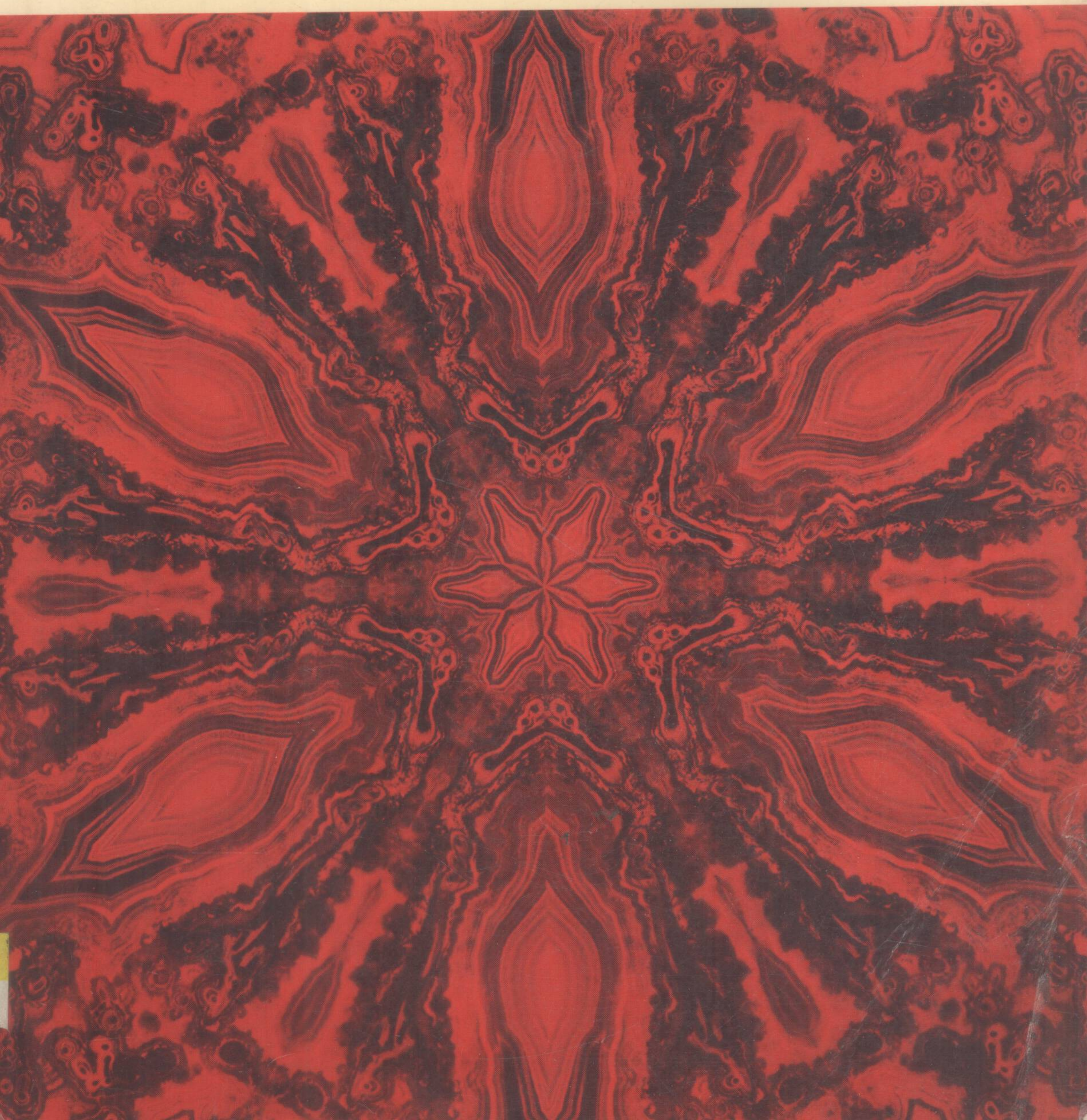
Experimental Chemistry

Richard C. Hatch



EXPERIMENTAL CHEMISTRY

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Preface

Current theories in chemistry, like those in any science, are accepted because they work; that is, they provide a reasonable interpretation of selected experimental observations. When a theory ceases to work in one aspect or another or as fresh information becomes available, hopefully it is revised. This continuing process of observation, interpretation, and revision is the essence of the scientific method. Although a full appreciation of the method requires an independent research experience, the experimental work described in this text provides a satisfactory introduction to the reasoning involved.

