Lawrence J. Sacks

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# Experimental Chemistry

LAWRENCE J. SACKS

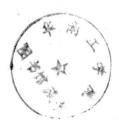
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# Preface

This book has accumulated over more than a decade largely because of disappointment with traditional laboratory experiments and some nagging questions about available lab manuals. For example: Why do we have to reteach simple lab operations in later courses, often requiring students to unlearn poor procedures taught earlier? Why don't college students retain the enthusiasm for chemistry that many high school graduates bring with them to college? Why do some experiments, present in most manuals, give results that defy any reasonable analysis on the basis of information available to the student? Why do so many students forget so much of what they have learned in a first-year lab course before finishing college? And why don't students keep the general chemistry lab manual for later use?

I think the last question sums up the others. Lab manuals aren't kept for future reference because they aren't worth keeping. There are, of course, some notable exceptions, but for the most part they are books designed for particular (usually homogeneous) groups of students. Much more commonly, the manual is that part of a required chem lab in which blank spaces must be filled in (often from material in the textbook) and turned in, so that a grade can be turned in, so that the student can get through Chem 197 and on to more of the same in Chem 198. Students look upon the lab as a place where their own observations and conclusions are not to be trusted; instead, the "right" observation or conclusion must be found in the text, if the blanks are to be filled in "correctly." Too often we are more concerned that a student left a blank page than that we left a blank in his understanding or his ability to reason.

This book is based on the conviction that chemistry is an experimental science, and that laboratory work in general chemistry is important and deserves the best possible presentation so that it can be an effective introduction to experimental work. Lab work is not incidental to chemistry—it is the essence of it. This presentation presumes that students conscientiously pursuing studies in one of the sciences deserve an equally conscientious instructor, equipment capable of providing reliable quantitative results, and instructions that make the best possible use of all of these.

Not all chemistry comes in three-hour packages and not all students can complete the same work in the same time. Many students enter college with substantial deficiencies in mathematics and science, as well as in English, whereas others have had advanced courses, sometimes at the college level. To complicate matters further, there is frequently little correlation between the first few weeks of lectures in general chemistry and the lab work being done. What kind of experiment can challenge the well-prepared student, help the poorly prepared student, and still stand independently, so that if, back at the classroom, atomic structure or history of chemistry is being discussed, the lab can still carry on?

The physical measurements in Section I have proved to be a highly satisfactory solution. Students proceed at different paces. Some of my students are still on Experiment 1, Part 1, when the majority of the class is on Experiment 2. As students gain lab technique, plan work better, and keep better records of results, some of the initial differences disappear, but there are numerous opportunities for flexibility in the extent of work to be done. Some students may skip parts of an experiment or an entire experiment, while others will find opportunities for more advanced work. Let's recognize that the number of experiments completed is not, in itself, much of a guide to lab proficiency. What is done must be done carefully and with understanding.

What should the lab work accomplish? As a part of a chemistry course, it must provide lab technique—specific training in chemical laboratory operations, including use and care of equipment and lab safety. Only those techniques that can be taught correctly should be attempted. But this is not a serious limitation if we are willing to relax some of our restrictions on equipment ordinarily reserved for upper-classmen. It has been my experience that properly instructed freshmen take much better care of equipment than do upperclassmen who were first taught on inferior equipment or without proper supervision. Before we decide that we cannot afford careful instruction with automatic balances, reliable burets, or reagent-grade chemicals, we should consider what it costs *not* to present good lab procedures the first time around, in terms of later use of equipment and, more importantly, in terms of attitudes developed during the first encounter with the chemistry laboratory.

Every chemistry experiment should encourage—and require—critical analysis of experimental evidence; the questions asked about the experiment have an important bearing here. By restricting these for the most part to the experimental results (and, occasionally, to closely related situations), the student is shown that he can, in fact, depend on his own results and his own judgment.

What topics should be included (or excluded)? In view of the great number of possible topics a matter of selection necessarily arose (and will arise again for the instructor, unless two labs per week are offered; there are suggestions for selection in the Instructor's Handbook). Most students taking this course will go on to organic chemistry, so organic reactions as such are not stressed. There is, however, a brief discussion of organic compounds in conjunction with halogenation reactions (Experiment 39), and organic compounds are frequently used.

