diluted to 1 L)

4 L 0.0500 M EDTA titrant

Exactly 18.6 g of disodium dihydrogen EDTA dihydrate, Na$_2$EDTA·2H$_2$O, should be diluted to 1.00 L in a volumetric flask.

2 L pH 10 ammonia/ammonium chloride buffer (67 g NH$_4$Cl added to 570 mL conc. NH$_3$ diluted to 1 L; Caution – stench!)

1% Eriochrome Black T indicator

Dissolve 1 g EBT in 100 mL distilled water and transfer to a dropper bottle. The indicator should not be kept for more than 1 week; keep refrigerated.

0.01 M Mg/EDTA solution (2.0 g MgCl$_2$·6H$_2$O and 3.7 g Na$_2$EDTA·2H$_2$O diluted to 1 L)

**Unknowns**

*Dissolved oxygen*

25 coded 4-ounce bottles (clean and dry)

2 L 0.06 M potassium iodate stock solution to serve as “dissolved oxygen” for the unknowns

Weigh 26±1 g of KIO$_3$ to the nearest 0.01 g and record; transfer quantitatively to a 2.00-L volumetric flask; add approximately 1 L of distilled water and shake to dissolve (KIO$_3$ is very slow to dissolve); dilute to 2.00 L with distilled water.

For the individual unknowns, pipet 75.0 mL of the stock KIO$_3$ solution to each bottle. Then, from a buret, add between 5 and 15 mL of distilled water to each bottle; record initial and final buret volumes to the nearest 0.01 mL; cap and shake the bottles. The instructor should be provided with the concentration of the iodate stock solution and with the buret volumes for the amount of water in each unknown.

*Chloride*

25 coded 4-ounce bottles (clean and dry)

1 L 0.40 M chloride ion stock solution

Weigh 23±1 g of NaCl to the nearest 0.01 g and record; transfer quantitatively to a 1.00-L volumetric flask; dissolve and dilute with distilled water to 1.00 L.

For the individual unknowns, pipet 75.0 mL of distilled water into each bottle. Then, from a buret, add between 5 and 15 mL of the chloride stock solution to each bottle; record initial and final buret volumes to the nearest 0.01 mL; cap and shake the bottles. The instructor should be provided with the concentration of the chloride stock solution, and the buret volumes for the stock solution in each unknown.
Calcium

25 coded 4-ounce bottles (clean and dry)
1 L 0.4 M calcium ion stock solution

Weigh 40±1 g of CaCO₃ to the nearest 0.01 g and record; transfer quantitatively to a 1.00-L volumetric flask; dissolve with shaking in the minimum quantity of conc. HCl (Caution!); dilute to 1.00 L with distilled water.

For the individual unknowns, pipet 75.0 mL of distilled water into each bottle. Then, from a buret, add between 5 and 15 mL of the calcium stock solution to each bottle; record initial and final buret volumes to the nearest 0.01 mL; cap and shake the bottles. The instructor should be provided with the concentration of the calcium stock solution and with the buret volumes for the stock solution in each unknown.

C. Answers to Pre-Laboratory Questions

1. Available oxygen represents the amount of oxygen dissolved in a water sample, plus any other oxidizing agents present. The analysis in this experiment does not distinguish between dissolved O₂ and other reducible materials.

2. Hard water is water that contains significant concentrations of ionic substances; it is most commonly thought of as water that causes traditional soaps to precipitate. Hard water may be temporary (HCO₃⁻ ion) or permanent (Ca²⁺, Mg²⁺ ions). Temporary hard water is treated by boiling to expel CO₂. Permanent hard water may be treated by removing the ions (e.g., by ion exchange), by complexing the ions (e.g., with EDTA), or by precipitating the ions before using the water.

3. mmol EDTA = (31.72 mL)(0.05048 M) = 1.601 mmol

   mmol Ca²⁺ = mmol EDTA

   M of Ca²⁺ in sample = (1.601 mmol)/(25.0 mL) = 0.0640 M

4. 

   HOOC—C—H₂
   HOOC—C—N—C—N—C—COOH
   H₂     H₂     H₂     H₂

5. a. Na₂S₂O₃
   b. KI
   c. Na₂CrO₄
   d. AgNO₃
   e. NH₄Cl
D. Answers to Post-Laboratory Questions

1. If the iodine evaporates from the solution, the amount of thiosulfate titrant required will be too small. If the amount of thiosulfate is too small, the reported available oxygen will be smaller than the true amount.

2. The endpoint of the Ca/EDTA/Eriochrome reaction is indistinct. When Mg is introduced into the system, a competition between Mg and Ca exists, and the color of the Mg/EDTA/Eriochrome endpoint can be used.

3. In order to degrade sewage, a large colony of bacteria is needed. The bacteria consume the oxygen in their life processes.
EXPERIMENT 23 Colligative Properties of Solutions

A. General Notes

The experiment presents both a quantitative choice (freezing point depression) and a more qualitative one (osmosis) illustrating the effect a solute has on the properties of a solvent. Before students attempt the experiment, the instructor should take a few minutes at the chalkboard to review these effects, including those effects (boiling point elevation, vapor pressure lowering) that are not demonstrated in the experiment. Students must be made to realize that these “mysterious” colligative properties are exactly what one would expect if one were to examine the constitution of a solution on a microscopic basis.

Choice I determines the molar mass of elemental sulfur as dissolved in naphthalene. This is instructive because it reaffirms to students that elements are not necessarily monatomic in the free state. Arriving at a molar mass that is eight times larger than the atomic mass of sulfur at first surprises students. The instructor may also wish students to determine the molar mass of another naphthalene-soluble substance if a true unknown is desired. The instructor should go over an example for the molar mass calculations at the chalkboard.

Choice II clearly demonstrates osmosis and dialysis if the system is set up correctly (especially as to the rinsing of the membrane tubing in the last portion of the experiment). From this choice, students should determine that water flows faster into the 25% NaCl solution than into the 5% solution and that substances dialyze through a membrane at a speed in inverse proportion to the size of the particles involved. (Chloride ion passes through the membrane almost immediately, whereas glucose requires 15–30 minutes, and starch never passes through the membrane.)

Estimated time to complete:

Choice I: 2 hours
Choice II: 2 hours (if Parts A and B are set up at same time)

B. Materials Required (given per 25 students)

Choice I

25 8-inch test tubes with 2-hole stoppers to fit
25 10–12-inch lengths of medium-gauge copper wire
600 g naphthalene
50 g 1,4-dichlorobenzene (p-dichlorobenzene)
1 L acetone (in hood)
50 g precipitated or powdered sulfur (not chunk or roll sulfur)
Choice II

freshly sliced cucumber
1 lb NaCl(s)
75 10–12-inch lengths of cellophane dialysis tubing (sold commercially)
several one-hole paper punches
2 L 5% sodium chloride (50 g NaCl diluted to 1 L)
1 L 25% sodium chloride (250 g NaCl stirred and diluted to 1 L)
1 L 5% dextrose/glucose (50 g dextrose diluted to 1 L)
1 L 1 % starch solution

Boil 1 L of distilled water. Make a slurry of 10 g starch in 10 mL cold distilled water, and pour the paste into the boiling water. Stir the mixture until it is homogeneous. Cool and decant from any lumps of undissolved starch.

100 mL 0.1 M silver nitrate (17 g of AgNO₃ diluted to 1 L)
100 mL 0.1 M iodine/potassium iodide

17 g KI and approximately 10 g of elemental I₂ diluted to 1 L. The solution is 0.1 M in KI and less than 0.1 M in I₂; iodine is not soluble to the extent of 0.1 M.

1 L Benedict’s reagent or 500 mL each of Fehling’s A and B reagents (sold commercially, or directions for preparation are in the CRC Handbook)

C. Answers to Pre-Laboratory Questions

Choice I

1. Colligative properties are those properties of a solution that depend only on the number of solute particles present and not on their identity. Boiling point elevation, freezing point depression, vapor pressure lowering, and osmotic pressure are all colligative properties.

2. \( K_f \) for benzene = 5.12°C/molal from the Introduction

\[
m = \frac{\Delta T}{K_f} = \frac{6.33°C}{5.12°C/molal} = 1.24 \text{ mol} 
\]

\[
m = 1.24 \text{ mol} /\text{kg} = \frac{\text{mol unknown}}{0.00851 \text{ kg solvent}} 
\]

\[
\text{mol unknown} = 0.0106 \text{ mol unknown} 
\]

molar mass = g/mol = 1.15 g unknown/0.0106 mol unknown = 108 g/mol

3. When 1 mol of an ionic substance is dissolved, the number of individual particles that are present in the solution will be greater than 1 mol. For example, if 1 mol of NaCl is dissolved, the solution will contain 2 mol of particles (1 mol of Na⁺ and 1 mol of Cl⁻). Since colligative properties depend on the number of particles dissolved—not on their identity—on a mole for mole basis, an ionic solute demonstrates a larger effect.
Choice II

1. If a solution having a higher or lower concentration than bodily fluids is injected into the bloodstream, osmosis/dialysis may occur into or out of the cells. If osmosis occurs into a cell, the cell may burst; if osmosis occurs from a cell, the cell structures may collapse.

2. 5% w/v dextrose = 5 g dextrose/100 mL solution  molar mass dextrose = 180 g/mol

\[ \text{5 g dextrose} \times \frac{1 \text{ mol}}{180 \text{ g}} = 0.0278 \text{ mol dextrose} \]

\[ 100 \text{ mL} = 0.100 \text{ L} \]

\[ M = \text{mol/L} = \frac{0.0278 \text{ mol}}{0.100 \text{ L}} = 0.278 \text{ M} \]

Note that the question contains only one significant figure for the % dextrose, and strictly speaking, the molarity should be reported as 0.3 M.

0.9% w/v NaCl = 0.9 g NaCl/100 mL solution  molar mass NaCl = 58.5 g/mol

\[ 0.9 \text{ g NaCl} \times \frac{1 \text{ mol}}{58.5 \text{ g}} = 0.0154 \text{ mol NaCl} \]

\[ M = \text{mol/L} = \frac{0.0154 \text{ mol}}{0.100 \text{ L}} = 0.154 \text{ M} \]

Note again that the question only contains one significant figure for the % NaCl, and strictly speaking the molarity should be reported as 0.2 M.

Since NaCl forms two particles per formula unit, the colligative molarity is twice the formal molarity = 2(0.154 M) = 0.307 M.

The solutions are not quite isotonic for the percentages solutes as given.

D. Answers to Post-Laboratory Questions

Choice I

1. Supercooling most commonly occurs when a process is performed in a container with very smooth sides (e.g., glass). In order for crystals to form, there must generally be some irregular point about which crystal formation can nucleate. (For example, in crystallization techniques one finds directions to “add a seed crystal” or to “scratch the walls of the container with a stirring rod.”)

2. \( K_f \) for naphthalene = 6.9°C/molal

3. If the solute were to dimerize when dissolved in the solvent, the apparent molar mass would be twice the true molar mass.

4. boiling point elevation = 2.04°C and therefore the solution is 2.04/0.51 = 4 m in glucose

\[ \text{mass of glucose} = 4 \text{ mol} \times 180 \text{ g/mol} = 720 \text{ g glucose} \]
Choice II

1. The smaller a particle, the faster it moves through the membrane. Chloride ion is detectable almost immediately; glucose is detectable after 15–20 minutes; starch, being colloidal and very large, should not pass through the membrane at all. A starch solution is really a colloidal dispersion.

2. Starch is a large polymeric molecule, and its molecules are too large to pass through the pores of the membrane.

3. When blood cells are placed in a medium that is hypotonic to the fluid inside the blood cells, osmosis of solvent into the cells occurs, causing them to burst. This is hemolysis. When blood cells are placed in a hypertonic medium, osmosis of water from the cells into the medium occurs, causing the cells to shrink and collapse. This is crenation. Either process destroys the blood cell.
EXPERIMENT 24 Colloids

A. General Notes

Students have trouble differentiating between true solutions and colloidal dispersions. To them, if you put a solute in water and the solute seems to disappear, then it must have “dissolved.” In actuality, many of the materials they come into contact with in everyday life are colloids or suspensions. Everyone, for example, has seen particles of dust in the air in a room when a sharp beam of light is present. Similarly, most students will appreciate how cigarette smoke forms a dispersion in the air of a room, making the room “smoky.” Students probably have not realized, however, that the same effects can occur when the solvent is a liquid (rather than air), as is demonstrated clearly in this experiment.

The experiment demonstrates that relatively concentrated colloids generally appear cloudy, whereas very dilute colloids may appear clear to the naked eye but display the Tyndall effect when a beam of high-intensity light is passed through the mixture.

Estimated time to complete: 100–120 minutes

B. Materials Required (given per 25 students)

250 g soluble starch
250 g gelatin
250 g sodium chloride
250 g glucose (dextrose)
5–6 high-intensity lamps (or small flashlights)
25 square glass jars (“French squares” or TLC chambers, or 25 tall-form beakers

the idea being that the height of the solution in the jar or beaker should be at the level reachable by the high-intensity lamp; if flashlights are used, the usual low-form beakers found in student lockers will suffice

ice

C. Answers to Pre-Laboratory Questions

1. A colloidal dispersion is a mixture in which small particles of solute are permanently dispersed throughout the solvent. The suspended particles are intermediate in size between large, macroscopic particles and individual molecules.

2. Brownian motion is the random and unceasing motion of the particles of a colloid, making the motion very much like that of the molecules in a gas. (One might expect the relatively macroscopic particles of a colloid to precipitate readily.) The Tyndall effect is the scattering of light by colloidal particles, making the beam of light visible as it passes through the colloid.
3. True solutions contain individual atoms, ions, or small molecules. Colloidal dispersions contain larger aggregates or very large individual molecules, ranging in size up to 1000 nm. Suspensions contain macroscopic particles larger than 1000 nm that can usually be seen easily with the naked eye. The colligative properties of solutions depend on the number of particles actually dissolved in the solvent: colloidal and suspended particles may not have the expected effect on a solvent’s properties, compared to a truly dissolved solute.

4. A gel is a jelly-like material which generally results from the coagulation of a colloid. The solute particles trap solvent molecules among them to form a semi-solid.

D. Answers to Post-Laboratory Questions

1. The distilled water was filtered primarily to remove any dust that might have been present from the air in the room or from the glassware used. The presence of dust would have resulted in a false Tyndall effect in the true solutions.

2. Many everyday materials are suspensions; examples include salad dressing, paint, milk of magnesia—basically anything that has to be shaken before use.

3. To say that milk has been “homogenized” means that it has been treated so that it is uniform throughout (homogeneous). Milk contains butterfat, which in milk that has not undergone treatment will rise to the top and separate. In milk that has been homogenized, the butterfat is made to form a colloidal dispersion in the aqueous portion.
EXPERIMENT 25 Rates of Chemical Reactions

A. General Notes

Chemical kinetics occupies a fair portion of time in the general chemistry course, and it is material that students usually enjoy. However, there appears to be no simple, completely reliable, quantitative kinetics experiment for students to work on in the laboratory. It is relatively easy to demonstrate that using higher concentrations of reagents does speed up a reaction, or that lowering the temperature does slow down a reaction, but it has been difficult to find an experiment that shows these phenomena with the quantitative agreement students have been told, in their lecture, to expect.

The reaction in this experiment, an iodine clock reaction, is perhaps the most useful of the currently available kinetics experiments. The instructor must be warned, however, that the reaction has often proved difficult to perform successfully, since there are many things that can go wrong with the experiment that are beyond the control of students.

It is strongly recommended that the instructor perform Run A of the procedure, using the reagents the students will be using, immediately prior to the laboratory period. The concentrations specified for the two redox reagents used in the clock reaction are concentrations that generally (but not always) give reasonable times for the iodine color to appear. For some reason (perhaps a self-catalytic decomposition), these concentrations sometimes give the iodine color too quickly; in this case, the instructor should dilute the potassium iodate until a better time is obtained. On the other hand, if the reaction is too slow, sulfuric acid can be added to the sodium bisulfite (Caution: stench!) until a better time is obtained. It is not really necessary to re-label the bottles with the new concentrations, since students do no calculations with these concentrations.

In any case, the reagents should be prepared as nearly as possible in time to the laboratory period, and fresh, previously unopened bottles of the reagents should be used. In particular, the starch decomposes relatively quickly because of bacterial action and/or acidic hydrolysis.

Students should be especially cautioned that cleanliness is important during the kinetic runs: a different graduated cylinder should be used for each of the solutions, and the thermometer should be rinsed and wiped when moving between solutions. Students should rinse all glassware with distilled water, since transition metals in tap water may speed up the reaction.

In the portion of the experiment illustrating the temperature-dependence of the rate, students need to be warned that all solutions must be equilibrated at the higher/lower temperature, and must be kept at that temperature during the course of the reaction. In our experience, students sometimes heat or chill the reagents, but then mix them together on the lab bench instead of in the heating/cooling bath.

Students will need a watch with a second hand/display for this experiment. It is worthwhile reminding students of this in advance of the laboratory period.