This text is designed for the laboratory program of a general chemistry course. Related experiments are grouped in a sequence of chapters similar to those found in most modern general chemistry textbooks. Pertinent theoretical concepts examined in a principles section at the beginning of each chapter often supplement material presented in these books.

Quantitative thinking and procedures are introduced early and emphasized throughout much of the text. Precision and accuracy in experimental measurements and the statistical analysis of data are thoroughly discussed. A number of experiments involve classical methods of gravimetric and volumetric analysis and provide the opportunity for replicate determinations. A chapter titled "Quantitative Chemical Analysis" is devoted solely to these methods because of the increasing tendency to offer in the general chemistry program material formally taught in the traditional quantitative analysis course. Wherever feasible, an experiment calls for the investigation of an unknown, a substance presented directly to a student or a compound that he must actually synthesize. Modern instrumental methods are featured in several experiments. Since the expense of the instrumentation may restrict the use of these experiments, alternate procedures have been provided.

Important details of descriptive chemistry have not been neglected. In addition to being a natural by-product of most experiments in the text, these details are the primary concern of Chapter 18, "Qualitative Analysis: Descriptive Chemistry of Selected Elements."

A number of experiments require two or more laboratory periods for completion since a lengthy project, treated in some depth, is often more stimulating than the customary single period experiment. Another equally attractive approach involves the use of group experiments where students are divided into small groups, each responsible for only a portion of the total data ultimately shared by all.

Guidelines for the preparation of laboratory reports are outlined in Chapter 4. Although students clearly benefit from organizing their own reports, an instructor does not always have time to examine a large number of these individual efforts and may wish to use the standard report forms which follow each experiment. Requiring formal reports for a few selected experiments is a desirable alternative.

For the most part, experimental procedures are rather detailed. However, toward the end of a course, an instructor may wish to set aside time for "open-ended" experiments where a student must first devise a method for solving a problem. Suggestions for this type of work appear at the conclusion of several experiments, and one entire chapter is devoted to selected projects with only a minimum of instructions. There is a wide variety of experiments in the book and some include alternate procedures. Therefore, an instructor should experience little difficulty in devising a schedule to fit the background and needs of his students.

Many individuals have contributed to this work. I am grateful to my colleagues Dr. Charles E. Mortimer for encouragement, Dr. David N. Stehly for many helpful suggestions, and Mrs. Elsie M. Schmoyer for typing the manuscript. I also wish to thank the publisher's staff, particularly Mr. Stephen Kraham, editor, and Miss Marie Louise Caspe, manuscript editor, for their generous assistance. My sincere thanks to my wife, Deborah, for her encouragement, constant help, and, most of all, patience.

RICHARD C. HATCH

Contents

1

Introduction: General Instructions

This introductory chapter presents an outline of general instructions for students working in the laboratory. Included is information concerning preparations for an experiment, laboratory work, safety precautions, and reports on experimental measurements.

1–1 PREPARATIONS FOR AN EXPERIMENT

Before a student enters a laboratory to perform a particular experiment, it is essential that he carefully study the description of the assigned project in order to acquire a clear understanding of its objectives and procedures. This study should be supplemented by an examination of reference sources for material which provides insight into the theory and practice relating to the experiment.

In order to make efficient use of library reference material, it is necessary to be familiar with the locations of periodicals such as the *Journal of Chemical Education*, the *Journal of the American Chemical Society*, and *Analytical Chemistry;* equally important is a knowledge of the locations for chemistry textbooks, treatises, and handbooks. A list of suggested readings has been provided at the conclusion of each chapter in this textbook.

The relatively small amount of time required for the preparation for an experiment enables one to accomplish more while expending less time and effort in the laboratory. Moreover, this small bit of planning often makes it possible to avoid much frustration once an experiment is underway.

1-2 LABORATORY WORK

1. *Many of the* experiments described in this textbook can be completed in a single three hour laboratory period. Others require two or more periods. These may be abridged, however, so that meaningful results are obtained in one laboratory session.

2. The actual laboratory work for an experiment may be preceded by a short briefing session. During this briefing, the instructor will initiate some discussion concerning the theory relating to the experimental problem and the techniques employed in the solution of that problem.

3. Two or more individuals may be required to work as a group while performing certain experiments. One advantage of such group projects is that they provide an opportunity for discussion of the experiment. Preliminary study for each project, however, and the composition of each laboratory report must be an individual effort.

