Experiments in Physical Chemistry

Carl W. Garland
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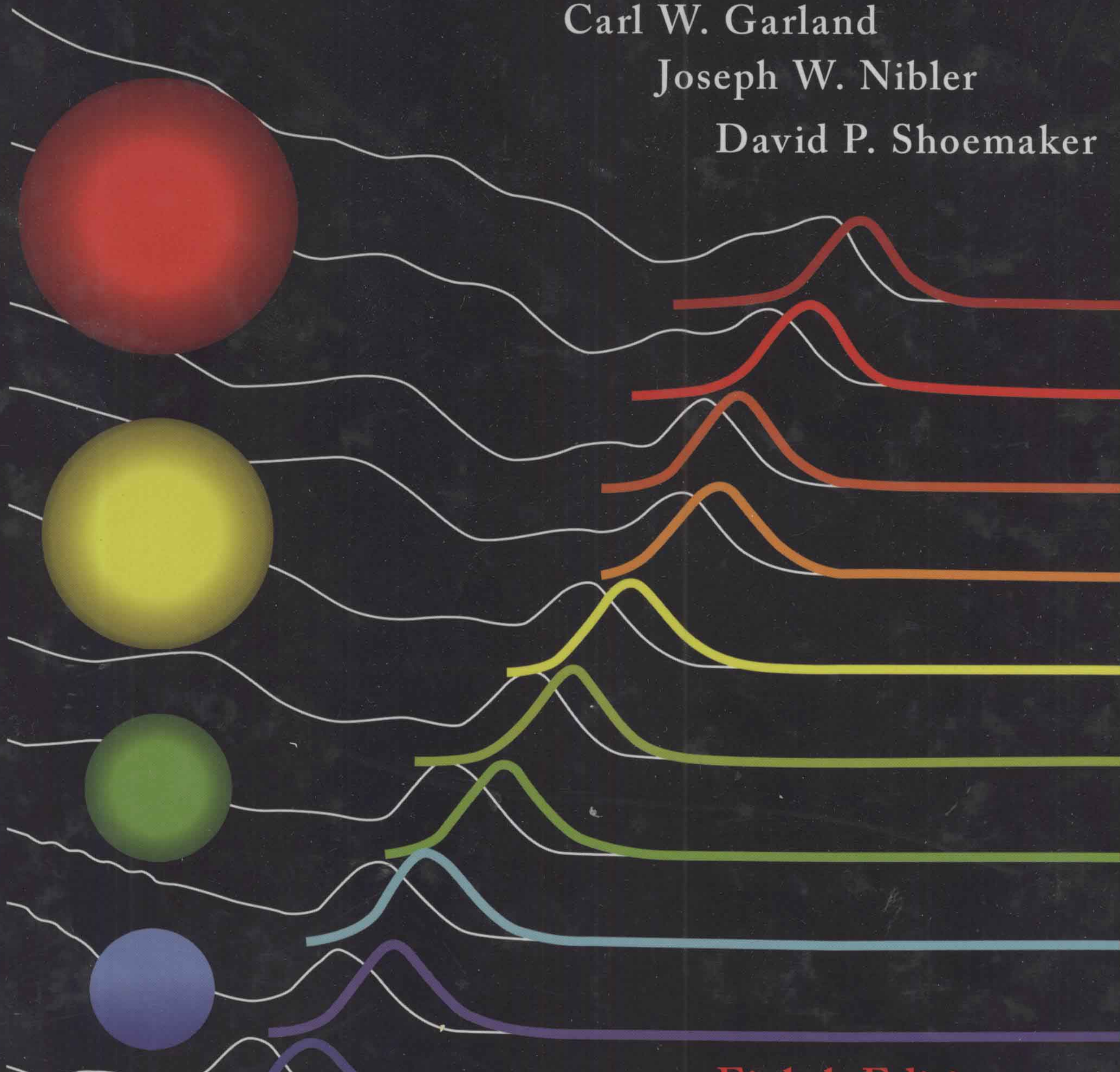

Eighth Edition

EXPERIMENTS IN PHYSICAL CHEMISTRY

EIGHTH EDITION

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EXPERIMENTS IN PHYSICAL CHEMISTRY, EIGHTH EDITION

Published by McGraw-Hill, a business unit of The McGraw-Hill Companies, Inc., 1221 Avenue of the Americas, New York, NY 10020.