Estimated time to complete: 150–180 minutes

B. Materials Required (given per 25 students)

5 L 0.024 M potassium iodate (5.1 g KIO₃ diluted to 1 L)

2 L 0.016 M sodium bisulfite/1% starch

For 1 L of the mixture, bring approximately 900 mL of distilled water to the boiling point. Make a slurry of approximately 10 g of starch in 50 mL of cold distilled water; add the starch paste to the boiling water; cool and decant the solution from any lumps of undissolved starch. When the mixture is cool, add 1.7 g NaHSO₃; transfer the mixture to a 1-L graduated cylinder and dilute to 1.0 L.
Do a test run of Kinetic Run A. If the time for the color change is too short, dilute the potassium iodate solution in proportion to the time increase desired; if the time for the color change is too long, add concentrated sulfuric acid (Caution!), a few drops at a time, to the sodium sulfite solution (with mixing) until the time is more reasonable.

C. **Answers to Pre-Laboratory Questions**

1. The reaction is first-order in both [A] and [B].

2. For a rate law of the form \( \text{Rate} = k[A][B] \) as in Question 1, and the rate in \( M/s \), the units of the rate constant are \( L/mol-s \).

3. The mechanism of a reaction is the series of elementary steps by which the reaction takes place on a microscopic basis. The combined stoichiometry of the mechanistic steps algebraically results in the overall stoichiometry of the reaction, but the overall rate of the reaction is controlled by the slowest elementary step in the mechanism (the rate-determining step). Determination of the species involved in the rate-determining step of a reaction, which shows the stoichiometry and species involved in an intermediate step of the reaction, often gives clues to what must happen in earlier and later steps of the mechanism.

4. Reactions are speeded up with an increase in temperature. At higher temperatures, a larger fraction of molecules will have kinetic energies equal to or greater than the activation energy for the reaction.

D. **Answers to Post-Laboratory Questions**

1. A similar set of reactions could be performed, in which the amount of potassium iodate used was kept constant, but in which the amount of sodium bisulfite used was systematically varied.

2. If the total volume of the solution had not been kept constant by addition of a complementary amount of water, then the actual concentrations of potassium iodate in the system after mixing would not have been varied in the systematic manner desired.

3. Because temperature also affects rate, any difference in temperature between solutions would not have isolated the desired effect on rate due to changes in concentration.

4. Rate is the derivative of concentration with respect to time; therefore, rate and time are inversely related; a higher rate means a smaller reaction time.
A. General Notes

This experiment presents both quantitative and qualitative aspects of systems in chemical equilibrium. Students have trouble appreciating what is meant by an equilibrium: too often they suppose that something is “wrong” with a reaction if the theoretical maximum amount of product is not produced. The esterification reaction in Choice I is especially nice, since the concentrations of all of the species at equilibrium are “normal”-size numbers that students feel more comfortable with. (All too frequently, the equilibrium constants we expect them to deal with—ionization constants and solubility products, for example—are very small powers of 10.)

Choice I studies the esterification reaction between 1-propanol and acetic acid. This experiment requires two weeks to complete, although the amount of work required each week will permit another short experiment to be performed if this is desired. Students are able to calculate the concentrations of all species present at equilibrium from a knowledge of what quantities of the two reactants were mixed initially, and from measuring the concentration of acetic acid still present at equilibrium. The only possible pitfall in the experiment is the need for a strong mineral acid catalyst: the concentration of mineral acid must be determined immediately after adding the catalyst to the organic reactant, before the esterification reaction has a chance to proceed very far. Students must be warned not to delay pipeting the samples of catalyzed reaction mixture: the catalyzed reaction mixture should require more standard NaOH to titrate than the uncatalyzed mixture did. If the instructor notices that students are requiring less NaOH to titrate the mixture after the mineral acid has been added, the experiment can be saved by having students titrate 1-mL portions of a blank: 33 mL of distilled water to which the same number of drops of mineral acid are added as were added to the organic reaction mixture.

Choice II of the experiment allows students to determine the equilibrium constant for the complexation reaction between iron(III) and the thiocyanate ion using a spectrophotometric method (the iron/thiocyanate complex is intensely colored). Whereas in Choice I, students are to determine only a single value for \( K \), in Choice II, students determine multiple values for \( K \) and see that the constant is, indeed, constant.

Choice III of the experiment applies Le Châtelier’s principle to some simple equilibrium systems. The instructor might want to spend a few minutes at the chalkboard discussing exactly what the equilibrium is in each system and how the changes made might be expected to affect each system.

Estimated time to complete:
- Choice I: 120 minutes (first week); 60 minutes (second week)
- Choice II: 75–90 minutes
- Choice III: 60 minutes

B. Materials Required (given per 25 students)

**Choice I**
- 25 50-mL titration burets
- 25 1-mL volumetric transfer pipets and rubber safety bulbs
- plastic food wrap
7 L 0.10 \textit{M} sodium hydroxide

It is only realistic to expect the determination of the equilibrium constant to be good to one or two significant figures; therefore the titrant may be made up determinately (4.0 g of NaOH diluted to 1 L; \textit{Caution}!)

1 L 1-propanol (\textit{n}-propyl alcohol): needed first week only

1 L glacial acetic acid (ethanoic acid): needed first week only; \textit{Caution}!

200 mL 1\% phenolphthalein indicator

Dissolve 2 g phenolphthalein in 100 mL 95\% ethanol and dilute to 200 mL with distilled water. Transfer to dropper bottles.

200 mL 6 \textit{M} sulfuric acid

330 mL conc. H\textsubscript{2}SO\textsubscript{4} (\textit{Caution}!) diluted to 1 L; transfer to dropper bottle; \textit{Caution}: heat evolved on dilution is very large; pack in ice bath.

Choice II

spectrophotometers (Spectronic 20 or other), cuvets

18 150-mm test tubes (5 per student)

10.0 mL Mohr pipets and rubber safety bulbs

5 L 2.00 \texttimes 10\textsuperscript{-3} \textit{M} iron(III) nitrate

Place 4.04 g of iron(III) nitrate nonahydrate in a 5-Liter volumetric flask and add approximately 3 L of water; add approximately 25 mL of concentrated nitric acid (\textit{Caution}!), mix, and then dilute to the calibration mark with water; Mix thoroughly and transfer to 1-L bottles for dispensing

5 L 2.00 \texttimes 10\textsuperscript{-3} \textit{M} potassium thiocyanate

Place 0.972 g of potassium thiocyanate in a 5-L volumetric flask and add approximately 3 liters of water; add approximately 25 mL of concentrated nitric acid (\textit{Caution}!), mix, and then dilute to the calibration mark with water. Mix thoroughly and transfer to 1-L bottles for dispensing

Choice III

250 mL saturated sodium chloride solution (stir until no more salt dissolves, filter before dispensing)

200 mL 12 \textit{M} (conc.) hydrochloric acid (dropper bottle); \textit{Caution}!

200 mL 1 \textit{M} hydrochloric acid (83 mL conc. HCl diluted to 1 L; transfer to dropper bottle); \textit{Caution}!

100 mL 0.1 \textit{M} iron(III) chloride (27 g FeCl\textsubscript{3} \cdot 6H\textsubscript{2}O diluted to 1 L with 1 \textit{M} HNO\textsubscript{3}; \textit{Caution}!)

100 mL 0.1 \textit{M} potassium thiocyanate (10 g KSCN diluted to 1 L)

500 mL 0.1 \textit{M} silver nitrate (17 g AgNO\textsubscript{3} diluted to 1 L)

100 mL concentrated ammonia (dropper bottle)

100 mL 1\% phenolphthalein indicator

Dissolve 1 g phenolphthalein in 50 mL 95\% ethanol and dilute to 100 mL with distilled water. Transfer to dropper bottles.

100 g ammonium chloride
C. Answers to Pre-Laboratory Questions

Choice I

1. \[ K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \]

   \[ K = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]} \]

   \[ K = \frac{[\text{CO}_2]^2}{[\text{CO}][\text{O}_2]} \]

2. \[ M = \frac{(0.10)(0.0234)}{(0.00100)} = 2.3\ M \]

   Only two figures are justified since the concentration of the base is only given to two figures.

Choice II

1. A calibration curve is a plot of the absorbance versus the concentration for a colored substance in solution (a Beer’s law plot). If it is assumed that the absorbance is a linear function of the concentration over all ranges of concentration, then an unknown’s concentration may be determined by finding its absorbance on the calibration curve and then reading down to the concentration axis to see what concentration gives rise to such an absorbance.

2. \[ \text{Absorbance} = 2 - \log(26.2) = 0.582 \]

Choice III

(a) Equilibrium is shifted to the right.

(b) Equilibrium is shifted to the right.

(c) Equilibrium is shifted to the right.

(d) No change occurs.

D. Answers to Post-Laboratory Questions

Choice I

1. Catalysts speed up the attainment of equilibrium but do not affect the position of the equilibrium.

2. Other acids might conceivably have been used (e.g., \( \text{H}_3\text{PO}_4 \) is sometimes used for esterification reactions). It is unlikely that \( \text{HCl} \) or \( \text{HNO}_3 \) would be used, however, because each of these is itself capable of reacting with organic acids or alcohols to give other products than the ester. (Students would not be likely to know this at this point.)

3. Solids and pure liquids are left out of equilibrium constant expressions when there exists a heterogeneous equilibrium. All of the reactants and products in this system are virtually completely miscible in each other in a single phase.
Choice II

1. Student results typically agree within a few percent, with the equilibrium constant having a value on the order of $10^2$.

2. The most common reason for lack of agreement is the student’s math in calculating the concentrations. Students should be warned not to round off numbers too soon in the calculations (when performing calculations consisting of several steps, some students have a habit of rounding off each intermediate step, and the cumulative round-off can become quite large).

Choice III

1. In a saturated solution that contains some undissolved solute, dissolving and crystallization are constantly going on at the same speed. (Two opposite processes going on at the same time at the same speed are the conditions that define a dynamic equilibrium.) The net concentration of solute in solution does not change if the solution is saturated, no matter what quantity of excess solute might be present.

2. The concentration of chloride ion in saturated NaCl is on the order of 5.4 $M$. Concentrated HCl contains a much larger concentration of chloride ion than does the saturated NaCl, and adding concentrated HCl to the NaCl shifts the equilibrium in the direction of precipitation. The much more dilute 1 $M$ HCl solution contains chloride ion at a much more dilute level than in the saturated NaCl. The relatively large amount of water in the dilute HCl prevents precipitation of NaCl. The 1 $M$ HCl effectively dilutes the saturated NaCl solution so that it is no longer saturated.

3. Silver ion precipitates thiocyanate ion as silver thiocyanate. Although silver ion is not part of the iron/thiocyanate equilibrium reaction, precipitation of the thiocyanate by silver does have an effect on the equilibrium (it removes thiocyanate from the system).

4. HCl is a strong acid and reacts both with the weak base ammonia itself and with the hydroxide ion that the ammonia produces when it ionizes.


**EXPERIMENT 27 The Solubility Product of Silver Acetate**

**A. General Notes**

This experiment, in which $K_{sp}$ is determined for a salt in several media, should help clear up some misconceptions students have about equilibria. Students have learned in lecture that equilibrium constants always have the same value unless the temperature is varied. An equilibrium constant calculated from true activities would indeed be constant, but one calculated from molar concentrations will necessarily show some variance—with changes in total ionic strength, for example. In this experiment, students should expect to see some variation in the values determined for $K_{sp}$ for several reasons. First of all, silver acetate is not a truly sparingly soluble salt; second, as mentioned above, one should not expect precise agreement under different experimental conditions for a concentration equilibrium constant; finally, the method used for measuring silver ion concentration is subject to difficulty in detecting the endpoint. The instructor may wish to discuss these points at the chalkboard. In spite of what has been said above, students will be able to determine the order of magnitude of $K_{sp}$ with little difficulty.

The endpoint of the titration may be difficult to detect, particularly since the solution becomes progressively more cloudy with AgCl precipitate. Students should titrate the first sample of each series fairly quickly to determine an approximate volume for the endpoint. They can then titrate the additional two samples rapidly to about 1 mL before the expected endpoint, and then dropwise, allowing the AgCl to settle between additions of silver acetate, which should make the appearance of the endpoint somewhat easier to see.

Although the procedure advises students to filter the silver acetate solutions if they are cloudy, it may be easier to decant the clear liquid from any remaining solid if the layer of solid can be left undisturbed.

Estimated time to complete: 3 hours

**B. Materials Required (given per 25 students)**

- 25 50-mL titration burets
- 25 rubber pipet safety bulbs
- 25 10-mL volumetric transfer pipets
- 25 25-mL volumetric transfer pipets
- 4 L 0.0500 M potassium chloride
  - The concentration of this reagent should be known to three significant figures. If a 4-L volumetric flask is available, add 14.9 g KCl and dilute to 4.00 L. If only a 2-L volumetric is available, two batches will be necessary: add 7.45 g KCl and dilute to 2.00 L.
- 1 L 5% potassium chromate (50 g K$_2$CrO$_4$ diluted to 1 L)
- 2 L saturated silver acetate (25 g AgC$_2$H$_3$O$_2$ diluted to 2 L; stir 1 hour)
- 2 L saturated silver acetate in 0.100 M KNO$_3$
  - To a 2-L volumetric container, add 25 g AgC$_2$H$_3$O$_2$ and 20.2 g KNO$_3$; dilute to nearly 2 L and stir 1 hour; dilute to 2.00 L.
2 L saturated silver acetate in 0.100 $M$ AgNO$_3$

To a 2-L volumetric container, add 10 g AgC$_2$H$_3$O$_2$ and 33.8 g AgNO$_3$; dilute to nearly 2 L and stir 1 hour; dilute to 2.00 L.

2 L saturated silver acetate in 0.100 $M$ sodium acetate

To a 2-L volumetric container, add 10 g of AgC$_2$H$_3$O$_2$ and 27.2 g NaC$_2$H$_3$O$_2$·3H$_2$O; dilute to nearly 2 L and stir 1 hour; dilute to 2.00 L.

C. Answers to Pre-Laboratory Questions

1. The solubility product constant is the equilibrium constant for the dissolving of a sparingly soluble ionic solid in water.

2. silver chloride, $K_{sp} = 1.77 \times 10^{-10}$
   silver bromide, $K_{sp} = 5.35 \times 10^{-13}$
   barium sulfate, $K_{sp} = 1.07 \times 10^{-10}$
   calcium carbonate, $K_{sp} = 4.96 \times 10^{-9}$
   silver acetate, $K_{sp} = 1.94 \times 10^{-3}$
   calcium hydroxide, $K_{sp} = 4.68 \times 10^{-6}$

3. (a) $[\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 2.0 \times 10^{-16}$
   $[\text{PbCrO}_4] = 1.4 \times 10^{-8} M$

(b) $[\text{Pb}^{2+}][0.100] = 2.0 \times 10^{-16}$
   $[\text{PbCrO}_4] = [\text{Pb}^{2+}] = (2.0 \times 10^{-16})/(0.100) = 2.0 \times 10^{-15} M$

(c) $[0.0010][\text{CrO}_4^{2-}] = 2.0 \times 10^{-16}$
   $[\text{PbCrO}_4] = [\text{CrO}_4^{2-}] = (2.0 \times 10^{-16})/(0.0010) = 2.0 \times 10^{-13} M$

D. Answers to Post-Laboratory Questions

1. See brief discussion in Part A.

2. Literature: $K_{sp} = 1.94 \times 10^{-3}$

3. Like any equilibrium constant, $K_{sp}$ varies with temperature. Depending on whether the solution process is endothermic or exothermic, $K_{sp}$ will either increase or decrease with increased temperature.
A. General Notes

This experiment is a very comprehensive demonstration of the properties of acids, bases, salts, and buffered systems and of the techniques used to measure pH.

The determination of pH with various indicators will give your students a chance to play detective. Students are familiar with universal indicator and pH paper from earlier experiments and will perhaps realize from this exercise that such general-purpose indicators are, in fact, usually mixtures of the individual indicators discussed here. It is suggested that students use a light box to illuminate their samples. If no such light box is possible, students should view their samples against a sheet of white paper in a well-lighted area of the laboratory.

Several pH meters will be needed for the experiment. (Ideally, there should be one meter for each four students.) The instructor should discuss the set-up and use of the meter. For example, it should be explained to students whether their meter is provided with separate pH and reference electrodes, or whether there is a single combination electrode; the instructor should explain the specific meter controls and should demonstrate how to calibrate the meter in standard reference buffered solutions. Students should be cautioned not to stir solutions with the electrode and to return the meter to the “stand-by” or the “off” setting when they are finished with it. The instructor will perform a brief demonstration with a lightbulb conductivity tester, to show that weak acid and weak base solutions conduct electricity poorly but that strong acid, strong base, and salt solutions conduct electricity readily.