4. Bring the regular textbook to every laboratory session. The text is a readily available reference which may be helpful in understanding experimental procedures and interpreting results.

5. It is often necessary to perform rapid calculations while in the laboratory. Use a slide rule for this purpose.

6. If a particular procedure can be modified so that a more precise measurement is obtained without expending a great deal of additional time and effort, do so. Attempts to achieve an unnecessary precision in a particular measurement, however, are inefficient as well as a sign of poor laboratory technique.

7. An analytical balance is assigned to each student. This instrument is used for accurate weighing, and since at least one such operation is required in most experiments, it is important that a student fully understand how to use a balance. For this reason, Chapter 6 is devoted solely to the construction and operation of this instrument. Each individual is responsible for keeping the table area around his assigned balance clean and neat.

8. Discard all solid wastes in the porcelain jars placed in the laboratory for this purpose. Do not throw solid materials into a sink. Liquid wastes should be placed in waste containers if they are available. If there are no such containers, flush liquids down a sink drain with a large volume of water.

9. Leave chemical reagent containers at their proper locations in the laboratory. Do not take these containers to a laboratory desk work area. Reagents may be transferred (i.e., poured) directly into a clean beaker, flask, or watch glass. Do not use a spatula, medicine dropper, or other transferal devices to remove reagents from their containers, since this practice may contaminate the reagent.

10. When transferring a quantity of a reagent from its container, do not measure out a large excess since chemicals are usually expensive. Never return used chemicals to their original containers since this is another possible source of contamination. Any excess should be discarded as described in item 8.

11. Distilled water is expensive to produce and therefore should not be wasted.

12. At the conclusion of each laboratory session, thoroughly clean the work area and glassware that has been used.

1–3 SAFETY PRECAUTIONS

The following safety precautions must be observed by a student working in the laboratory:

1. Wear a pair of laboratory safety glasses at all times.

2. It is advisable, although not mandatory, to wear a lab coat or apron in order to protect clothing.

3. The directions provided for each experiment in this textbook are designed to minimize the possibility of accidents. If a student desires to change or supplement an experimental procedure, he must first consult with his laboratory instructor. Do not attempt unauthorized experiments.

4. Learn the locations of the several items of safety equipment provided in the laboratory. This equipment may include a fire extinguisher, safety shower, fire blanket, eye-wash bottles and sinks, and first aid kits.

5. Keep the laboratory desk work area clean and uncluttered.

6. Read the labels on all chemical reagent containers before using their contents. The use of an improper reagent can lead to a serious accident.

7. Since most chemical reagents are poisonous to some degree, one should assume that a particular reagent is hazardous unless he knows for sure that it is not. Never taste a chemical or extensively inhale its vapors.

8. Several experimental procedures described in this textbook require the use of a ventilating hood in order to avoid prolonged contact with vapors or gases which are poisonous or have an objectionable odor.

9. One potential mode of poisoning is often overlooked—namely, a chemical being absorbed through the skin. Because of this danger, it is wise to get in the habit of washing one's hands immediately after they come in contact with any chemical. It is particularly important to wash the hands just prior to leaving the laboratory for the day.

10. When a chemical reagent is not in use, its container should be tightly closed. Containers of particularly volatile materials should be kept in a ventilating hood.

11. Never pipet any liquid by applying suction with the mouth; use a mechanical pipetting device. This operation is described in Chapter 5.

12. If a chemical reagent gets into the eyes or mouth, or on the skin, immediately wash the affected area with a large amount of water. An eye-wash device is often available. After washing, report the accident to your laboratory instructor.

13. In order to neutralize acids spilled on clothing, use a very dilute ammonia or sodium bicarbonate solution. When bases are spilled, first neutralize with a dilute acetic acid solution and then wash the affected area with dilute ammonia solution.

Acids or bases spilled on the laboratory desk or floor are effectively neutralized with solid sodium bicarbonate followed by rinsing with water.

14. Keep flammable materials far away from all flames. If it is necessary to heat such materials, use an electrical heating device.

15. Never add water to a concentrated acid solution since this generates a great deal of heat energy which may crack the container causing a dangerous spill.

Always mix a concentrated acid and water by pouring the acid into the water slowly, with constant stirring.

16. When heating the contents of a test tube, be sure to point the open end of the tube away from all individuals including yourself. A vapor pocket formed beneath the surface of the contents may lead to "bumping," a process which causes the contents to be violently ejected from the tube.