Analytical and physical chemistry posed different problems. Quantitative procedures pervade all of chemistry and the other sciences as well. By introducing them here, time in a subsequent quant course can be utilized for more specialized methods. But other areas also deserve attention in the laboratory. Many topics from physical chemistry are appropriate, but others were avoided, partly for reasons of space; but more important, current practice notwithstanding, I consider a great deal of physical chemistry too advanced for beginning students. The inclusion of a section on electron-transfer reactions results from insufficient attention and poor presentation of this topic in most textbooks. The elimination of a separate qualitative analysis scheme resulted from the evolution of Experiments 17 and 18. The same equilibrium concepts can be presented without going through the usual group separations. Unknowns can be introduced (as is done in most of the experiments) and provide at least as much student interest with equal or greater understanding. My intention is to emphasize how we learn about separations, rather than to present a particular scheme for separating particular ions.

Edison's estimate of the proportion of perspiration to inspiration (99:1) applies almost as well to writing as to inventing. I hope this book will save other instructors from some of the perspiration in preparing lab experiments suitable for their students. I am grateful to my former students whose efforts justified mine. I particularly thank Carol Czaplinski for checking several new procedures. For helpful criticisms, I am indebted to Professors Fred Tabbutt, Donald McMasters, R. H. Schwendeman, and Loren Hepler; and to (Mrs.) Barbara Rosen (who learned me better grammer and speling). The editors of The Macmillan Company have shown great patience and consideration in adjusting deadlines and obtaining reviews so that academic, rather than commercial, criteria could determine the content and format of this book. Special thanks go to my wife, Ruth, who helped retype and proofread the many drafts. For the remaining errors the author accepts full responsibility; corrections and suggestions from colleagues and students will be greatly appreciated.

L. J. S.

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#### To the Student

When many of us now teaching chemistry started out, we knew less about the subject than many of you now do, yet we managed to survive; you will, too. But the first chemistry course and the first college year should be more than just "survival." This section, then, might be called "Beyond Survival." It is here to help you get maximum benefit from the time you spend. As an added bonus, you might even find that some of the working habits learned here will help you in later courses.

Despite references to "the scientific method" it is difficult to find any unique method of solving problems—scientific or other. There are, however, some approaches that are demonstrably more successful in solving problems than others. These invariably involve careful observations, accurate recording of these observations, and thoughtful interpretation of the results. Frequently, careful planning of an experiment is necessary to furnish relevant, reliable information. But it is difficult to plan an experiment if you don't know what options exist, so a major objective of this book is to help you develop lab skills and learn experimental methods.

How much you gain from the lab work depends primarily on you. These directions will, hopefully, be a help, and there's no way of doing experimental work without a lab to work in, preferably a well-equipped one. Your instructor will be very important, too, but it's up to you to learn. Sometimes this just means following the directions carefully. This is much easier to do if you read through the experiments before lab and prepare an outline of the procedures to be followed. If you do not prepare adequately for lab you will fall behind, but there will be many occasions when you will learn more by repeating a part of an experiment (or the entire experiment) or by performing a variation of an experiment than by forging on to a new topic. It is more important to understand one experiment than to do two not knowing what's going on.

Particularly in the first experiment you may think that there is an enormous amount of new material to learn. Agreed. But we don't expect perfection for the first experiment you do in lab—regardless of what it is. The lab is a room for improvement. If you know how to do every operation perfectly the first time (including use of the notebook and preparation of the report) rush up to your instructor and ask for more advanced work, within this course or elsewhere. If you're like most students, you will instead find some parts quite straightforward, others complicated, some quite confusing. If you have trouble with an experiment, there are optional parts that can be omitted to provide you more time to work out the difficulties. If, after giving a problem a serious attempt, you still cannot solve it, ask your instructor.