Estimated time to complete: 3 hours

B. Materials Required (given per 25 students)

25 100-mL unknown samples for indicator pH determination

These samples are most easily prepared by dispensing commercial standard reference buffered solutions into coded 2-ounce bottles. If it is desired to home-prepare such solutions, instructions for many buffered systems are provided in the CRC Handbook.

100 mL each of 1% solutions of the following indicators in dropper bottles (1 g of the indicator dissolved in 50 mL 95% ethanol diluted to 100 mL with distilled water): methyl violet, malachite green, cresol red, thymol blue, bromphenol blue, methyl orange, bromcresol green, methyl red, methyl purple, bromthymol blue, litmus. Other indicators you have on hand might be substituted for some of these, as long as the approximate pH ranges are similar. The pH ranges and colors of the indicators should be provided to students if a substitution is made.

2 L each of pH 0, 1, 2, 3, 4, 5, and 6 standard reference buffers

Standard reference buffers are sold commercially, either as ready to use or as a concentrate. Be certain the buffers you purchase are not colored. (This is sometimes done to make it possible to identify the buffer at a glance.)

4 L pH 7 standard reference buffer (for electrode calibration)

5–6 pH meters with electrode systems (electrode placed in distilled water and the meter plugged in at least 2 hours before the laboratory period)
500 mL of each of the following 0.1 M salt solutions (the amount of anhydrous salt needed for 1 L of 0.1 M solution is indicated after the name of the salt)

- sodium chloride: 5.9 g
- potassium bromide: 12 g
- sodium nitrate: 8.5 g
- potassium sulfate: 17 g
- sodium acetate: 8.2 g of the anhydrous salt (or 14 g of the trihydrate)
- ammonium chloride: 5.4 g
- potassium carbonate: 14 g
- ammonium sulfate: 13 g
- copper(II) sulfate: 25 g of the pentahydrate
- iron(III) chloride: 27 g of the hexahydrate, freshly prepared

25 50-mL titration burets

unknown solid acid samples

The simplest compounds for this purpose are listed below. The amount indicated is sufficient to prepare 100 mL of 0.1 M solution of the acid. The samples should be dispensed in coded polyethylene bags.

- sodium hydrogen sulfate: 1.2 g
- potassium hydrogen sulfate: 1.4 g
- potassium hydrogen phthalate: 2.0 g

1 L 0.2 M NaOH for titration of the above salts (since only one significant figure is indicated the solution may be made up determinately; 8 g NaOH diluted to 1 L; Caution!)

100 mL 1% phenolphthalein in dropper bottle (1 g phenolphthalein dissolved in 50 mL 95% ethanol diluted to 100 mL with distilled water)

100 mL 0.1 M HCl in dropper bottle (8.3 mL conc. HCl diluted to 1 L; Caution!)

100 mL 0.1 M NaOH in dropper bottle (4 g NaOH diluted to 1 L; Caution!)

universal indicator solution (several dropper bottles)

light bulb conductivity tester (instructor demonstration)

0.1 M solutions of HCl, NaOH, ammonia, and acetic acid (instructor demonstration)
C. Answers to Pre-Laboratory Questions

1. Acids: HCl, HBr, HNO3, H2SO4, HClO4
   Bases: Group IA and IIA hydroxides

2. HCN  \( K_a = 6.2 \times 10^{-10} \)
   HF  \( K_a = 7.2 \times 10^{-4} \)
   HCOOH  \( K_a = 1.8 \times 10^{-4} \)
   CH₃NH₂  \( K_b = 3.7 \times 10^{-4} \)
   CH₃COOH  \( K_a = 1.8 \times 10^{-5} \)

3. Indicators show different colors at different pH values and change color at characteristic pH values. By testing an unknown sample with several indicators, it should be possible to bracket the approximate pH of the unknown by reference to the indicator colors.

4. The membrane that responds to hydrogen ion is most commonly made of glass.

D. Answers to Post-Laboratory Questions

1. It is mostly CO₂ in the air that lowers the pH of distilled water to values less than 7.
   \[ \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \]

2. Among the important buffered solutions in the body are the H₂CO₃/HCO₃⁻ system and the various buffered mixtures formed by proteins and amino acid molecules. Buffers in the body are vital because most biochemical processes are strongly affected by pH.

3. The buffer capacity of a buffer reflects how much strong acid or strong base a given amount of the buffer could consume before its pH changes drastically. Although all equimolar mixtures of a given weak acid and its conjugate would have the same pH, the amount of strong acid or strong base that the buffer could consume would be dictated by the molar concentrations of the components. For example, a buffer containing HAc and NaAc each at 0.5 \( M \) could consume five times the amount of added acid or base as a buffer in which the concentrations were only 0.1 \( M \).
A. General Notes

Choice I of this experiment is the students’ first complete volumetric analysis, in which they first prepare the titrant, standardize the titrant, and then analyze an unknown sample. Although other acids could be used for the standardization of the NaOH titrant, potassium hydrogen phthalate is used because it is easily available in a high state of purity at relatively low cost. Earlier experiments have made use of titration as an analytical technique, but many of these were designed to result in only two or three significant figures in the data, to obtain a “ballpark” estimate of some property of the system (such as the determination of the equilibrium constant in Experiment 26). In Choice I of this experiment you should insist that students make all determinations and calculations to four significant figures, and you should be far more critical in grading their results. The instructor in particular should remind students that the endpoint of the titration is the first appearance of the faintest pink color.

Choice II of the experiment will be perhaps more “relevant” to students, since it is the analysis of an everyday pharmaceutical material. Because of the nature of the manufacturing process, one would probably not bother analyzing an antacid tablet to the precision of four significant figures expected for Choice I. For this reason, the addition of standard HCl is made only with a graduated cylinder, and so only three figures should be reported by students. Again, because of differences among the antacid tablets due to manufacturing, shipping, and storage, I would not hold students to the exact assay of the tablet as reported on the label.

Estimated time to complete:

<table>
<thead>
<tr>
<th>Choice</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choice I</td>
<td>180 minutes</td>
</tr>
<tr>
<td>Choice II</td>
<td>120 minutes</td>
</tr>
</tbody>
</table>

B. Materials Required (given per 25 students)

Choice I

50 50-mL titration burets
25 5-mL volumetric transfer pipets and rubber safety bulbs
25 1-L glass or plastic bottles (if not locker equipment)
250 g sodium hydroxide pellets
500 g potassium hydrogen phthalate (potassium acid phthalate, potassium biphthalate)

The KHP should be stored, with the cap removed from the bottle, in an oven at 110°C. A pair of tongs or heat-proof gloves should be kept near the oven so that students can remove the KHP safely.

500 mL 1% phenolphthalein (set out 5 dropper bottles of 100 mL each)

Dissolve 5 g phenolphthalein in 250 mL 95% ethanol and dilute to 500 mL with distilled water.
1 L vinegar unknown solution (a single group unknown is adequate)

The vinegar unknown may be commercial white vinegar (not brown cider vinegar), or a 5% acetic acid solution may be prepared by diluting 48 mL concentrated CH$_3$COOH to 1 L with distilled water; Caution!

solid acid unknowns

Since the students standardized their NaOH against KHP, it is best if the unknowns are also made from KHP. Commercial analyzed KHP unknowns may be purchased, or they may be home-made by diluting reagent grade KHP with an inert salt such as NaCl and grinding in a ball mill to homogenize the samples. (The unknowns should contain between 40 and 70% KHP by mass, and all weighings when preparing the unknowns should be made to four significant figures.) Dispense about 8 g of the unknown samples in coded, sealed polyethylene bags. The instructor should be provided with the percentage KHP in each sample so that he or she can guide students as to how large a sample should be weighed out for the analysis.

Choice II

25 50-mL titration burets

6 L 0.1 M sodium hydroxide solution

This solution is needed only if students did not perform Choice I of the experiment. Three-significant-figure precision is needed for the solution’s concentration. Since 6-L volumetric flasks are not generally available, the solution should be prepared as three 2-L batches and then combined, with the average molarity being reported to the students. For 2 L, weigh out 8 g of NaOH to the nearest 0.01 g, transfer quantitatively to a 2-L volumetric flask, and dilute to 2.00 L with distilled water; Caution!

12 L 0.1 M hydrochloric acid solution

Three-significant-figure precision is needed for the solution’s concentration. The solution is best prepared in 2-L batches and then combined, with the average molarity being reported to students. For 2 L, transfer 17 mL of concentrated HCl to a 2-L volumetric flask, and dilute to 2.00 L with distilled water. The assay provided by the manufacturer on the label of the concentrated HCl should be used in calculating the exact molarity of the solution; Caution!

500 mL 1% bromphenol blue indicator (set out 5 dropper bottles of 100 mL each)

Dissolve 5 g of bromphenol blue in 500 mL distilled water.

500 g sodium bicarbonate

Antacid tablet samples

Each student will be titrating a total of 4 tablets. More than one brand of tablet should be available. There are many suitable brands of such tablets, and whichever is cheapest or most readily available may be used.
C. Answers to Pre-Laboratory Questions

Choice I

1. KHP, molecular formula KHC$_8$H$_4$O$_4$, molar mass 204.2 g

2. An indicator (in acid–base titrations) is typically an organic dye that changes color over a particular pH range and which may be used to mark the endpoint of a titration. The choice of indicator for a titration is based on the pH expected at the equivalence point for the substances being reacted.

3. mol KHP = (0.4538 g)/(204.2 g/mol) = $2.222 \times 10^{-3}$ mol

mol NaOH = mol KHP at the endpoint

$M = \text{mol/L} = \frac{2.222 \times 10^{-3} \text{ mol}}{0.04412 \text{ L}} = 0.05037 \text{ M}$

Choice II

1. A standard solution is one whose concentration has been determined to a high level of precision, typically four significant figures.

2. CaCO$_3$ Molar mass = 100 g

(1.00 g)(1 mol/100 g) = 0.0100 mol

(0.0100 mol)/(0.100 M) = 0.100 L = 100 mL

NaHCO$_3$ Molar mass = 84.0 g

(1.00 g)(1 mol/84.0 g) = 0.0119 mol

(0.0119 mol)/(0.100 M) = 0.119 L = 119 mL

Mg(OH)$_2$ Molar mass = 58.3 g

(1.00 g)(1 mol/58.3 g) = 0.0172 mol

(0.0172 mol)/(0.100 M) = 0.172 L = 172 mL

Al(OH)$_3$ Molar mass = 78.0 g

(1.00 g)(1 mol/78.0 g) = 0.0128 mol

(0.0128 mol)/(0.100 M) = 0.128 L = 128 mL
D. Answers to Post-Laboratory Questions

Choice I

2. The equivalence point of a titration is the point where the titrant has been added to the sample in an exactly stoichiometrically equivalent amount. The endpoint of a titration is the point where the indicator or instrument we use to detect the completion of the neutralization gives its response. For example, in a strong acid/strong base titration using phenolphthalein as indicator, the equivalence point would come at exactly pH 7 (neutral), whereas the endpoint for phenolphthalein comes at around pH 8. However, the amount of additional base required to go from pH 7 to pH 8 is only a fraction of a drop. Indicators must be carefully chosen for titrations to have color changes in the region of the pH expected at the equivalence point.

3. The endpoint represents an observable phenomenon, such as the color change of an indicator. The equivalence point represents when the titrant has been added in exactly the stoichiometric amount required to react with the analyte. If the indicator is chosen correctly, the endpoint represents a good approximation to the equivalence point.

Choice II

2. The bases used in antacids are either weak bases (NaHCO₃) or very insoluble bases [Mg(OH)₂, CaCO₃]. If a strong, soluble base like NaOH were used, it would undoubtedly neutralize stomach acidity, but it would probably destroy the lining of the mouth and esophagus on the way down!

4. There are several dangers. One danger is described as the “acid rebound” effect: when stomach acid is neutralized, this only causes the acid-secreting cells of the stomach to produce more acid. A second danger lies in those antacids that contain magnesium ion: magnesium ion is a strong purgative, and abuse leads to chronic diarrhea and dehydration.
EXPERIMENT 30 Determination of Calcium in Calcium Supplements

A. General Notes

EDTA titrations of calcium and magnesium ions in “hard water” have long been a part of the traditional general chemistry laboratory curriculum. With the recent indications that dietary calcium deficiencies may be involved in the development of osteoporosis, it seems desirable to adapt this traditional experiment for students to a more urgent “real world” analysis. In this experiment, students will determine the amount of calcium ion in a commercial product (most typically, an antacid tablet containing calcium carbonate as the active ingredient).

The instructor should be warned that the endpoint of the titration in this experiment is rather unusual. As the titration is begun, the sample is wine-red in color. As the titration progresses, the sample gradually begins to turn gray, but this gray color is not the endpoint. As the titration proceeds further, the gray color diminishes until the sample is bright blue. The endpoint is taken to be the point when all the gray color has disappeared, and the sample is colored bright, pure blue. To a first approximation, the gray color arises as the blue color of the titrated metal ion mixes with the original red color of the untitrated metal: the sample is titrated until there is no trace of red or gray present. Needless to say, this endpoint is not as distinct as many, and the margin of error is larger.

It is essential that the indicator used for the titration be freshly prepared (within a day of the laboratory section). If the indicator must be kept for later lab sections, it should be refrigerated. If the indicator solution appears not to work, an additional small quantity of the powdered indicator dye can be added to the solution.

The pH buffer used in this experiment contains concentrated ammonia solution. The buffer should be kept and dispensed in an exhaust hood: students should take their samples to the hood to add the buffer (once the buffer is diluted by adding to the sample, the odor decreases substantially).

B. Materials Required (given per 25 students)

25 25-mL volumetric transfer pipets
25 pipet safety bulbs
25 50-mL burets and buret stands/clamps
25 250-mL volumetric flasks
1 L 3 M HCl (250 mL concentrated HCl diluted to 1 L in exhaust hood; Caution!)
8 L 0.0500 M Na₂EDTA (18.6 g Na₂EDTA 2H₂O diluted to 1.00 L volumetrically)
1 L pH 10 ammonia buffer (67 g NH₄Cl added to 570 concentrated NH₃ diluted to 1L; Caution!)
25 calcium supplement tablets
   Many over-the-counter antacids have calcium carbonate as the active ingredient; each tablet should contain 500 mg CaCO₃, which is equivalent to 200 mg Ca²⁺. It might also be interesting for students to compare prices for an equivalent amount of calcium.

dropper bottles of Eriochrome Black T indicator solution
   For 100 mL, dissolve with stirring 1 g EBT, 0.20 g MgCl₂·6H₂O, and 0.37 Na₂EDTA 2H₂O in 100 mL water. Keep refrigerated until the laboratory period and between sections. If the indicator appears to have stopped working after a few days, an additional amount of EBT powder may be added.
C. Answers to Pre-Laboratory Questions

1. The most obvious use of calcium in the body is in bones and teeth.

2. EDTA has many uses: in rust removers, in some drain cleaners, as an additive to fertilizers (to boost the solubility of trace-metal components, and in medicine as a treatment for lead poisoning.

3. ETDA is ethylenediamine-N, N', N'-tetraacetic acid. The substance is usually used as its disodium salt.

   \[
   \text{HOOC--C}^\text{H_2} \text{C--COOH} \\
   \text{HOOC--C--N--C--N--C--COOH}
   \]

4. Molarity of Ca\(^{2+}\) ion = \((27.2 \text{ mL})(0.02053 \text{ M})/25.0 \text{ mL} = 0.02234 \text{ M}\)

   \[
   \text{mg of Ca}^{2+} = 25.0 \text{ mL} \times (1 \text{ L/1000 mL}) \times (0.02234 \text{ mol/L}) \times 40.08 \text{ g/mol} = 0.02238 \text{ g} = 22.4 \text{ mg}
   \]

D. Answers to Post-Laboratory Questions

1. Answer depends on student results. In general,

   \[
   \text{mass CaCO}_3 = \text{(mass Ca)} \times (100.1 \text{ g CaCO}_3/40.08 \text{ g Ca})
   \]

2. Student mechanical errors; indistinctness of the endpoint; manufacturer’s tolerances; etc.

3. The primary natural sources of calcium include milk and other dairy products, as well as many vegetables and meats.
A. General Notes

This experiment introduces the use of oxidation–reduction reactions in chemical analysis. (In a later experiment, students will study electrochemistry in some detail.)

Potassium permanganate is a widely used redox titrant. It does have some disadvantages, however. Since permanganate is such a strong oxidizing agent, it reacts with practically anything and is hard to obtain in a pure state. Permanganate solutions cannot be kept for very long without their concentration changing significantly. Therefore, in order to be able to complete the analysis of this experiment in one lab period, students prepare and standardize their permanganate solution and then use it to analyze the unknown sample, all in one lab period. To accomplish this, only three standardization and unknown titrations are performed.

Students might be told that the analysis in this experiment does not represent a typical analysis for iron in a “real” sample. Ordinarily, a real sample would probably consist of an iron ore, in which the iron would be present in both +2 and +3 oxidation states. Such an ore would require extensive pretreatment with acid to get the iron into solution, and then reduction to get all of the iron into the +2 oxidation state.