17. Never throw lighted matches into a sink where they might ignite a discarded flammable liquid.

18. Do not heat glassware such as graduate cylinders and reagent bottles since these items break rather easily. When the contents of a beaker or flask are heated, place the vessel on an asbestos wire gauze to insure an even distribution of heat. Never fill a vessel to more than about seventy percent capacity during a heating operation or its contents may overflow.

19. Cracked or severely broken glassware may cause an injury or, at the very least, fall apart during an experiment. Replace such damaged glassware immediately.

20. When a piece of glass tubing or a thermometer is inserted into the hole of a rubber stopper, lubricate both the surface of the glass and the hole. A soap solution is an excellent lubricant. Wrap the tube with a cloth towel and hold it near the end which is to be inserted.

When trying to remove glass tubing from a stopper or other rubber fitting, pry the rubber away from the glass and drop a bit of lubricant into the opening. Wrap both the tubing and the fitting in a cloth towel and attempt to twist off the fitting without applying too much force. If the fitting cannot be removed intact, cut it off with a knife.

21. Fire polish the ends of all freshly cut glass tubing in order to eliminate sharp edges.

22. Never eat or smoke in the laboratory.

NOTE: Additional safety precautions will be outlined by your laboratory instructor when necessary.

1–4 REPORTS ON EXPERIMENTAL MEASUREMENTS

Write your report on an experiment as soon after its completion as possible. If the interval between the completion of a project and the writing of a report is too long, the experimenter's impressions of and appreciation for the project tend to fade.

Avoid getting into a position where several reports must be written simultaneously. When this happens, each of the reports tends to be poorly constructed. Detailed instructions for writing a laboratory report are presented in Chapter 4.

2

Chemical Symbols and Units

Chemists use a variety of symbols and units when discussing experimental procedures and results. This chapter briefly describes some of them as they are used in this laboratory text.

2–1 FORMULAS

Chemical compounds composed of molecules are represented by molecular formulas indicating the number of each type of atom in a single molecular unit. For example, the formula for hydrogen peroxide, H_2O_2, shows that a molecule of this compound incorporates two atoms of both hydrogen and oxygen. Frequently, formulas are presented in a way which suggests something about the arrangement of atoms within a molecule. Thus, a more descriptive formula for hydrogen peroxide is HOOH.

Empirical formulas are used to represent the smallest whole number ratio of the different ions in an ionic compound. For instance, the formula for sodium chloride, NaCl, shows that this substance contains a one to one ratio of Na^+ and Cl^- ions.

2–2 EQUATIONS

Chemical equations describe the changes that occur when compounds react (e.g., bond rearrangements and change in oxidation state). The reaction of solid carbon and oxygen gas to produce gaseous carbon dioxide is represented as

$$\underbrace{C(s) + O_2(g)}_{\text{(reactants)}} \rightarrow \underbrace{CO_2(g)}_{\text{(products)}}.$$

The arrow does not necessarily indicate a complete reaction, that is, a complete conversion of one or more reactants to products. When the conversion is incomplete and the reaction system reaches a state of dynamic equilibrium, the arrow is often replaced by a double arrow, $\rightleftharpoons$.

The physical states of participants in a reaction are designated by letters placed after the formulas in an equation. The letter symbols include (s) for solids, (l) for liquids, and (g) for gases. A fourth symbol, (aq), indicates that a participant is a component in an aqueous solution. The use of (aq) is illustrated here in the equation depicting a reaction between zinc 2+ ion and hydrogen sulfide in an aqueous solution:

$$Zn^{2+}(aq) + H_2S(aq) \rightarrow ZnS(s) + 2H^+(aq).$$

(Note that a hydrogen ion in an aqueous environment is portrayed as $H^+(aq)$ rather than H_3O^+ which represents the ion associated with a single water molecule. The latter symbol is not used since the exact nature of a hydrogen ion in aqueous media is still being debated.)

In the description of an experimental procedure, chemical reagents in aqueous solution are often represented with the (aq) symbol; typical examples are:

Hydrochloric acid	$HCl(aq)$	Aqueous ammonia	$NH_3(aq)$
Nitric acid	$HNO_3(aq)$	Aqueous sodium hydroxide	$NaOH(aq)$.
Sulfuric acid	$H_2SO_4(aq)$		

A chemical equation should describe the condition of reaction participants as accurately as possible without being too lengthy. In the previous illustration, the aqueous solution of H_2S also contains $HS^-(aq)$ and $S^{2-}(aq)$ ions. Experimental evidence indicates, however, that the predominate sulfur-containing species are H_2S molecules; consequently, only the formula $H_2S(aq)$ appears in the equation. As a general rule, when there is a choice of several reaction participants (e.g., H_2S, HS^-, and S^{2-}), the one with the highest concentration is represented.