Learn to keep data in neat, labeled tables; record observations completely, even if you aren't certain you'll need the information later. Think about what you're doing and what you hope to find. The questions at the end of the experiment help pinpoint the more important aspects of the experiment. In a few cases they should be answered before lab, since they check your understanding of some mathematical operations,

balancing of equations, and so forth. However, it is neither expected nor acceptable for you to answer the questions relating to the experimental work except on the basis of your own results. You will be judged on all aspects of your lab work—lab technique, accuracy of results, and your evaluation of those results, as reflected in your reports. That is why the evaluation of experimental results is a part of the *first* experiment, and all subsequent experiments in which quantitative results are obtained.

The chemistry laboratory is potentially a dangerous place. So is the automobile, the kitchen, or the basketball court. However careful you are, somebody else can smash into your car, just as someone else can spray you with sulfuric acid in the laboratory. The Laboratory Regulations sheet lists some rules that have been established for the convenience of the class and the safety of each member. They are nonnegotiable. If you don't want to wear safety glasses of some sort, stay out of the laboratory. If your creative spirit moves you to do something original without the approval of your instructor, write a poem. If you write it in your lab notebook (or even as you use the notebook for strictly lab work, as intended), follow the guidelines on the Laboratory Notebook sheet.

Most of my former students, who helped formulate this approach to chemical experimentation, liked lab work and found themselves well prepared for later courses. I hope the same will be true for you.

## Laboratory Regulations

1. Safety is a prime requisite for laboratory work. Eye protection is required at all times unless explicitly stated otherwise. Prescription glasses afford the minimum acceptable protection; safety glasses or goggles are preferred. A lab apron will prove a good investment for protecting clothing.

Learn the location of the safety equipment: fire extinguisher, safety shower, and eye wash fountain. Injuries should be treated immediately

and reported to your instructor.

2. Lab work is to be done on an *individual* basis unless you are instructed otherwise. Prepare for lab by reading the experiment and preparing an outline of the procedure.

3. Record your results immediately and directly in your notebook.

4. The most productive research demands original work, and this is strongly encouraged. *However*, for safety reasons this may be done *only* with the approval and supervision of the instructor. *Unauthorized experiments are strictly forbidden*.

5. Students are allowed in the laboratories only during regularly scheduled class periods unless special permission is explicitly given by

the instructor.

- 6. Keep your lab clean. Wipe up spilled materials immediately. Only soluble, harmless materials should be put in the sink, and these should be washed down with plenty of water. Insoluble or toxic materials should be put in the containers provided. If in doubt, *don't* pour a substance down the drain; it will soon be carried to a water-treatment plant and possibly pass through into a stream. Heed the warnings on the reagent bottles.
- 7. Balances and other delicate instruments require special care. Follow carefully the directions for their use.

### Laboratory Notebook

The notebook is to contain a *permanent*, *accurate record* of your work in lab. Therefore, the book should be bound and have a hard cover. It should have at least 60 pages, which you must number if they are not prenumbered. Quadrille pages are preferable, but lined pages will suffice. A book about 7 by 9 inches is preferred.

The first two sheets (pages 1 through 4) are reserved for the table of contents, which is to be kept up to date with the number of each experiment, its title, and the page on which it begins.

Each experiment should begin with its title, object, and procedure followed (or reference to the source of the procedure). Date each page. If you continue the work later, note this. Always begin an experiment on a new page.

All entries in the notebook must be in ink. Record data as you gather them *directly in the notebook*. Use right-hand pages only, unless a double page is needed for a large table. In general the left-hand pages should be used for notes or calculations for the experiment, or left blank. *Never* record data on loose slips of paper for later transfer to the notebook. Should a correction be necessary, draw a single, light line through the erroneous value and enter the correct value. The original value must remain legible (you may later decide to use it). Wherever possible, tables of data are preferred to isolated values; in either case, all values must be clearly labeled so that your notebook is comprehensible to someone with training comparable to your own.

Leave sufficient space on each page for corrections, yours or your instructor's. Leave about a 1-inch margin all around each page.

The notebook should be brought to each lab and used for no other purpose.

# Section I

## Identification of Substances by Physical Properties

#### Introduction

In this section methods for characterizing solid and liquid substances by selected physical properties will be investigated and unknown samples will be identified on the basis of such information.