Estimated time to complete: 150–180 minutes

B. Materials Required (given per 25 students)

25 50-mL titration burets
25 500-mL volumetric flasks and stoppers
250 g potassium permanganate
500 g ferrous ammonium sulfate
2 L 6 M sulfuric acid (330 mL concentrated H\textsubscript{2}SO\textsubscript{4} diluted to 1 L; use extreme caution in diluting; considerable heat is evolved; pack container in ice; Caution!)

iron unknown samples

Commercial unknowns consisting of diluted FAS are available for this purpose. Alternatively, pure iron(II) salts can be dispensed. Students should be told how much sample to weigh out so as to require approximately 25 mL to titrate. Typically, students will require on the order of 7–8 g.
C. Answers to Pre-Laboratory Questions

1. \[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \]
   \[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
   \[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+} \]

2. Permanganate can be used in the redox analysis of practically any oxidizable substance. Permanganate has also been used in medicine as an antifungal agent.

3. Molar mass FAS = 392.2 g
   
   \[
   (1.041 \text{ g FAS})(1 \text{ mol/392.2 g}) = 0.002585 \text{ mol Fe}
   \]
   
   \[
   (0.002585 \text{ mol Fe})(1 \text{ mol KMnO}_4/5 \text{ mol Fe}) = 5.171 \times 10^{-4} \text{ mol KMnO}_4
   \]
   
   \[
   M = 5.171 \times 10^{-4} \text{ mol KMnO}_4/0.02623 \text{ L} = 0.01971 M
   \]

4. mol KMnO\text{\textsubscript{4}} used = (0.02845 L)(0.01971 M) = 5.568 \times 10^{-4} mol
   
   \[
   (5.568 \times 10^{-4} \text{ mol KMnO}_4)(5 \text{ mol Fe/1 mol KMnO}_4) = 0.002784 \text{ mol Fe}
   \]
   
   \[
   (0.002784 \text{ mol Fe})(55.85 \text{ g/1 mol}) = 0.1555 \text{ g Fe}
   \]
   
   \[
   \%\text{Fe} = (0.1555 \text{ g Fe}/2.893 \text{ g sample})(100) = 5.374 \%\text{Fe}
   \]

D. Answers to Post-Laboratory Questions

1. If the unknown had not been dried, part of the presumed sample weight would have been adsorbed water. The apparent percentage iron determined would have been less than if the sample had been dried.

2. Sulfuric acid is added as the source of hydrogen ion indicated in the balanced chemical equation for the reaction.

3. Iron can also be determined by titration with other redox reagents (for example, potassium dichromate). Iron in solution is often determined spectrophotometrically as the complex with 1,10-phenanthroline. Iron can also be precipitated and weighed as the hydroxide (although this is a very time-consuming procedure).
EXPERIMENT 32 Electrochemistry I: Chemical Cells

A. General Notes

You will find that students love this experiment: everyone is familiar with electrical batteries, and students find it very reassuring to be able to prepare batteries that actually work.

The construction of the voltaic cells in Part C calls for porous porcelain cups rather than a U-tube salt bridge; such cups are much easier to deal with and set up reliably (but are much more expensive), and they enable students to set up several cells quickly. If a U-tube is used, it is absolutely essential that the arms of the tube be filled to the rim before inverting into the half-cells: if there is an air space, the battery will not work at all. To assist students in setting up the cell and to avoid disappointment, you may wish to prepare the U-tubes in advance, filling them with a gel of 1 M NaCl in agar. Another alternative is to use strips of filter paper soaked in a conductive salt solution, but using this method often results in the cell potential drifting during measurement.

If at all possible, students should be provided with a volt meter so that they can determine their cell’s potential. Such meters are relatively expensive, but the measurement takes only a few seconds and 1–2 meters should suffice. If it is at all possible, the wires provided to students for hooking their battery to the volt meter should be plastic-coated and equipped with alligator clips at each end. (This makes connection of the wires take only a second.)

Really adventurous instructors might want to stop by the local electronics store and purchase small buzzers, light-bulbs, or motors which will run on voltages less than 2 volts: students are even more impressed with the batteries they construct if they can see them make some device actually work! We typically pick up a pack of 1-v LEDs for lab: but realize, these will disappear and/or burn out very quickly. You can also use higher-voltage devices: students will figure out that if they connect two cells in series they get a higher voltage.

Estimated time to complete: 120–150 minutes

B. Materials Required (given per 25 students)

25 porous cups
short strips of zinc (cut from zinc ribbon to 1–2-mm width); or mossy zinc
short strips of copper (cut from copper wire or fine turnings)
magnesium turnings
50 2-foot lengths of plastic-coated copper wire (with alligator clips at both ends if possible)
several voltmeters
250 mL 1 M sulfuric acid (56 mL concentrated H₂SO₄ diluted to 1 L; Caution!)
250 mL 1 M sodium sulfate (142 g anhydrous Na₂SO₄ diluted to 1 L)
2 L 1 M copper(II) sulfate (250 g CuSO₄·5H₂O diluted to 1 L)
1 L 0.1 M copper(II) sulfate (25 g CuSO₄·5H₂O diluted to 1 L)

2 L 1 M zinc sulfate (287 g ZnSO₄·7H₂O diluted to 1 L)

1 L 0.1 M zinc sulfate (29 g ZnSO₄·7H₂O diluted to 1 L)

2 L 1 M MgSO₄ (247 g MgSO₄·7H₂O diluted to 1 L)

sandpaper for cleaning electrodes (check your local “dollar” store for inexpensive sandpaper)

1 cm × 10-cm strips of copper, zinc, and magnesium

C. Answers to Pre-Laboratory Questions

1. Oxidation is defined in the Introduction as a loss of electrons by a species. The correspondence to oxidation being an increase in oxidation number is most easily seen for simple monatomic ions. In the process Zn → Zn²⁺ + 2e⁻, the zinc atoms are losing electrons (negative charge) and so are increasing in oxidation number.

2. A voltaic cell represents a spontaneous redox reaction that has been set up in such a manner that the electrons transferred pass through an external circuit. In an electrolysis cell, electrical current from an external source is used to make an otherwise non-spontaneous redox reaction occur in the cell.

3. The voltage developed by a cell is related to the concentration of ions in the form specified by the Nernst equation.

4. The nickel reaction will be the oxidation.

\[ \text{Ni} \rightarrow \text{Ni}^{2+} + 2e^- \]

\[ \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} \]

The overall reaction is

\[ \text{Ni} + \text{Pb}^{2+} \rightarrow \text{Ni}^{2+} + \text{Pb} \]

with potential of 0.10 volt for a standard cell.
D. Answers to Post-Laboratory Questions

1. A standard cell is one in which the activities of all species are unity (to an approximation, this means the concentrations of all ions are 1 M, the pressures of any gases are 1 atm), and the cell is at 25°C. Assuming the temperature was near 25°C, the initial student’s cell was effectively a standard cell.

2. As the cell runs, the concentration of reactant ions drops and the reduction of these ions occurs less frequently. According to the Nernst equation, a drop in concentration of the reactant ions leads to a decrease in the cell potential. (The denominator of the ratio gets smaller, so the ratio itself becomes larger, and because a function of the log of this ratio is subtracted from the standard cell potential, the actual potential decreases.)

3. a. \[ \text{Mg(s)} || \text{Mg}^{2+}(1 \text{ M}) || \text{Al}^{3+}(0.01 \text{ M}) || \text{Al(s)} \]
   \[ E = 0.71 - 0.0592/6[\log(0.01/1)] = 0.71 - (-0.020) = 0.73 \text{ V} \]

   b. \[ \text{Al(s)} || \text{Al}^{3+}(0.1 \text{ M}) || \text{Ag}^+(0.01 \text{ M}) || \text{Ag(s)} \]
   \[ E = 2.46 - 0.0592/3[\log(0.01/0.1)] = 2.46 - (-0.020) = 2.48 \text{ V} \]

   c. \[ \text{Zn(s)} || \text{Zn}^{2+}(0.1 \text{ M}) || \text{Ag}^+(1 \text{ M}) || \text{Ag(s)} \]
   \[ E = 1.56 - 0.0592/2[\log(1/0.1)] = 1.56 - 0.03 = 1.53 \text{ V} \]
A. General Notes

In Choice I, students electrolyze water and measure the relative volumes of the gases produced and then test the gases for their nature (using tests that have been developed in earlier experiments). Choice II of the experiment makes the point that the actual electrolysis that occurs when a current is passed through a solution is the easiest possible reaction.

Both choices call for a source of dc electrical current for the electrolysis. The simplest, and safest, source of current would be a 9-volt “transistor” battery. Alternatively, several 1.5-volt flashlight batteries could be connected in series. The instructor may wish, on the other hand, to use power supplies that plug into the wall current. *This is not recommended for student use* because of the danger of electrical shock, particularly when the students would be working in contact with conductive ionic solutions. Such a power supply might be useful, however, if the experiment were to be performed by the instructor purely as a demonstration. At this point, mini-apparatuses for electrolysis are available commercially, and these might be tried.

Estimated time to complete: 60–75 minutes for each choice

B. Materials Required (given per 25 students)

Both choices

25 9-volt transistor batteries and snap-on connectors
50 2-foot lengths of copper wire terminating in alligator clips
50 3–4-inch thin graphite rods to serve as electrodes

Choice I

500 mL 1 M sodium sulfate (142 g Na₂SO₄ diluted to 1 L)
wooden splints
rulers

Choice II

500 g potassium iodide
50 g sodium thiosulfate pentahydrate
100 mL universal indicator solution (dropper bottle)
wooden splints
100 mL 1% starch solution (heat 50 mL water to boiling; make a paste of 1 g soluble starch in 25 mL water; add to the boiling water and stir to dissolve; dilute to 100 mL)
C. Answers to Pre-Laboratory Questions

Choice I

1. Oxygen is soluble to the extent of 3.16 cm\(^3\) per 100 mL H\(_2\)O at 25°C, whereas hydrogen is soluble to the extent of 1.91 cm\(^3\) under the same conditions. The gases are generated relatively quickly and do not have much of a chance to dissolve.

2. \[2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2.\]
   If 25 mL of hydrogen were collected, one would expect 12.5 mL of oxygen according to the stoichiometric coefficients of the balanced reaction equation.

3. If a glowing wooden splint burns vigorously in a colorless, odorless gas, the gas is almost certainly oxygen. If a colorless, odorless gas is less dense than air, and if it explodes when mixed with air but burns quietly when limited oxygen is available, the gas is almost certainly hydrogen.

Choice II

1. The actual reaction that occurs is always the reaction that can occur most easily—with the smallest expenditure of energy. This can be determined by reference to a table of standard reduction potentials for half-cells. In the case of many salts, water is preferentially oxidized or reduced.

2. NaCl:  
   reduction:  \[2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-\]
   oxidation:  \[2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-\]
   overall:  \[2\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow \text{H}_2 + 2\text{OH}^- + \text{Cl}_2\]

KBr:  
   reduction:  \[2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-\]
   oxidation:  \[2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-\]
   overall:  \[2\text{H}_2\text{O} + 2\text{Br}^- \rightarrow \text{H}_2 + 2\text{OH}^- + \text{Br}_2\]

CuCl\(_2\):  
   reduction:  \[\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}\]
   oxidation:  \[2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-\]
   overall:  \[\text{Cu}^{2+} + 2\text{Cl}^- \rightarrow \text{Cu} + \text{Cl}_2\]
D. Answers to Post-Laboratory Questions

Choice I

1. For the electrolysis of water, a higher voltage could be used.

2. Sodium sulfate was added as an ionic electrolyte to carry charge between the electrodes. Another salt—as long as its components were not easily oxidized or reduced—could have been used.

3. Using standard cells (with 1 M H⁺ and 1 M OH⁻ present in the anode and cathode chambers, respectively) the potential required is 2.06 V. In pure water where [H⁺] = [OH⁻], the potential required is 1.23 V. See Zumdahl text.

Choice II

1. Sodium thiosulfate would reduce any I₂ present (brown color) to I⁻ ion. The reaction is

\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^- \]

2. If the solution were concentrated enough, Br₂ would produced. If the solution were too dilute, water would be oxidized. Water would be reduced in either case.
A. General Notes

Some may argue that gravimetric analysis is archaic. The method has been virtually replaced in the traditional 
analytical chemistry course by instrumental and advanced titrimetric methods. The methods of gravimetric 
analysis however, offer a good demonstration of more advanced stoichiometric principles and permit the 
instructor to determine the laboratory skills of his or her students.

Each of the choices of this experiment makes use of sintered glass filtering funnels/crucibles. In spite 
of their relatively high cost, such funnels are recommended for several reasons: the funnels are relatively easy to 
clean and bring to constant weight, they are easier for students to filter through because suction can be used, and 
they avoid the need for techniques such as ashing of a filter paper. Students should be asked to clean the 
funnels when they finish the experiment, because it is easier to remove the precipitates while they are still 
relatively fresh. If students neglect to clean the funnels, they can be cleaned by the instructor by soaking for 
several days in a mixture of 6 M HCl and 6 M HNO₃. (Any dirt not removed by this acid soak can be assumed 
to be imbedded in the frit plate of the funnel and is not likely to be removed by subsequent student use.)

A drying oven is needed for this experiment; it should be reliably controllable at 110°C. Students 
should be warned to dry their crucibles in a beaker that is labeled. (The label should not be affixed to the 
crucible itself to avoid mass effects.) All too often, students think that they will remember what their funnels 
look like and where they were placed in the oven.

Students should be cautioned to clamp their suction flasks securely when filtering the precipitates. One 
of the most common accidents in the lab is for a filter flask to tip over during aspiration. Not only is there a 
danger of the flask breaking, but the precipitate is usually lost.

Instructors are reminded that each analysis is done only in duplicate, and therefore the accuracy of the 
mean determination may not be up to analytical standards.

Estimated time to complete: 150–180 minutes for either choice

B. Materials Required (given per 25 students)

Both choices

50 medium-porosity 30-mL sintered glass filtering crucibles

oven set reliably to 110°C

Choice I

500 mL 6 M nitric acid (378 mL concentrated HNO₃ diluted to 1 L: Caution!)

2 L 5% silver nitrate (50 g AgNO₃ diluted to 1 L)

chloride ion unknown samples

Each student will need approximately 2 g of the sample. These may be commercial analyzed chloride 
unknowns, or you may dispense simple chloride salts such as NaCl, KCl, etc. The unknowns may be 
dispensed in sealed, coded polyethylene bags.
Choice II

500 mL 6 M hydrochloric acid (500 mL concentrated HCl diluted to 1 L; Caution!)

3 L 5% barium chloride (50 g BaCl$_2$ diluted to 1 L)

hotplates

100 mL 0.1 M silver nitrate (17 g AgNO$_3$ diluted to 1 L)

unknown sulfate ion samples

Each student will need approximately 2 g of the sample. Commercial analyzed sulfate ion samples may be used, or such compounds as Na$_2$SO$_4$ and K$_2$SO$_4$ may be used. (Make sure the salts are anhydrous and are handled under water-free conditions while dispensing.) The unknowns may be dispensed in sealed, coded polyethylene bags.

C. Answers to Pre-Laboratory Questions

Choice I

1. g Cl$^-$ = (0.7409 g AgCl)(35.45 g Cl$^-$/143.35 g AgCl) = 0.1832 g Cl$^-$
   
   % Cl$^-$ = (0.1832 g Cl$^-$/0.4032 g sample) x 100 = 45.43 %Cl$^-$

2. AgCl $\rightarrow$ Ag$^+$ + Cl$^-$
   
   $[\text{AgCl}] = (1.8 \times 10^{-10})^{1/2} = 1.34 \times 10^{-5}$ M

   Molar mass AgCl = 143.35 g/mol

   (1.34 $\times$ 10$^{-5}$ mol/L)(143.35 g/mol) = 1.923 $\times$ 10$^{-3}$ g/L

Choice II

1. g SO$_4^{2-}$ = (0.2321 g BaSO$_4$)(96.06 g SO$_4^{2-}$/233.36 g BaSO$_4$) = 0.09554 g SO$_4^{2-}$
   
   % SO$_4^{2-}$ = (0.09554 g SO$_4^{2-}$/1.5618 g sample) x 100 = 6.117 %SO$_4^{2-}$

2. BaSO$_4$ $\rightarrow$ Ba$^{2+}$ + SO$_4^{2-}$
   
   $[\text{BaSO}_4] = (1.1 \times 10^{-10})^{1/2} = 1.049 \times 10^{-5}$ M

   (1.049 $\times$ 10$^{-5}$ mol/L)(233.36 g/mol) = 2.448 $\times$ 10$^{-3}$ g/L
D. Answers to Post-Laboratory Questions

Choice I

1. A slight excess of the precipitating reagent has been shown to assist coagulation of the precipitate into larger crystals and to reduce adsorption of impurities on the crystals.