The representation of the reaction between zinc 2+ ions and hydrogen sulfide in aqueous solution is an example of an ionic equation. If zinc chloride ($ZnCl_2$) is the source of zinc 2+ ions, the equation could be written as

$$ZnCl_2(aq) + H_2S(aq) \rightarrow ZnS(s) + 2HCl(aq).$$

Since chloride ions, however, are not altered chemically as a result of this process, there is no pressing need to include them in the equation.

Stoichiometry A chemical equation must be quantitatively, as well as qualitatively, accurate; it must reflect the fact that the total number of atoms and ions of a particular element are conserved in a reaction. In addition, the equation must also indicate that electrical charge is conserved. These two conservation principles are employed to balance an equation. For example, in the equation representing the zinc 2+ ion and hydrogen sulfide reaction, the total number of atoms and ions of the element H are balanced by placing the number 2 before the $H^+(aq)$ formula; this also serves to balance the net electrical charge (2+). Numbers which appear before formulas in a balanced equation are referred to as stoichiometric coefficients. When there is no number, it is understood that the coefficient is one. These numbers represent the relative numbers of the various molecules and ions involved in a reaction, or the relative number of moles of reactants and products. A mole is an Avogadro number (6.023×10^{23}) of particles. Additional discussion of these coefficients appears in Chapter 9.

2–3 SOLUTION CONCENTRATIONS

A chemical reagent used in the laboratory is often dissolved in an appropriate liquid. If a known amount of reagent is needed, it may be obtained by measuring out a specified volume of the solution, provided that the composition is known. Composition, or the quantity of reagent in a fixed volume or mass of solution, is expressed as a concentration in the following ways.

1. Percentage by mass: number of grams of reagent per 100 grams of solution. For example, a 36% aqueous solution of hydrochloric acid contains 36 grams of hydrogen chloride, HCl, per 64 grams of water, H_2O.

2. Mass per unit volume: number of grams of reagent per unit volume of solution. The 36% hydrochloric acid solution contains 425 grams of HCl per liter of solution.

3. Mole fraction, X: number of moles of reagent divided by the total number of moles of all the components in a solution. In the hydrochloric acid solution, $X_{\mathrm{HCl}} = 0.217$ and $X_{\mathrm{H_2O}} = 0.783$.

4. Molality, m: number of moles of reagent (solute) per 1000 grams of solvent (major component). The molality of the hydrochloric acid solution is 15.4 moles of HCl per 1000 grams of water or simply 15.4 molal.

5. Molarity, M: number of moles of reagent per liter of solution. The hydrochloric acid solution contains 11.7 moles of HCl per liter of solution and therefore its concentration is 11.7 M. Molar concentrations are commonly represented by square brackets enclosing the formula for a reagent (e.g., [HCl] = 11.7 M).

Molarity is a particularly convenient concentration unit to work with as far as stoichiometric relationships are concerned. If some specific number of moles of a solute are needed, they are present in a volume V of a solution where the solute concentration is M, that is,

$$\text{number of moles of solute} = M\ (\text{moles liter}^{-1}) \times V\ (\text{liters}).$$

3

Reliability of Experimental Measurements

The majority of experiments in this textbook are quantitative in nature since they require accurate measurements of properties such as mass, volume, and concentration. The values of these properties, expressed as numbers with appropriate units, constitute the data for an experiment. Once the data has been collected, it is used to compute the experimental results. Finally some consideration must be given to the reliability of both the data and the results.

3–1 *ACCURACY AND PRECISION*

All experimental measurements are subject to error. Error is defined as the difference between a measured value and the "true" value of a property. If this difference is small compared to the magnitude of the true value, then the measurement is said to be accurate. Expressing the reliability of a measurement in terms of its accuracy is not often possible, since there are relatively few instances where the true value of a property is known. Counted numbers of objects or events are true values; so are the rational or irrational numbers which appear in mathematical formulas. For example, the numbers 2 and π in the formula for the area of a circle (Area $= \pi r^2$) are known to any desired accuracy.

Since an experimental measurement is subject to error, a property determined by that measurement can never have a true value in the same sense that a counted number does. However, in some cases a property does have a value which is accepted as true by the scientific community. An accepted value may be defined.