It is a relatively simple matter to bring about a chemical reaction. There are almost unlimited numbers of substances that will undergo a chemical change under suitable conditions. Even as you read this page your body is performing hundreds of chemical changes, while many others are occurring all around you. Some of these reactions are quite well understood; both reactants and products have been determined, the energy of the reaction has been determined, and a reasonable path for the reaction has been formulated on the basis of sound experimental and theoretical conclusions. In other cases relatively little is known about the reaction.

For reactions carried out in the laboratory, the reactants are usually known and, in simpler cases, only one or two predictable products result under a given set of conditions; but such cases represent only a minute fraction of all chemical changes. You must therefore learn to identify chemical substances if you are to understand chemical reactions. More immediately, you must recognize that before a chemical equation can be written, the correct reactants and products must be determined. Usually you will know the reactants, and before long you will be able to predict the products of certain reactions. But the proof is in the putting—of the substances to the test of analysis.

In this section we will learn to measure certain physical and thermal properties of liquids and solids; in later sections we will investigate chemical behavior. By selecting more easily measured physical and chemical properties we can frequently simplify identification; by making use of these and other more esoteric measurements, samples of considerable complexity can be identified. We shall postpone, at least temporarily, the equally challenging task of obtaining pure materials from mixtures—samples furnished for the experiments in Section I will be

pure substances, either (solid) metallic elements or (liquid) organic compounds.

You will be given sufficient sample for the tests to be performed, provided you don't waste any. Perform nondestructive tests first and be careful not to contaminate or lose the sample.

CAUTION: Unless you have explicit information to the contrary, consider all liquids as *flammable* and *toxic*. Avoid breathing vapors and keep the liquids off the skin. In case some spills on you, wash it off immediately with plenty of water (then attend to the desk or floor). Since most liquid samples will be rather volatile, they should be kept in tightly closed bottles.

The experiments in this section should provide you with sufficient information to predict the identity of your unknown samples. You will also be expected to defend your selection; hence you should obtain as much evidence as possible—don't rely on one or two measurements if others are also available.

## Reliability of Quantitative Measurements

You will be making quantitative measurements on your samples—you will be recording numbers and their units, such as 4.336 g, 6 cm, 12.3 ml, or 102.2°C. How much confidence can you have in your values? For example, suppose you measure the boiling point of a liquid (as in Experiment 3) and record the value 86°C. You suspect that the compound is allyl formate, but when you find a reference value for this compound, it is listed as 83°C. Could you have this compound? It depends on whether the allowable range of values for your compound and for the reference compound have common ground. Might your value be off by a degree or two? Might the reference value? To answer these questions it is necessary to have some quantitative estimate of the errors encountered in taking measurements. "Pretty good" or "probably way off" isn't much help. Instead, we will use generally accepted methods for reporting uncertainties which come from statistics.\* Usually we will not obtain enough readings to warrant use of the more sophisticated statistical methods, but even the simpler tests will aid greatly in evaluating the data. Such evaluation must consider two distinct but related estimations of the validity of the measurements, precision and accuracy.

#### **Precision and Accuracy**

**Precision** refers to the *reproducibility* or closeness of replicate (repeated) measurements and is related to the *dispersion* (scatter) of the

<sup>\*</sup> For an excellent introduction to statistics by self-study, see R. J. Flexer and A. S. Flexer, *Introduction to Statistics*, Vol. 6 in Programmed Reviews of Mathematics, Harper & Row, New York, 1967. An introduction to useful statistical methods for this course is given in Appendix A.

values. High precision (low dispersion) suggests that the next measurement will be close to the average of those already taken, while a large uncertainty (high dispersion) reflects much scattering, hence less confidence in the average value. Some uncertainty is present in every measurement. Identical values usually reflect a rounding off in the taking and/or the reporting of the data. Your estimate of the uncertainty of a measurement should always accompany the value.

Accuracy is the closeness of the individual values (or, more commonly, their average) to the *true* value. The difference between the experimental and true values is the **error** in the experiment:

experimental value — true value = error

and

$$\frac{\text{experimental value} - \text{true value}}{\text{true value}} = \text{relative error}$$

Note that the error can be positive or negative, showing whether the experimental value is above or below the true value.