2. If the precipitate were exposed to light, silver ion would be reduced to metallic silver, and chloride ion would be oxidized to elemental chlorine gas. If chlorine gas is evolved from the AgCl precipitate, the experimentally determined amount of chloride ion would be less than the true amount that was present in the sample originally.

3. Other ions in the solution from which precipitation occurs may be trapped within the crystals of solid if the precipitation occurs too quickly or from too concentrated a medium. If other ions are trapped within the crystals of precipitate, and the precipitate is then weighed, the mass of the precipitate will be too large.

Choice II

1. Occlusion of foreign ions is prevented by precipitating from a relatively dilute solution, and by digesting the precipitate to allow foreign ions to escape from the crystals as the crystals are growing larger.

2. Barium sulfate is highly opaque to X rays. In addition to its insolubility in water, barium sulfate coats the lining of the digestive tract when ingested and makes any imperfections visible to X rays.

3. The precipitation of carbonate was avoided by using an acidic medium.
EXPERIMENT 35 Coordination Compounds

A. General Notes

The study of coordination compounds is sometimes omitted from the general chemistry course because of time constraints, but students usually find laboratory work with such compounds to be great fun because so many of the compounds are beautifully colored—so many of the compounds used in general chem lab are white!

Choice I of this experiment prepares the tetrammine complex of copper(II) and is virtually foolproof. The synthesis is relatively brief, however.

Choice II is a considerably more involved synthesis of the hexammine complex of cobalt(III), requiring students to oxidize the cobalt(II) starting material with an air bubbler and then to recrystallize the product.

Although they may be pretty to look at, the products of these syntheses are toxic, and copper and cobalt compounds are hazardous to the environment. The product should be collected by the instructor and disposed of properly.

Students should be cautioned to clamp their suction flasks securely before filtering the products of the reactions: otherwise, the flask will tip over during the filtration.

Estimated time to complete:

Choice I: 2 hours
Choice II: 3 hours

B. Materials Required (given per 25 students)

Choice I

75 g copper(II) sulfate pentahydrate
500 mL conc. ammonia
1 L 95% ethanol
100 mL conc. hydrochloric acid (dropper bottle); Caution!
1 vial pH test paper

Choice II

125 g cobalt(II) chloride hexahydrate
100 g ammonium chloride
two-hole rubber stoppers
short lengths of rubber tubing for use as connectors
500 mL conc. ammonia; Caution!
500 mL conc. hydrochloric acid; Caution!
1 vial pH test paper
500 mL 95% ethanol
100 g activated charcoal (decolorizing carbon)

C. Answers to Pre-Laboratory Questions

Choice I

1. Molar mass CuSO₄·5H₂O = 249.5
   
   \[(1.00 \text{ g})(1 \text{ mol/249.5 g}) = 0.00401 \text{ mol}\]

   Molar mass [Cu(NH₃)₄]SO₄·H₂O = 245.5
   
   \[(0.00401 \text{ mol})(245.5 \text{ g/1 mol}) = 0.984 \text{ g}\]

2. A ligand is a neutral or negative species capable of forming coordinate covalent bonds to the d-orbitals of a metal ion. A molecule or ion must contain at least one pair of nonbonding electrons for forming the coordinate bond to the metal ion.

3. The approach of ligand molecules to a transition metal ion causes the otherwise degenerate d-orbitals of the metal to split into two sets of orbitals of slightly different energy. The energy difference between these split d-orbitals corresponds to wavelengths of visible light.

Choice II

1. Molar mass CoCl₂·6H₂O = 237.9

   \[(4.00 \text{ g})(1 \text{ mol/237.9 g}) = 0.0168 \text{ mol}\]

   Molar mass [Co(NH₃)₆]Cl₃ = 267.4

   \[(0.0168 \text{ mol})(267.4 \text{ g/1 mol}) = 4.50 \text{ g}\]

2. The half-reactions are

   \[
   \begin{align*}
   \text{Co}^{3+} + e^- & \rightarrow \text{Co}^{2+} & E^o &= 1.95 \text{ V}\\
   \text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O} & E^o &= 1.23 \text{ V}
   \end{align*}
   \]

   The overall standard potential is \((1.95 - 1.23) = 0.73 \text{ V}\).
D. Answers to Post-Laboratory Questions

Choice I

1. The coordination complex can form only with molecular ammonia, NH$_3$, since the coordinate bond requires the nonbonding electron pair on the nitrogen atom. If an ammonium salt were used, a double salt might crystallize if the ammonium salt were added in the correct stoichiometric amount.

2. The tetramminecopper(II) ion is relatively stable to substitution by other ligands but could be replaced by strong-field ligands such as CN$^-$ or ethylenediamine. See the Zumdahl text.

3. Nearly all tetravalent copper(II) complexes are square-planar in geometry.

Choice II

1. The effect is partly steric and partly electronic/electrostatic. If ligand molecules are surrounding and blocking a metal ion, it will have less tendency to attract electrons for undergoing reduction. Ligand molecules are polar, and the negative end of the dipole is directed toward the metal ion, leaving the positive end of the dipole directed outward from the complex and also lowering the tendency of the metal ion to attract electrons. By accepting the coordinate covalent bond from the ligand molecules, the metal ion has effectively already gained electrons and has more completely filled its outer shell.

2. Charcoal serves as a surface upon which the oxidation can take place more readily; the charcoal adsorbs oxygen and provides a greater area.

3. The complex would be less soluble in a concentrated chloride ion solution than in water. Chloride ion is at a concentration of 12 M in concentrated HCl.

4. The complex is octahedral, with bond angles of 90°.
A. General Notes

When trying to set up a laboratory schedule in general chemistry that complements and reinforces the lecture material, there oftentimes comes a point where students are just not ready for new material (perhaps a holiday or vacation period intervened). Sometimes an experiment is needed for lab that can stand apart from the lectures but which still gives students some insight into chemical principles and is not just “busy work.” The three syntheses in this experiment, though simple in nature and able to be placed most anywhere in the syllabus, are nonetheless derived from important industrial processes.

In Choice I, students prepare sodium thiosulfate pentahydrate and investigate the properties of this substance that make it important in photography. The synthesis is interesting in that one of the reactants (sulfur) would ordinarily not be soluble in water: in this process, sulfur dissolves by reacting with the sodium sulfite solute. Students are asked to monitor the pH changes during the heating process as an indication that the reaction has proceeded; to make this work, the detergent used to promote wetting of the sulfur should be as nearly neutral as possible.

Choice II allows students to prepare some truly beautiful crystals of copper(II) sulfate pentahydrate. If the diluted solution can be left undisturbed for a week (or possibly longer if the humidity of the laboratory is high), typically a large, single, almost perfectly shaped crystal will form. If you desire to preserve some of the better crystals, they will have to be sealed to prevent the waters of hydration from being lost to the atmosphere.

The synthesis of sodium hydrogen carbonate in Choice III mimics the industrial synthesis. In the industrial method, however, there is a great deal of recycling of materials (for example, the ammonium bicarbonate side-product is reclaimed and converted back into ammonia and carbon dioxide for further use). It might be helpful to your students’ understanding of real-world chemistry to discuss the industrial methods. Students are instructed to have their filtration apparatus set up and ready to use before mixing the reagents: the product must be filtered near 0°C, or it will dissolve to too great an extent, and students must have the filtration equipment ready at the right moment. The heating of the product mixture must be performed over a water bath: the decomposition of ammonium bicarbonate is accompanied by a lot of spattering, and sodium bicarbonate does decompose to sodium carbonate if the material is heated too strongly.

Estimated time to complete:

Choice I: 120–150 minutes
Choice II: 120 minutes
Choice III: 150 minutes

B. Materials Required (given per 25 students)

Choice I

500 g sodium sulfite
300 g powdered sulfur
100 mL concentrated laboratory detergent (dropper bottle)
1 vial pH test paper
25 evaporating dishes
25 glass crystallizing dishes (or Petri dishes)
100 mL 0.1 M potassium iodide/iodine (dropper bottle; 17 g KI and approx. 10 g I₂ diluted to 100 mL)
200 mL 0.1 M sodium bromide (10 g NaBr diluted to 1 L)
100 mL 0.1 M silver nitrate (dropper bottle; 17 g AgNO₃ diluted to 1 L)

Choice II

250 g copper(II) oxide (cupric oxide, black)
3 L 6 M sulfuric acid (330 mL concentrated H₂SO₄ diluted to 1 L; use extreme caution in diluting; heat is evolved; pack container in ice.); Caution!
25 evaporating dishes
25 crystallizing dishes

Choice III

500 g sodium chloride
1500 mL concentrated ammonia; Caution!
crushed dry ice (to fill a volume of approx. 4 L)
100 mL 3 M hydrochloric acid (250 mL concentrated HCl diluted to 1 L; dropper bottles); Caution!

C. Answers to Pre-Laboratory Questions

Choice I

1. Na₂SO₃ + S + 5H₂O → Na₂S₂O₃·5H₂O
2. Molar mass Na₂SO₃ = 126
   Atomic mass S = 32
   (15 g sodium sulfite)(1 mol/126 g) = 0.119 mol sodium sulfite
   (10 g S)(1 mol/32 g) = 0.313 mol
   Sulfur is in excess by (0.313 – 0.119) = 0.194 mol = 6.21 g sulfur in excess
3. I₂ + 2S₂O₃²⁻ → 2I⁻ + S₄O₆²⁻
   AgBr + 2S₂O₃²⁻ → Ag(S₂O₃)₂³⁻ + Br⁻

Choice II

1. Four of the five water molecules are coordinately covalently bonded to the copper(II) ion in a square-planar complex. The fifth water molecule is hydrogen-bonded to the sulfate ion.
Experiment 3
Inorganic Preparations

2. \( \text{CuO} + \text{H}_2\text{SO}_4 + 4\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \)

Molar mass CuO = 79.5

Molar mass \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) = 250

\[(5.0 \text{ g CuO})(1 \text{ mol}/79.5 \text{ g}) = 0.063 \text{ mol CuO}\]

\[\text{mol CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{mol CuO}\]

\[(0.063 \text{ mol CuSO}_4 \cdot 5\text{H}_2\text{O})(250 \text{ g}/1 \text{ mol}) = 16 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O}\]

Choice III

1. Substance at 0°C in hot water
   
   - \( \text{NaHCO}_3 \) 6.9 16.4 g at 60°
   - \( \text{NH}_4\text{Cl} \) 29.7 75.8 at 100°
   - \( \text{NH}_4\text{HCO}_3 \) 11.9 decomposes

The data above are from the CRC Handbook of Chemistry and Physics, which is what most students will report. (The CRC Handbook does not provide solubility data at 20° for these substances.) It should be clear to your students that ammonium chloride is considerably more soluble than the other two salts at 0°C.

2. Sodium hydrogen carbonate is used as a leavening agent in baking powders, as an antacid, and as an aid in deodorizing, among other uses.

D. Answers to Post-Laboratory Questions

Choice I

1. The detergent is a surfactant, which enables water molecules and sulfur atoms to come in closer contact and mix better.

2. The sulfite ion undergoes hydrolysis.

   \( \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_3^- + \text{OH}^- \)

3. The waters of hydration of sodium thiosulfate may be lost to the atmosphere.

4. If a strong acid were added to a solution of sodium thiosulfate, the free weak acid would be produced. \( \text{H}_2\text{S}_2\text{O}_3 \) is unstable and decomposes into elemental sulfur, water, and sulfur dioxide gas.

   \( \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{S}_2\text{O}_3 \rightarrow \text{S} + \text{SO}_2 + \text{H}_2\text{O} \)
Choice II

1. \[ \text{Cu} + \text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{H}_2 \]

Elemental Cu is attacked only by relatively concentrated sulfuric acid, and obviously there is a danger in handling the concentrated acid. Hydrogen is produced by the process, and provision would have to be made for venting the hydrogen to prevent a fire hazard. Finally, using the oxide more closely resembles the industrial process. (Copper ores are typically sulfides, which are then converted to oxides by roasting.)

2. In two cases, a relatively concentrated solution was cooled rapidly, causing nucleation of small, usually irregular crystals. In the third case, a dilute solution was allowed to evaporate slowly, allowing time for the ions to migrate to the first site of nucleation and to build up a single crystal. (The crystal is more perfectly shaped because as solvent evaporates, the crystal will eventually be in equilibrium with dissolved solute; rough points on the crystal can re-dissolve and then re-precipitate.)

3. electroplating, fungicide, wet-cell batteries, algae control in pools, paint pigments, color fixer for textiles

Choice III

1. \[ \text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3 \]

This reaction illustrates why students were not able to prepare a sodium hydroxide solution determinately in Experiment 29: sodium hydroxide absorbs carbon dioxide from the atmosphere.

2. \[ 2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]

3. Sodium carbonate: manufacture of glass, soap, paper, cleaners, water softeners

Sodium hydrogen carbonate: baking powders, antacids, spill kits for acids, toothpastes, air fresheners
A. General Notes

This experiment should be “exciting” to students, because the sodium fusion often is accompanied by a big puff of black smoke. Students have learned from their lectures, and from their previous laboratory experience with sodium, that it is a very reactive substance and is consequently dangerous to handle and use. For this reason, the experiment is written in terms of the instructor performing the fusions for the students in the fume exhaust hood. It is recommended that test tubes be set up for the instructor before lab, each containing one small pellet of sodium, in a number equal to the number of students or groups in the lab section. The test tubes can be covered with plastic wrap or foil to protect the sodium from air oxidation, but usually the oil remaining on the sodium is sufficient for this. It is our experience that students are nervous about sodium because of what they have heard in lectures, and typically do not heat it strongly or quickly enough for a good fusion: slow heating produces oxidation of the sodium, rather than vaporization.

Sodium may be obtained commercially as very small pellets of 1–2 mm in diameter. This commercially prepared material should be used, rather than the instructor’s trying to cut small pellets from chunk sodium. (If the sodium is exposed to the air during cutting, it will oxidize too much to permit a good fusion.) Sodium usually is packaged with the metal stored under a layer of a hydrocarbon solvent: this solvent should be removed from the pellets before dispensing. A simple technique is to transfer a scoopful of sodium pellets to a paper towel, pat the pellets almost dry with additional towels, and then transfer the pellets to the test tubes with forceps.

Depending on the materials used as the known and unknown, the samples may smoke considerably upon their addition to the sodium vapor. For this reason, the fusion must be done in the exhaust hood. For a proper fusion, the sodium must be melted and vaporized within a matter of a few seconds. The burner should be adjusted to give the hottest possible flame before it is placed under the test tube containing the sodium. If the sodium turns white, rather than melting and then forming a dark vapor, the heating has been too slow and the sodium has been oxidized. Because students are naturally apprehensive about handling the sodium, they tend to use too cool a flame in first heating the metal.

Excess sodium is destroyed, before water is added to dissolve the ionic products of the fusion, by the use of methanol. The test tube’s sides will have blackened in a good fusion, and students may have trouble telling whether the sodium has been completely destroyed by the methanol. One method is to have students listen to the test tube: if any sodium is still present, it will be fizzing as it reacts with the methanol. In any case, at least 5 minutes should be allowed for the methanol/sodium reaction before any water is added.

Estimated time to complete: 120 minutes

B. Materials Required (given per 25 students)

25 18×150-mm Pyrex test tubes, each containing a single 1–2-mm pellet of sodium (Instructor only!)

250 mL methanol

1 vial pH test paper

1 vial lead acetate test paper

100 mL 0.5 M iron(II) sulfate (dropper bottle)

Dissolve 139 g FeSO₄·7H₂O (ferrous sulfate) and diluted to 1 L; the solution must be freshly prepared and should be pale green in color (not yellow, which indicates iron(III) is present).
100 mL 3 M potassium hydroxide (dropper bottle; 168 g KOH diluted to 1 L)
100 mL 0.5 M iron (III) chloride (dropper bottle)
   135 g ferric chloride hexahydrate, FeCl₃⋅6H₂O, diluted to 1 L or 81 g of the anh. salt diluted to 1 L)
250 mL 3 M sulfuric acid
   dropper bottle; 167 mL concentrated H₂SO₄ diluted to 1 L; use caution; considerable heat evolved; pack container in ice; Caution!
100 mL 5% sodium nitroprusside (dropper bottle; 50 g Na₂[Fe(NO)(CN)₅]⋅2H₂O diluted to 1 L)
250 mL 3 M acetic acid (dropper bottle; 170 mL concentrated CH₃COOH diluted to 1 L); Caution!
100 mL 0.1 M silver nitrate (dropper bottle; 17 g AgNO₃ diluted to 1 L)
100 mL 3 M ammonia (dropper bottle; 200 mL concentrated NH₃ diluted to 1 L); Caution!
250 mL 3 M nitric acid (dropper bottle; 200 mL concentrated HNO₃ diluted to 1 L); Caution!
250 mL 0.1 M ferric nitrate (40 g Fe(NO₃)₃⋅9H₂O diluted to 1 L with 1 M HNO₃); Caution!
500 mL methylene chloride (dichloromethane)
250 mL 0.1 M potassium permanganate (16 g KMnO₄ diluted to 1 L)

C. Answers to Pre-Laboratory Questions

1. The molecular formula might be determined from a quantitative elemental analysis (see the Zumdahl text), combined with a molar mass determination. The structure of the compound might be elucidated by various techniques (infrared spectroscopy, mass spectrometry, x-ray diffraction, etc.).

2. Prussian blue is an iron/cyanide complex containing the iron in both oxidation states, Fe₄[Fe(CN)₆]₃.

3. A reducing agent is a substance that is itself easily oxidized and that therefore causes the reduction of some other species. Because sodium itself is easily oxidized, it makes a good reducing agent. An example of sodium behaving as a reducing agent is the reaction:

\[ 2Na + Cl₂ \rightarrow 2NaCl \]

4. Sodium must be kept away from water. Sodium reacts vigorously with water generating hydrogen gas, and usually enough heat to ignite the hydrogen gas. In this experiment, after the sodium fusion is complete, any traces of elemental sodium must be reacted with methanol before water can be added to dissolve the ionic products of the fusion. Methanol also reacts with sodium to generate hydrogen, but at a much lower rate and there is far less danger of the hydrogen igniting.

\[ 2Na(s) + 2H₂O(l) \rightarrow 2NaOH(aq) + H₂(g) + \text{heat} \]
D. Post-Laboratory Questions

1. If the sodium vapor were not hot enough, the reduction of the organic compound would have been incomplete. This is especially a problem for nitrogen: if the sodium vapor is not hot enough, the cyanide ion will not readily form.

2. Lead acetate test paper contains lead acetate in the solid state impregnated on the paper. The paper is moistened because otherwise it would be relatively difficult for a gas/solid reaction to take place.

3. Sulfide and cyanide ion interfere with the tests for the halogens because these ions also form precipitates with silver ion. In particular, silver sulfide and silver cyanide are dark-colored and would completely mask any white silver halide precipitate.

4. Chloride is identified as a precipitate with silver ion, which dissolves in ammonia but re-precipitates in acid.

Iodide ion is identified by mild oxidation to convert the species to the free element, which is then identified by the color of its methylene chloride extract.

Bromide ion is identified by oxidation with a stronger oxidizing agent to the free element, which is also then identified by the color of its extraction in methylene chloride.
Experiment 37  Qualitative Analysis of Organic Compounds
A. General Notes

The amount of organic chemistry that can be covered in the general chemistry course is admittedly small, but one should still try to give students a feel for the subject. Undoubtedly the lecturer will have discussed at least the most important functional groups, and this experiment gives students a chance to see illustrated some of the properties of the various families of compounds.

Parts of this experiment are intended to be performed by the instructor purely as a demonstration. Under no circumstances should students be allowed to attempt this material themselves.

Because most of the sample compounds in this experiment are both highly volatile and flammable, as much of the experiment as possible should be performed in the exhaust hood. The laboratory should be kept well ventilated, and no open flames should be permitted. (For those portions of the experiment requiring a hot-water bath, hotplates should be provided.)

All organic products and excess reagents should be collected for proper commercial disposal.

Estimated time to complete: 120–150 minutes

B. Materials Required (given per 25 students)

Instructor’s demonstration:

1-mL samples of the following hydrocarbons: hexane, 1-hexene, cyclohexane, cyclohexene, toluene

Student experiment:

50 mL hexane (mixed isomers may be used)
50 mL 1-hexene
50 mL cyclohexane
50 mL cyclohexene
50 mL toluene
100 mL 1% bromine in methylene chloride

Add 1 mL of elemental bromine to 100 mL methylene chloride; dispense in a glass dropper bottle with glass dropping pipet. Elemental bromine causes extremely severe burning if spilled on the skin, and its vapor is extremely toxic and corrosive. Prepare the bromine solution in the exhaust hood, and wear thick gloves while handling.

100 mL 1% potassium permanganate (dropper bottle; 16 g KMnO₄ diluted to 1 L)
100 mL methanol (methyl alcohol)
100 mL ethanol
100 mL 2-propanol (isopropyl alcohol)
100 mL 1-butanol (n-butyl alcohol)
100 mL 1-pentanol (\(n\)-pentyl alcohol, \(n\)-amyl alcohol)
100 mL 1-octanol (\(n\)-octyl alcohol)
2 L acidified 5\% potassium dichromate
   50 g \(\text{K}_2\text{Cr}_2\text{O}_7\) and 55 mL of conc. \(\text{H}_2\text{SO}_4\) diluted to 1 L with distilled water; \textit{Caution}!
approx. 5 g sodium pellets 1–2 mm-diameter; \textit{Caution}!
100 mL 10\% formaldehyde (270 mL commercial 37\% solution diluted to 1 L)
100 mL 10\% acetaldehyde (100 mL acetaldehyde diluted to 1 L)
100 mL acetone
100 mL 10\% glucose (100 g glucose diluted to 1 L)
100 mL 10\% fructose (100 g fructose diluted to 1 L)
1 L Benedict’s qualitative reagent
100 mL glacial acetic acid (ethanoic acid)
100 mL propionic acid (propanoic acid)
100 mL butyric acid (butanoic acid)
1 L 10\% sodium bicarbonate (100 g \(\text{NaHCO}_3\) diluted to 1 L)
1 vial pH test paper
100 mL concentrated ammonia
100 mL 10\% \(n\)-butylamine (10 mL \(n\)-butylamine diluted to 100 mL)
1 M copper(II) sulfate (254 g \(\text{CuSO}_4\cdot5\text{H}_2\text{O}\) diluted to 1 L; stir 1 hour)
8–10 hotplates
UV lamp or high-intensity incandescent lamp

C. \textbf{Answer to Pre-Laboratory Question}

<table>
<thead>
<tr>
<th>Name Given</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>hexane</td>
</tr>
<tr>
<td>isopropyl alcohol</td>
<td>2-propanol</td>
</tr>
<tr>
<td>1-hexene</td>
<td>1-hexene</td>
</tr>
<tr>
<td>formaldehyde</td>
<td>methanal</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>cyclohexane</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>ethanal</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>cyclohexene</td>
</tr>
<tr>
<td>acetone</td>
<td>propanone (2-propanone)</td>
</tr>
<tr>
<td>toluene</td>
<td>toluene or methylbenzene</td>
</tr>
</tbody>
</table>
D. Answers to Post-Laboratory Questions

1. The test is not specific for organic acids, because the net reaction is that of hydrogen ion (from whatever source).

   \[ H^+ + HCO_3^- \rightarrow H_2CO_3 \rightarrow H_2O + CO_2 \]

2. In going from permanganate to manganese(IV) oxide, there is a change in oxidation state for manganese: this is a redox reaction. The alkene is converted to a glycol (two –OH groups).

3. Aldehydes usually have lower boiling points than organic acids and can be distilled off from the mixture as they form.

4. A primary amine (–NH₂ group) contains a nitrogen atom with an unshared pair of electrons. Such an amine can act as a ligand, forming a coordination complex with copper(II) ion, similar to the tetrammine complex formed by ammonia.

6. acetic acid, \( K_a = 1.8 \times 10^{-5} \)

   \( n \)-butylamine, \( K_b = 4.1 \times 10^{-4} \)
EXPERIMENT 39 The Preparation and Properties of Esters

A. General Notes

Students don’t always like organic chemistry. To many of them, it seems that the lectures are just endless lists of names, formulas, and reactions to study and that in the laboratory, everything smells bad and has to be refluxed for 3 hours before it will react! Although there are not too many simple organic syntheses that can be performed by students at the introductory level, luckily for motivational purposes, the synthesis of esters is fairly easy. Esters, for the most part, are pleasant compounds to deal with, and the syntheses called for in this experiment may help to pique your students’ interest in organic chemistry.

In Choice I, students prepare aspirin and methyl salicylate from salicylic acid, and the Introduction to the experiment seeks to explain the reasoning that went into the development of these materials as drugs. Students always enjoy these syntheses and frequently ask whether they may take their aspirin product home with them (the answer must be no) to show their friends or families. Students also perform a qualitative version of the USP test for unreacted salicylic acid on their aspirin and compare the results to the same test applied to a commercial aspirin tablet. Because the student aspirin has been freshly prepared, their aspirin often gives less of a purple color with iron(III) than does the commercial aspirin, and students become very proud of their keen synthetic technique!

Choice II of the experiment is mostly for fun. Students synthesize esters that are components of the essential oils of various fruits. I would assign all students to prepare ethyl or methyl butyrate, because the change in odor between butyric acid and the ester product is remarkable.

Estimated time to complete:

Choice I: 120 minutes
Choice II: 60 minutes

B. Materials Required (given per 25 students)

Choice I

hotplates set up in the exhaust hoods
150 g salicylic acid
250 mL acetic anhydride; Caution!
200 mL 50% sulfuric acid (dropper bottle); Caution!
Place a beaker containing 100 mL distilled water in a reservoir of ice; cautiously and slowly, over a 10-minute period, add 100 mL of concentrated H$_2$SO$_4$ (Caution!); cool to room temperature; transfer to dropper bottle.
500 mL 95% ethanol
100 g sodium bicarbonate
100 mL 0.5 M iron(III) chloride (dropper bottle; dissolve 14 g FeCl$_3$·6H$_2$O in 100 mL 1 M HCl)
300 mL methanol
commercial aspirin tablets (these may be the cheapest generic product)
Thiele tube melting point baths (optional)
melting point capillaries (optional)

**Choice II**

hotplates set up in the exhaust hoods
plastic pipets whose stems have been cut to approx. 1 inch
50 mL each of the following alcohols
  - *n*-propyl alcohol (1-propanol)
  - methyl alcohol (methanol)
  - isobutyl alcohol (2-methyl-1-propanol)
  - *n*-octyl alcohol (1-octanol)
  - isoamyl alcohol (2-pentanol)
  - ethyl alcohol (ethanol)
  - benzyl alcohol (α-hydroxytoluene)
50 mL or 50 g each of the following acids
  - acetic acid (ethanoic acid)
  - butyric acid (butanoic acid – *Caution: stench!*)
  - propionic acid (propanoic acid)
  - 2-aminobenzoic acid (anthranilic acid)
200 mL 50% sulfuric acid (dropper bottle); *Caution!*
Place a beaker containing 100 mL distilled water in a reservoir of ice; cautiously and slowly, over a 10-minute period, add 100 mL of concentrated H$_2$SO$_4$ (*Caution!*); cool to room temperature; transfer to dropper bottle.
100 mL methyl salicylate
500 mL 20% NaOH (100 g NaOH dil. to 500 mL); *Caution!*
C. Answers to Pre-Laboratory Questions

Choice I

1. salicylic acid, molar mass = 138 g
   acetylsalicylic acid, molar mass = 180. g

2. \( (5.0 \text{ g salicylic acid})(1 \text{ mol/138 g}) = 0.036 \text{ mol salicylic acid} \)
   \[
   \text{mol salicylic acid} = \text{mol acetylsalicylic acid}
   \]
   \( (0.036 \text{ mol acetylsalicylic acid})(180. \text{ g/1 mol}) = 6.5 \text{ g acetylsalicylic acid} \)

Choice II

1. \[
   \begin{align*}
   \text{CH}_3 & \quad \text{COO} \quad \text{CH}_2\text{CH}_2\text{CH}_3 \\
   \text{CH}_3 & \quad \text{COO} \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
   \text{CH}_3\text{CH}_2\text{CH}_2 & \quad \text{COO} \quad \text{CH}_3 \\
   \text{CH}_3 & \quad \text{COO} \quad \text{CH}_2\text{CH}_2\text{CH}_3 \\
   \text{CH}_3\text{CH}_2 & \quad \text{COO} \quad \text{CH}_2\text{CH}_3\text{CH}_3 \\
   \text{CH}_3 & \quad \text{COO} \quad \text{CH}_2\text{CHCH}_3
   \end{align*}
   \]

2. \( \text{R-CO-OR'} + \text{NaOH} \rightarrow \text{R'-OH} + \text{R-COO Na}^+ \)
   methyl salicylate + NaOH → methyl alcohol + sodium salicylate
**D. Answers to Post-Laboratory Questions**

**Choice I**

1. Esterification involves dehydration and condensation of the organic acid and the alcohol. Sulfuric acid is a good dehydrating agent. Mechanistically, a strong protonating agent is needed. Other acids could be used, but $\text{H}_2\text{SO}_4$ helps to drive the equilibrium more to the right than most acids.

2. Acetaminophen is $\text{N}$-acetyl-$\text{4}$-aminophenol

    Ibuprofen is $2$-(4-$\text{isobutyl}$phenyl)$\text{-propanoic}$ acid.

    Neither compound is an ester.

3. acetic anhydride + water $\rightarrow$ 2 acetic acid

4. Generally, the students’ purified aspirin shows less color with iron(III) than do the commercial tablets, which makes them feel very proud of their synthetic skills.

**Choice II**

1. One simple method might be to use a chemical dehydrating agent to remove water as it is produced, thus shifting the equilibrium to the right.

3. Hydrolysis literally means “breakdown by water”; hydrolysis is generally taken to mean the reaction of a substance with, or through the action of, water. In organic chemical reactions, hydrolysis is often facilitated by hydroxide ion or hydronium ion.
EXPERIMENT 40 Proteins

A. General Notes

Although the amount of biochemistry that can be covered in a general chemistry course is necessarily limited, students should be introduced at least to some of the “mysteries” of the subject and should gain a clear appreciation of why the subject is so complicated (but rewarding) to study.

Initially in the experiment, students perform some classical tests for proteinaceous materials, using several real-world samples. Students are asked at one point to donate a small bit of hair for testing; fingernail clippings could be substituted. Students also study how proteins can be denatured by almost any change in their environment. The instructor may wish to lead a discussion and solicit suggestions from students about other ways in which proteins may be denatured—and let them test their suggestions.

B. Materials Required (given per 25 students)

1% albumin (1 g albumin diluted to 100 mL)
nonfat milk (powdered milk may be used)
1% alanine (1 g alanine diluted to 100 mL)
10% NaOH (10 g NaOH diluted to 100 mL); Caution!
3% CuSO₄ (3 g CuSO₄ pentahydrate diluted to 100 mL)
gelatin

Prepare unflavored gelatin at double the strength listed on the package. Pour into shallow tray. Cut into small (1-cm) cubes. Another alternative is to transfer the gelatin to 24-well plastic test plates: the tests can then be conducted directly in the 24-well plate. Ask students to remove the gelatin from the plates when finished however.

6 M HNO₃ (approximately 35 mL concentrated HNO₃ added to 70 mL water; Caution!)
6 M NaOH (24 g NaOH diluted to 100 mL)
5% lead acetate (5 g lead acetate hydrate diluted to 100 mL)
3 M HCl (25 mL concentrated HCl diluted to 100 mL); Caution!
3 M NaOH (12 g NaOH diluted to 100 mL); Caution!
saturated NaCl (approx 35 g NaCl diluted to 100 mL; stir; decant from excess solid)
ethyl alcohol
C. Answers to Pre-Laboratory Questions

1. The term alpha refers to the older nomenclature system for organic acids. The carbon atom next to the carboxyl carbon was referred to as the alpha carbon (what we would refer to as the number-2 carbon in the IUPAC system).

2. These structures are given in the Zumdahl text. This question is included here to give students practice in drawing more complicated molecules.

3. The primary structure of a protein is the specific order of the amino acids in the polymeric chain of the protein. The secondary structure of a protein describes in general terms how the long chain of amino acids (the primary structure) as a whole is arranged in space (e.g., whether as a helix or as part of a pleated sheet). The tertiary structure of the protein describes the specific folding of the primary/secondary structures in three-dimensional space (e.g., whether hydrophobic substituent groups are oriented to the inside or to the outside of the helix).

4. A protein is said to be denatured when it loses its ability to function as intended. This may come about through any disturbance in the protein’s structure (tertiary, secondary, or primary) caused by heat, cold, a change in pH, addition of a heavy metal, etc.

D. Answers to Post-Laboratory Questions

1. The biuret test is a test for the peptide linkage between two amino acids. Because there is no such linkage in an isolated molecular amino acid, the test is negative.

2. Much of the tertiary structure of a protein comes about through hydrogen bonding between various H and OH portions of the polymer. When the pH of a protein’s environment is changed, these portions of the polymer can be protonated or deprotonated (depending on the change in the pH), which changes their interaction with each other.

3. 

\[
\begin{align*}
\text{gly-ala} & \quad \text{ala-gly} \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{H}_2\text{N} \\
\text{CH}_2 \text{C} & \quad \text{CH} \\
\text{NH} & \quad \text{NH} \\
\text{CH} & \quad \text{CH}_2 \\
\text{COOH} & \quad \text{COOH} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
A. General Notes

Biochemistry is of course a very challenging subject for beginning students, but often it is a very interesting one. Even those students who may have wondered, “Why do I have to study chemistry?” can see the importance of this aspect of the subject!!