Let's take an example. To determine the density of a solid it is necessary to measure both its mass and its volume. Suppose we use a coarse lab balance that repeats weighings on the object only to within 0.2 g. If the average of several trials is 17.23 g, we would report the weight as  $17.2 \pm 0.2$  g, or 17.2 g  $\pm 1\%$ .\* For an irregularly shaped block, the volume might have to be reported as  $11.6 \pm 0.7$  cm³, or 11.6 cm³  $\pm 6\%$ . The density would then be 17.2 g/11.6 cm³ = 1.48 g/cm³, with an uncertainty that should not exceed 7%: density =  $1.5 \pm 0.1$  g/cm³. Note that in this case use of a better balance would reduce the uncertainty only slightly. For better precision, improvement in the volume measurement is required.

If our estimations of uncertainties are good ones, we would expect the density to be between 1.4 and 1.6 g/cm³. How confident are we that it's not 1.3 g/cm³? Or 1.8 g/cm³? It depends entirely on the validity of our uncertainty estimates. Since we took a series of weighings, we might be willing to give odds of as much as 10:1 that the weight is within the range 17.0 to 17.4 g. How confident are we of the volume estimate? It's a matter of judgment—in a wider interval there is more chance of including the true value, but the density is less reliable. How was the volume estimated? Here, we don't know, so we can't do more than use the 6% uncertainty as a rough estimate. Therefore, we can't really exclude either 1.3 or 1.8 g/cm³, but we would certainly not accept either value without other checks on the substance.

Where does the *true* value come from? Usually we take a prior measurement given in a reliable reference work. Some of the more common references are given at the end of this section. The author of the reference book has selected from values given in one or more chemical or

<sup>\*</sup> A more precise estimate of the uncertainty would be the sample deviation (see Appendix A). If you don't understand why the numbers are rounded off as shown, review the section on significant figures in your text book.

related journals. We hope that he used good judgment and that no experimental (or typographical!) errors went undetected. For greater reliability we should check two or more sources or the original report. Always cite properly the source of your reference value.

#### **Evaluation of Experimental Results**

The most reliable method for identifying a compound is to compare, in side-by-side tests, samples of the unknown compound and of the suspected compound. But this is not always practicable, and even if it were, it would remove much of the necessity of making decisions—and learning to use good judgment is one of the key reasons for running unknowns. Therefore, we will not have samples of knowns available, at least not until you have made your identification. However, the compound benzene ( $C_6H_6$ ) has properties quite similar to most of the liquid samples, so it can be used to evaluate each procedure in terms of the accuracy and precision possible.\*

#### Reporting the Results

The ultimate goal of these measurements is the identification of the substance. The more immediate—and more important—goal is gaining experience in making the measurements and in interpreting the results. Therefore, your report will be judged on how well each measurement is made (accuracy and precision) and how well you discuss the identification of the compound—not whether you are able to make the correct assignment. Unless other directions are given, prepare a table of results

TABLE I-1. Abbreviated Sample Report Form for Identification of the Unknown Liquid Sample

	Identification: <i>n</i> -heptane		
Sample No. 16 Property	Experimental Value	Reference Value	Error
Molar Mass	$76~\pm~20~\mathrm{g/mole}$	100 g/mole*	(—)34 g/mole <sup>†</sup> (—)34%
Boiling Point	$98.2 \pm 0.4$ °C	98.42°C*	$(-)0.2^{\circ}C^{\dagger}$
Density	0.6814 g/ml at 24°C	0.68376 g/ml 20°C*	(-)0.0024 g/ml (-)0.4% <sup>†</sup>

<sup>\*</sup>Handbook of Chemistry and Physics, 48th ed., p. Bl, 415, C. D. Hodgman, Ed., Chemical Rubber Publ. Co., Cleveland, Ohio (1967).

<sup>†(</sup>A discussion of each of these errors should now be presented, with an evaluation of the likely sources of error and of the uncertainty estimates if not discussed in the individual experiments.) Note that since temperature is on the Celsius scale, no per cent error can be given (if you don't see why this is so, consider an error in the freezing point of water or in the boiling point of liquid nitrogen).

<sup>\*</sup>Benzene is an abundant, important liquid. As a result it is available in high purity at low cost. Its properties have been very carefully studied by many scientists, so it is an ideal reference or standard compound for these experiments.