In this experiment, students see the action of some common enzymes that we make use of or deal with in everyday life. Rather than using reagent enzymes from a chemical specialty supplier, the experiment makes use mostly of natural sources for several enzymes. For those enzymes that are to be used from a fruit or vegetable, it is important that the plant material be freshly cut up just before the lab, so that the enzymes will not be oxidized by the air.

Estimated time to complete: 120 minutes

B. Materials Required (given per 25 students)

- soda or “oyster” cracker (no added flavorings)
- 5% lead acetate solution (5 g lead acetate diluted to 100 mL)
- 0.1 M I₂/KI solution
- gelatin samples
  - Prepare plain gelatin at twice the strength indicated on the package; pour into a shallow tray; cut into small (1-cm) cubes. The gelatin may also be prepared in 24-well plastic test plates and then the tests done in the 24-well plates.
- meat tenderizer (Check the package to make sure the active ingredient is an enzyme.)
- contact lens cleaner solution
  - Check package label to make sure that the active ingredient is an enzyme. Prepare at twice the strength indicated on the package.
- fresh pineapple (many supermarkets now sell fresh, sliced pineapple in the produce section: this works fine)
- canned/cooked pineapple
- 6% hydrogen peroxide solution
  - Sold in the hair coloring section of drugstores; 3% H₂O₂ may be used if necessary, but the 3% solution does not bubble as readily.
- yeast suspension
  - Add 1 package of dry yeast powder to 100 mL of water; add a few grams of table sugar to allow the yeast to multiply.
- freshly cut potato (it’s best to cut the potato after lab starts to make sure the surface has not dried out)
- cooked potato (may be precooked, or students may boil pieces of the fresh potato)
C. **Answers to Pre-Laboratory Questions**

1. An enzyme is a biological molecule that catalyzes and controls the speed of the reactions of another molecule or molecules. Enzymes are typically mostly proteinaceous in nature.

2. In the lock-and-key model, the enzyme and its substrate have complementary structures that enable them to fit together closely in space. The enzyme fits together closely enough to act only with its correct substrate, and not with other molecules that may be present. A given enzyme acts only on a single molecule or functionality.

3. Answers depend on student choice. See the Zumdahl text.

D. **Answers to Post-Laboratory Questions**

1. Cooking *denatures* the enzymes in pineapple and potato and they no longer have their catalytic action. Enzymes contain protein which is denatured by heating.

2. Heating, change in pH, change in solvent system, heavy metal ions, etc.

3. Some drugs work by having structures that are similar enough to the structure of the substrate of a particular enzyme of a microorganism to fool the enzyme. The drug molecule attaches itself to the enzyme either permanently (irreversible inhibition) or in competition with the substrate (reversible inhibition). If enough of the microorganism’s enzyme is tied up with the drug molecule, the microorganism will die.
A. General Notes

Although polymeric substances are most important to our present-day lives, aside from the synthesis of nylon (Choice II), there are no simple syntheses of such polymers that are appropriate at the introductory level. Thus Choice I considers the differences in properties between elemental sulfur as students usually encounter it and the polymeric sulfur formed when molten sulfur is quenched rapidly.

An oil bath is used in Choice I, rather than the direct heat of a burner flame, so that students can observe the changes in sulfur as it is heated more slowly. Sulfur passes from the solid state first to a straw-colored, easily flowing liquid and then to a dark red viscous liquid prior to reaching the boiling point. When the sulfur has reached the viscous red form, it may be poured into the quenching bath. A solubility test with carbon disulfide is used to distinguish the normal form of sulfur from the polymer. Carbon disulfide is very volatile, extremely flammable, and extremely toxic. All use of carbon disulfide must be confined to the exhaust hood. Students are asked to examine the crystalline shape of the recrystallized orthorhombic sulfur: if the evaporation of CS₂ is not too fast, they should notice a few regularly shaped crystals around the edge of the material being evaporated.

The reagents used in Choice II are volatile, toxic, and flammable, and the use of these reagents must be confined to the hood. Students should not handle the nylon until it has been washed. The nylon is synthesized in microscale, giving a filament only about 2 inches long. The instructor may wish to perform a macroscale synthesis as a demonstration so that students can have a better appreciation for the reaction.

Estimated time to complete:
- Choice I: 120 minutes
- Choice II: 90 minutes

B. Materials Required (given per 25 students)

Choice I

- hotplates set up in exhaust hood
- oil baths (250-mL beaker half filled with paraffin oil) for hotplates
- chunk (or crushed roll) sulfur
- 100 g powdered sulfur
- 100 mL carbon disulfide (stored in exhaust hood – highly toxic/highly flammable); Caution!
- 5–6 magnifying glasses

Choice II

- 30 mL 10% adipoyl chloride in hexane (30 mL adipoyl chloride in 70 mL hexane); Caution!
- 60 mL 20% 1,6-hexanediamine (20 mL hexamethylenediamine in 80 mL water)
- 250 mL 1 M sodium hydroxide (40 g NaOH diluted to 1 L); Caution!
C. Answers to Pre-Laboratory Questions

Choice I

1. A polymer is a large, usually chainlike molecule built from many small molecules (monomer units).

2. Sulfur usually exists as $S_8$ rings. As the sulfur is heated, these rings open. If heating is continued, the open chains attach to one another to form the long-chain polymer.

3. See the Zumdahl text for this phase diagram.

Choice II

1. The properties of nylon depend very much on its preparation: approximate properties are density, ~1.1 g/mL; melting point, ~250°C; color, colorless or white

2. The functional group is the amide linkage $-\text{C(=O)--N-}$.

3. This equation is given in the Introduction to the choice, and is repeated here to give students practice in writing the formulas of larger molecules.

D. Answers to Post-Laboratory Questions

Choice I

1. Many polymeric substances are insoluble, which is one of their more desirable properties. The polymeric sulfur chains are simply too big to dissolve.

2. When a substance is heated, the energy absorbed is usually converted to the kinetic energy of the molecules. For most substances, the molecules move more rapidly and more easily when heated. As the polymerization begins to happen for sulfur, however, the molecules are becoming so large that they cannot move easily.

3. On standing, the polymeric sulfur reverts to the rhombic form.

Choice II

1. The adipoyl chloride solution is less dense than the aqueous solution.

2 and 3. See the Zumdahl text for such examples.
A. General Notes

Traditional inorganic qualitative analysis has had a resurgence in popularity over the last few years. Just a few years ago, general chemistry texts were almost exclusively theoretical in nature, and students often emerged with a knowledge of many hypotheses and theoretical explanations but with very little practical knowledge of chemistry. Qualitative inorganic analysis is proving to be one of the best ways to teach descriptive chemistry: not only do students encounter many prettily colored precipitates, but they also learn a great deal about solubility, oxidation–reduction, and acid–base chemistry along the way.

In this and following experiments on qualitative analysis, students should apply the techniques, in parallel, to both a known and unknown sample, so that comparisons between positive and negative tests can be made.

Students often become lost in the qualitative analysis scheme, and having the unknown side-by-side for comparison is very helpful. The unknowns should contain only the cations of the current group: a full progressive separation scheme takes too long, and the results are often disappointing. All too often a student will discard a supernate from an unknown, only to discover the following week that it contained the next group to be studied!

Students will need centrifuges for this and the following few experiments. Ideally, there should be one centrifuge for every two students. The instructor should demonstrate this week how to insert the sample tubes into the centrifuge, and how to balance the centrifuge, and should remind students of the need to balance in the following weeks also.

Undeniably, a lot of reagents are needed for qualitative analysis, and the method used for dispensing these reagents should make it as easy as possible for the students to find the reagent they need. Ideally, each student should have a complete set of the reagents for his or her own use. Although expensive and time-consuming, it may be possible to prepare sets of small, individual dropper bottles for each student. Since most of the reagents used have reasonably long shelf lives, such a set of individual bottles may be kept from term to term. If such dropper bottles are not possible, you might have students obtain several milliliters of each reagent in clean semimicro test tubes at the beginning of the lab period, so that they will not have to go back to the reagent area again. In either case, students should not have to search through the general reagent area every time they need a drop or two of a solution. The amounts given in Part B represent each student taking approximately 5 mL of most reagents to his or her own bench. (If individual dropper bottles are to be set up, the overall amounts will of course have to be adjusted depending on the size of the bottles used.)

Estimated time to complete: 120–150 minutes

B. Materials Required (given for 25 students)

10–12 student centrifuges

Make sure the centrifuges are in good working order and that they can be placed in a position in the lab where not much damage will be done if there is a balancing problem. In spite of warning them, it is almost certain someone will forget to balance a centrifuge tube

100 centrifuge tubes to fit the above; make sure the necessary collars for the centrifuges are available.

disposable pipets (or medicine droppers, 10–12 per student)
125 mL 6 M hydrochloric acid (500 mL conc. HCl diluted to 1 L; Caution!)
125 mL 6 M acetic acid (340 mL conc. CH₃COOH diluted to 1 L; Caution!)
125 mL 0.2 M potassium chromate (39 g K₂CrO₄ diluted to 1 L; Caution!)
125 mL 6 M ammonia (410 mL conc. NH₃ diluted to 1 L; Caution - stench!)
125 mL 6 M nitric acid (380 mL conc. HNO₃ diluted to 1 L; Caution!)
50 g potassium iodide
1 vial pH paper

Group I known
Prepare 100 mL of the mixture by dissolving approximately 2 g AgNO₃, 3.5 g Pb(NO₃)₂, and 5.5 g Hg₂(NO₃)₂·2H₂O and diluting to 100 mL. This mixture is approximately 0.1 M in each ion.

Group I unknowns
Prepare 100 mL of individual 0.2 M stock solutions of each of the ions: 4 g AgNO₃; 7 g Pb(NO₃)₂; 11 g Hg₂(NO₃)₂·2H₂O. Having a higher concentration here allows for the concentration of each ion in a mixture to be similar to that in the known. For ease of dispensing, transfer to dropper bottles.
Prepare 2-mL individual unknowns in coded, polyseal vials, using one, two, or all three of the ions. For unknowns containing a mixture, roughly equal volumes of the component solutions should be used.

C. Answers to Pre-Laboratory Questions

1. Substance  | Cold water       | Hot water
AgCl         | 0.000089 at 10°  | 0.0021 at 100°
PbCl₂        | 0.99 at 20°      | 3.34 at 100°
Hg₂Cl₂       | 0.00020 at 25°   | 0.001 at 43°

Data represent g solute/100 mL and are from the CRC Handbook.

2. A general discussion of flow charts for qualitative analysis is given in the Zumdahl text. The specific flow chart for this analysis is given there. The flow chart students prepare is intended to get them to read through the experiment ahead of time, and to write down the important tests and what is concluded from those tests. They do not have to be fine artwork.
D. Answers to Post-Laboratory Questions

1. The ideal of classifying cations in groups is based on their solubility with a specific reagent. We want to separate the whole scheme of cations into smaller groups quickly and simply. Although the Group I cations might also precipitate as the sulfides, no separation of these cations from the other cations would be achieved.

2. Excess chloride ion can cause some metal chlorides to re-dissolve as the chloro-complexes. We add the HCl dropwise so that we can tell when the cations have just barely been precipitated completely.

3. The acid is added to ensure that the chromate ion does not convert to dichromate (changing the color of the precipitate).

4. The ammonia is intended to complex and dissolve the silver ion so that it can be separated from the mercurous precipitate. If lead ion were still present in solution, it would be carried along with the dissolved silver ion and would interfere with the test for silver ion in the next step.

5. An unbalanced centrifuge will creep along the lab bench and might fall to the floor. Also, an unbalanced centrifuge will vibrate badly, and the sample tubes might be shattered by the vibrations and the broken glass dispersed into the room.

6. Silver iodide
EXPERIMENT 44 Qualitative Analysis of the Group II Cations

A. General Notes

Group II in qualitative analysis includes those cations whose sulfides are insoluble under very acidic conditions. Hydrogen sulfide is generated through the use of thioacetamide to prevent too bad a stench from arising in the laboratory. Students should be warned about the dangers of thioacetamide and hydrogen sulfide.

The experiment calls for short-range pH paper to ensure that the acidity of the solution has been adjusted to the correct level. This is available commercially, covering typically pH 0–3. Homemade methyl violet paper is to be used only as a last resort, because this method allows no real numerical determination of the pH.

Estimated time to complete: 3 hours

B. Materials Required (given for 25 students)

1 vial short-range (pH 0–3) pH paper
125 mL 6 M hydrochloric acid (500 mL conc. HCl diluted to 1 L; Caution!)
125 mL 6 M ammonia (410 mL conc. NH₃ diluted to 1 L; Caution!)
125 mL 1 M thioacetamide (75 g thioacetamide diluted to 1 L)
125 mL 1 M ammonium chloride (54 g NH₄Cl diluted to 1 L)
125 mL 3 M potassium hydroxide (168 g KOH diluted to 1 L)
125 mL 6 M nitric acid (380 mL conc. HNO₃ diluted to 1 L; Caution!)
125 mL 0.1 M tin(II) chloride (19 g SnCl₂ diluted to 1 L)
125 mL 6 M acetic acid (340 mL conc. CH₃COOH diluted to 1 L; Caution!)
125 mL 0.5 M potassium hexacyanoferrate(II) (211 g K₄Fe(CN)₆·3H₂O diluted to 1 L)
50 g sodium dithionite (sodium hydrosulfite), Na₂S₂O₄ (Caution: Keep dry.)

Group II known

Prepare 100 ml of the mixture by dissolving 3 g BiCl₃, 2 g CdCl₂, 2 g CuCl₂, and 3 g SnCl₄ in 100 mL 1 M HCl. This mixture is approximately 0.1 M in each ion.

Group II unknowns

Prepare 100 mL each of individual 0.2 M stock solutions of each of the ions in 1 M HCl: 6 g BiCl₃, 4 g CdCl₂, 3 g CuCl₂, and 6 g SnCl₄. Having a higher concentration here allows for the concentration of each ion in a mixture to be similar to that in the known. For ease of dispensing, transfer to dropper bottles.

Prepare 2-mL individual unknowns in coded, polyseal vials, using one, two, three, or all four of the ions. For unknowns containing a mixture, roughly equal volumes of the ion solutions should be used.
C. **Answers to Pre-Laboratory Questions**

1. There are several schemes of qualitative inorganic analysis, and different sources will quote different methods of identification of a given ion. One such scheme is given here. Mercury may be identified by dissolving the HgS precipitate in a mixture of HCl and HNO$_3$ (aqua regia), which results in the formation of the soluble HgCl$_2$$^{2–}$ ion. The solution of HgCl$_2$$^{2–}$ is then treated with stannous chloride, which reduces the mercury complex to a mixed precipitate of Hg and Hg$_2$Cl$_2$ (gray or black). Arsenic sulfide may be dissolved in concentrated nitric acid with heating; ammonium molybdate, followed by stannous chloride, is then added, resulting in a deep blue color (due to the reduction of an arsenic/molybdenum complex by the Sn$_2^+$) to confirm arsenic. Alternatively, the arsenic sulfide can be oxidized to arsenate ion, AsO$_4^{3–}$, with hydrogen peroxide in a strongly basic medium, with the arsenate then being precipitated as the mixed magnesium/ammonium salt. Antimony sulfide may be oxidized to Sb(V) by a mixture of sodium nitrite and HCl, and the antimony then confirmed by the purple color formed when Rhodamine B dye is added. Alternatively, antimony can be converted to the chloro complex and then reduced to the free element by aluminum metal.

2. A discussion of flow charts for qualitative analysis is given in the Zumdahl text.

D. **Answers to Post-Laboratory Questions**

1. If the pH had not been adjusted to this low a value, the sulfides of the Group III cations would also have precipitated. The Group III sulfides are not soluble at the very low pH called for in this experiment. The idea for the cation groups is to be able to separate the general scheme of cations into smaller groups quickly and simply.

2. Thioacetamide was preferred because it generates hydrogen sulfide slowly, and still in solution. Hydrogen sulfide gas has a noxious odor and is highly toxic: other methods would have introduced too much hydrogen sulfide into the room air.

3. $\text{Cu}^{2+} + \text{S}_2\text{O}_4^{2–} \rightarrow \text{Cu} + 2\text{SO}_2$

4. $2\text{Br}^{3+} + 3\text{Sn}^{2+} \rightarrow 2\text{Bi} + 3\text{Sn}^{4+}$
EXPERIMENT 45 Qualitative Analysis of the Group III Cations

A. General Notes

Group III includes those cations whose sulfides are insoluble under conditions of higher pH than the Group II cations. This analysis, because the group contains a larger number of cations than the previous groups, causes students more trouble. In this experiment, it is almost essential that students perform the test on a known and unknown sample in parallel. Encourage students to label their test tubes as they work, indicating what ions the test tube contains at each point in the scheme. It is easy for students to get lost in the many steps involved in the separation and confirmation of the ions.

Please refer to the notes for Experiment 38 in this guide for information on the preferred method of dispensing reagents.

Estimated time to complete: 3 hours

B. Materials Required (given per 25 students)

25 casseroles
1 vial pH test paper
125 mL 1 M ammonium chloride (54 g NH₄Cl diluted to 1 L)
125 mL 6 M ammonia (410 mL conc. NH₃ diluted to 1 L; Caution-stench!)
125 mL 1 M thioacetamide (75 g thioacetamide diluted to 1 L; Caution!)
125 mL 6 M hydrochloric acid (500 mL conc. HCl diluted to 1 L; Caution!)
125 mL 6 M nitric acid (380 mL conc. HNO₃ diluted to 1 L; Caution!)
125 mL saturated ammonium thiocyanate

NH₄SCN is very soluble in water; dissolve, with stirring, in 125 mL distilled water until no more dissolves.

125 mL 1% dimethylglyoxime (10 g DMG diluted to 1 L with 2-propanol)
125 mL 6 M sodium hydroxide (240 g NaOH diluted to 1 L; Caution!)
125 mL commercial household bleach
125 mL 1 M potassium thiocyanate (97 g KSCN diluted to 1 L)
125 mL 2% aluminon reagent (20 g aurintricarboxylic acid diluted to 1 L)
125 mL 0.1 M barium nitrate (26 g Ba(NO₃)₂ diluted to 1 L)
125 mL 3% hydrogen peroxide (commercial solution)
Group III known

Prepare 250 mL of the mixture by dissolving 10 g Cr(NO$_3$)$_3$·9H$_2$O, 10 g Fe(NO$_3$)$_3$·9H$_2$O, 10 g Al(NO$_3$)$_3$·9H$_2$O, 7 g Ni(NO$_3$)$_2$·6H$_2$O, and 7 g Co(NO$_3$)$_2$·6H$_2$O in 250 mL 1 M HNO$_3$. This mixture is approximately 0.1 M in each ion.

Group III unknowns

Prepare 250 mL each of individual 0.2 M stock solutions of each of the ions in 1 M HNO$_3$: 20 g Cr(NO$_3$)$_3$·9H$_2$O, 20 g Fe(NO$_3$)$_3$·9H$_2$O, 20 g Al(NO$_3$)$_3$·9H$_2$O, 14 g Ni(NO$_3$)$_2$·6H$_2$O, and 14 g Co(NO$_3$)$_2$·6H$_2$O. Having a higher concentration here allows for the concentration of each ion in a mixture to be similar to that in the known. For ease of dispensing, transfer to dropper bottles.

Prepare 10-mL individual unknowns in coded stoppered vials or test tubes, using one or more of the ions. For unknowns containing a mixture, roughly equal volumes of the component solutions should be used.

C. Answers to Pre-Laboratory Questions

1. There are many different qualitative analysis schemes. The information quoted here is from only one possible scheme. If zinc were present in the mixture, it would occur in the same subgroup from Part B containing Al(OH)$_4^–$ and CrO$_4^{2–}$ as a zinc/hydroxide complex; a specific reagent (dithiazone) causes a pink color when added to zinc(II) in this form. An alternative test is to dissolve zinc sulfide in HCl and then to precipitate the zinc ion with potassium ferrocyanide. If manganese were present, it would be isolated as the hydroxide in the same step as Fe(OH)$_3$. After redissolving in HCl, tartrate ion is added to complex the iron present, the solution is made alkaline, and a specific reagent (benzidine) is added, producing a blue color in the presence of manganese. Alternatively, Mn(OH)$_2$ could be oxidized to MnO$_4^{2–}$ and identified by its color.

2. A discussion of flow charts for qualitative analysis is given in the Zumdahl text.

D. Answers to Post-Laboratory Questions

1. Adding ammonia to an acidified solution results in a buffered mixture.

2. The half-reactions are

   \[
   \begin{align*}
   \text{Fe}^{2+} &\rightarrow \text{Fe}^{3+} + e^- \\
   \text{ClO}^- + \text{H}_2\text{O} + 2e^- &\rightarrow \text{Cl}^- + \text{OH}^- \\
   \text{Cr}^{3+} + 4\text{H}_2\text{O} &\rightarrow \text{CrO}_4^{2–} + 8\text{H}^+ + 3e^-
   \end{align*}
   \]

3. The half-reactions are

   \[
   \begin{align*}
   \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{H}^+ + e^- \\
   8\text{H}^+ + 4e^- + \text{CrO}_4^{2–} &\rightarrow \text{Cr}^{2+} + 4\text{H}_2\text{O}
   \end{align*}
   \]

   The color persists only briefly because Cr$^{2+}$ is easily oxidized by oxygen in the air (or oxygen in the water).

4. Aluminum hydroxide is amphoteric, dissolving both in strong acids and in strong bases.
EXPERIMENT 46 Qualitative Analysis of the Group IV and V Cations

A. General Notes

These groups consist of all remaining ions whose chlorides and sulfides are soluble. Sodium, potassium, and the ammonium ion are detected by flame tests on the original known or unknown solution—so many of the reagents used for qualitative analysis contain these ions that the tests must be performed on the original solution. There are, however, other tests for these ions, in which a precipitate involving the ion is isolated. Students are usually taught that, as a rule of thumb, all sodium and potassium salts are very soluble in water: they should be made aware however, that there are a few slightly soluble salts involving these ions that can be made use of in qualitative analysis.

Estimated time to complete: 150–180 minutes

B. Materials Required (given per 25 students)

25 casseroles
25 6-inch lengths of nichrome wire for flame tests
25 squares of cobalt blue glass
1 vial pH test paper
125 mL 6 M hydrochloric acid (500 mL conc. HCl diluted to 1 L; Caution!)
125 mL 6 M ammonia (410 mL conc. NH₃ diluted to 1 L; Caution-stench!)
125 mL 1 M ammonium carbonate (114 g (NH₄)₂CO₃ diluted to 1 L)
125 mL 6 M acetic acid (340 mL conc. CH₃COOH diluted to 1 L; Caution!)
125 mL 1 M potassium chromate (194 g K₂CrO₄ diluted to 1 L; Caution!)
125 mL 1 M potassium oxalate (184 g K₂C₂O₄·H₂O diluted to 1 L)
125 mL 6 M sodium hydroxide (240 g NaOH diluted to 1 L; Caution!)

Groups IV and V known

Prepare 250 mL of the mixture by dissolving the following in 250 mL water: 3 g CaCl₂, 6 g BaCl₂, 2 g NaCl, 2 g KCl, and 2 g NH₄Cl. This mixture is approximately 0.1 M in each ion.

Groups IV and V unknowns

Prepare 250 mL each of individual 0.2 M stock solutions of each of the ions: 6 g CaCl₂, 12 g BaCl₂, 3 g NaCl, 3 g KCl, and 3 g NH₄Cl. Having a higher concentration here allows for the concentration of each ion in a mixture to be similar to that in the known. For ease of dispensing, transfer to dropper bottles.

Prepare 10-mL individual unknowns in coded stoppered vials or test tubes, using one or more of the ions. For unknowns containing a mixture, roughly equal volumes of the component solutions should be used.
C. **Answers to Pre-Laboratory Questions**

1. Magnesium may be detected using a specific reagent (p-nitroazobenzene-α-naphthol) that produces a bluish green precipitate in basic solution. Magnesium may also be precipitated as the white mixed salt MgNH$_4$PO$_4$ by adding ammonia and disodium hydrogen phosphate, Na$_2$HPO$_4$.

2. Sodium forms the bright yellow triple salt NaZnUO$_2$(CH$_3$COO)$_9$·6H$_2$O, which is only very slightly soluble in water. Potassium forms an insoluble yellow salt with the hexanitrocobaltate(III) ion, K$_3$[Co(NO)$_6$] and a red/yellow salt with the reagent dipicrylamine.

3. Flow charts for qualitative analysis are developed in the Zumdahl text.

D. **Answers to Post-Laboratory Questions**

1. Many of the reagents added to separate and confirm cations in the earlier groups have been sodium and potassium salts. There could be no distinction made between sodium and potassium from the original sample and that which had been added.

2. The glass appears blue to our eyes specifically because it absorbs orange-yellow wavelengths of light.

3. The samples were buffered by adding a mixture of NH$_3$ and HCl, adding NH$_3$ until the response to pH paper was basic. The solution was buffered in the basic range because the carbonates would dissolve if the solution were acidic (releasing CO$_2$).

4. With excessive heating, the carbonates could be degraded to release carbon dioxide.

5. \[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

If the solution is heated, NH$_3$ will be driven off as a gas.
A. General Notes

Although progressive separation and confirmation schemes exist for a general mixture of anions, such procedures tend to be time-consuming and require a very large number of reagents. Furthermore, many of the anions tested for are those that occur less commonly. This experiment provides some sense of the gross separation scheme, offering some quick precipitation tests, followed by specific confirmatory tests for sulfate, sulfite, carbonate, nitrate, phosphate, and the halides.

In a departure from the earlier experiments on the analysis of cations, both known and unknown samples in this experiment are provided as solids. In particular, the unknowns consist of a solid sample of a pure compound. (There are no mixtures among the unknowns.)

As with the cation analyses, it would be most convenient for students to have individual sets of the test solutions. The amounts specified below assume each student takes 5 mL of the reagent.

Estimated time to complete: 3 hours

B. Materials Required (given per 25 students)

50 g of each of the following anions for use as student authentic samples; in each case, either the sodium or potassium salt may be used: sulfate, sulfite, carbonate, nitrate, phosphate, chloride, bromide, iodide. The materials may be set up in small, labeled 2-ounce bottles or vials.

125 mL 0.1 M barium chloride (21 g BaCl₂ diluted to 1 L)
125 mL 6 M nitric acid (380 mL conc. HNO₃ diluted to 1 L; Caution!)
250 mL 6 M sulfuric acid (330 mL conc. H₂SO₄ diluted to 1 L; use extreme caution)
125 mL 0.1 M silver nitrate (17 g AgNO₃ diluted to 1 L)
125 mL 0.5 M ammonium molybdate
   This reagent should be prepared the day before the laboratory is to meet; the reagent is generated by dissolving molybdic acid in a buffered ammonia solution (not by dissolving solid ammonium molybdate); detailed directions for its preparation are given in the CRC Handbook.
125 mL 1 M iron(II) sulfate
   This reagent should be freshly prepared to prevent oxidation of the iron(II); 278 g FeSO₄·7H₂O diluted to 1 L
125 mL methylene chloride (dichloromethane)
125 mL 1 M potassium nitrite (85 g KNO₂ diluted to 1 L)
125 mL 0.1 M potassium permanganate (16 g KMnO₄ diluted to 1 L)
125 mL 6 M ammonia (410 mL conc. NH₃ diluted to 1 L; Caution!)
C. Answer to Pre-Laboratory Question

As with the cations, there may be several possible tests for the given anions. An older test for nitrite ion involves a material called Griess’s reagent (a mixture of sulfanilic acid and α-naphthylamine), which causes an intensely red color to appear with nitrite ion, which very quickly changes to yellow. A second test for nitrite is the formation of the brown coordination complex Fe(NO)$_2^{+}$ when acidified iron(II) is added to the sample. Acetate ion can usually be identified by the odor of acetic acid produced when the sample is treated with a strong mineral acid and boiled.

Many precipitation tests can be applied for the sulfide ion, because so many metals form colored precipitates with the ion. Perhaps the simplest test, however, is to acidify the sample with a strong mineral acid: the rotten egg odor of H$_2$S will be all too noticeable.

D. Answers to Post-Laboratory Questions

1. Nitrite ion is a weaker oxidizing agent than is permanganate. The idea is to oxidize only the iodide ion at this point; if permanganate were used, it would oxidize both iodide ion and bromide ion.

2. Several methods might be applied, such as determining the gases evolved when a solid sample is heated (for example, bicarbonates evolve both water vapor and carbon dioxide, whereas carbonates evolve only carbon dioxide). A classical chemical test is to add mercury(II) ion to a dissolved sample: carbonates are precipitated by Hg$^{2+}$ whereas bicarbonates are not.

3. $3\text{Fe}^{2+} + \text{NO}_3^{-} + 4\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{NO} + 2\text{H}_2\text{O}$
A. General Notes

This experiment will prove most challenging to your students—and possibly also to your own patience and teaching skills! Students will be given a sample of an unknown ionic salt, with instructions to find out as much as they can about their unknown in the time available. They are asked to make quantitative physical measurements, as well as to determine qualitatively what ions are present in the salt.

The experiment will challenge the instructor’s patience in that each of the students will, in all likelihood, perform different reactions and tests, and the instructor will undoubtedly be bombarded with many questions. The best approach is to circle continually through the laboratory, checking exactly what tests students are performing and why. Some guidance from the instructor at the outset will prevent a lot of wasted time and a lot of confused questions as to what to try next. Be especially vigilant in pointing out the obvious to students. For example, if their unknown is bright green, what ions have been encountered earlier that are bright green? In case students want to supplement the confirmatory tests in this manual, the instructor should have on hand a CRC Handbook and one or more texts on qualitative analysis.

The stockroom staff will also be taxed by this experiment, because just about all the reagents from the previous experiments on qualitative analysis are needed for this experiment, as well as some of the measuring instruments from earlier experiments. Here again, guidance from the instructor can make a big difference. For example, very few ionic salts have melting points that can be easily measured, and although a melting point determination might be useful for a few salts (e.g., NaC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} hydrate), in most cases it is a waste of time.

Students are told that in most cases, their unknowns contain a single cation and a single anion but that there is a possibility that some unknowns may be double salts. It is suggested that the better students in the class be assigned these double salts as an extra challenge.

Estimated time to complete: 3 hours

B. Materials Required (given per 25 students)

The list that follows is compiled from the earlier experiments on qualitative analysis.

1 vial pH test paper
1 vial short-range (0–3) pH paper
100 centrifuge tubes
10–12 student centrifuges
125 mL 0.1 M barium chloride (21 g BaCl\textsubscript{2} diluted to 1 L)
125 mL 0.1 M barium nitrate (26 g Ba(NO\textsubscript{3})\textsubscript{2} diluted to 1 L)
125 mL 0.1 M potassium permanganate (16 g KMnO\textsubscript{4} diluted to 1 L)
125 mL 0.1 M silver nitrate (17 g AgNO\textsubscript{3} diluted to 1 L)
125 mL 0.1 M tin(II) chloride (19 g SnCl\textsubscript{2} diluted to 1 L)
125 mL 0.2 M potassium chromate (39 g K\textsubscript{2}CrO\textsubscript{4} diluted to 1 L); Caution!
125 mL 0.5 M ammonium molybdate (see the CRC Handbook for recipe)
125 mL 0.5 M potassium hexacyanoferrate(II) (211 g K₄Fe(CN)₆·3H₂O diluted to 1 L)
125 mL 1 M ammonium carbonate (114 g (NH₄)₂CO₃ diluted to 1 L)
125 mL 1 M ammonium chloride (54 g NH₄Cl diluted to 1 L)
125 mL 1 M iron(II) sulfate (278 g FeSO₄·7H₂O diluted to 1 L)
125 mL 1 M potassium chromate (194 g K₂CrO₄ diluted to 1 L; Caution!
125 mL 1 M potassium nitrite (85 g KNO₂ diluted to 1 L)
125 mL 1 M potassium oxalate (184 g K₂C₂O₄·H₂O diluted to 1 L)
125 mL 1 M potassium thiocyanate (97 g KSCN diluted to 1 L)
125 mL 1 M thioacetamide (75 g thioacetamide diluted to 1 L)
125 mL 1% dimethylglyoxime (10 g DMG diluted to 1 L with 2-propanol)
125 mL 2% aluminon reagent (20 g aurintricarboxylic acid diluted to 125 mL)
125 mL 3 M potassium hydroxide (168 g KOH diluted to 1 L; Caution!
125 mL 3% hydrogen peroxide (commercial solution)
125 mL 6 M acetic acid (340 mL conc. CH₃COOH diluted to 1 L; Caution!)
125 mL 6 M ammonia (410 mL conc. NH₃ diluted to 1 L; Caution-stench!)
125 mL 6 M hydrochloric acid (500 mL conc. HCl diluted to 1 L; Caution!)
125 mL 6 M nitric acid (380 mL conc. HNO₃ diluted to 1 L; Caution!)
125 mL 6 M sodium hydroxide (240 g NaOH diluted to 1 L; Caution!)
125 mL commercial household bleach
125 mL methylene chloride (dichloromethane)
125 mL saturated ammonium thiocyanate
25 6-inch lengths of nichrome wire for flame tests
25 casseroles
25 squares of cobalt blue glass
250 mL 6 M sulfuric acid (330 mL conc. H₂SO₄ diluted to 1 L; use extreme caution; considerable heat evolved; pack container in ice when diluting); Caution!
50 g potassium iodide
50 g sodium dithionite (sodium hydrosulfite), Na₂S₂O₄ (Caution: keep dry.)
disposable (Pasteur) pipets (or medicine droppers)
unknowns

Each student should be given approximately 5 g of an ionic salt or double salt in a coded vial. Almost any salt containing the ions studied in the qualitative analysis experiments may be used.