This book is printed on recycled, acid-free paper containing 10% postconsumer waste.

1 2 3 4 5 6 7 8 9 0 QPD/QPD 0 9 8

ISBN 978–0–07–282842–9
MHID 0–07–282842–0

Publisher: *Thomas Timp*
Senior Sponsoring Editor: *Tamara L. Hodge*
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Associate Design Coordinator: *Brenda A. Rolwes*
Cover Designer: *Studio Montage, St. Louis, Missouri*
Compositor: *Laserwords Private Limited*
Typeface: *10/12 Times Roman*
Printer: *Quebecor World Dubuque, IA*

Cover description: The figure depicts the absorption and emission spectra of CdSe nanocrystals, whose color is a sensitive function of size. The figure is based on spectral data provided by NN-Labs. The authors thank both NN-Labs and Evident Technologies for CdSe samples used in the development of the quantum dot experiment.

Library of Congress Cataloging-in-Publication Data

Garland, Carl W.
Experiments in physical chemistry.—8th ed. / Carl W. Garland, Joseph W. Nibler, David P. Shoemaker.
p. cm.
Includes index.
ISBN 978–0–07–282842–9—ISBN 0–07–282842–0 (hard copy : acid-free paper)
1. Chemistry, Physical and theoretical—Laboratory manuals. I. Nibler, Joseph W.
II. Shoemaker, David P. III. Title.
QD457 .S56 2009
541.078—dc22

2007043492

www.mhhe.com

PHYSICAL CONSTANTS AND CONVERSION FACTORS[a]

1. Values of Some Fundamental Constants

Speed of light in vacuum	c	299792458 $m\ s^{-1}$ (defined)
Permeability of vacuum	μ_0	$4\pi \times 10^{-7} = 1.25663706 \times 10^{-6}$ $N\ A^{-2}$ (defined)
Permittivity of vacuum	ε_0	$(\mu_0 c^2)^{-1} = 8.8541878 \times 10^{-12}$ $F\ m^{-1}$ (defined)[b]
Elementary charge	e	$1.6021765 \times 10^{-19}$ C
Planck constant	h	6.626069×10^{-34} J s
Avogadro constant	N_0	6.022142×10^{23} mol^{-1}
Rest mass of electron	m_e	9.109383×10^{-31} kg
Rest mass of proton	m_p	1.672622×10^{-27} kg
Atomic mass unit (amu)	m_u	1.660539×10^{-27} kg
Faraday constant	$\mathcal{F}$	96485.34 C mol^{-1}
Bohr radius	a_0	$5.2917721 \times 10^{-11}$ m
Bohr magneton	μ_B	9.27401×10^{-24} J T^{-1}
Nuclear magneton	μ_N	5.050783×10^{-27} J T^{-1}
Rydberg constant	$\mathcal{R}_\infty$	10973731.57 m^{-1}
Hartree	E_h	4.359744×10^{-18} J
Gas constant	R	8.31447 J K^{-1} mol^{-1}
Boltzmann constant	k	1.38065×10^{-23} J K^{-1}
Gravitational constant	G	6.674×10^{-11} $m^3\ kg^{-1}\ s^{-2}$
Standard gravity	g	9.80665 $m\ s^{-2}$ (defined)
Triple point of water	T_{tp}	273.16 K = 0.01° Celsius (defined)
Normal atmosphere	p_0	101325 Pa (defined)
Standard volume	V_0	
V_0(101325 Pa ≡ 1 atm, 273.15 K)		22.4140 L mol^{-1}
(10^5 Pa = 1 bar, 273.15 K)		22.7110 L mol^{-1}

2. Conversion of Units (see Appendix B for SI units)

Angstrom (Å)	1 Å = 10^{-10} m = 0.1 nm
Micron (μ)	1 μ = 1μm = 10^{-6} m
Inch (in.) ≡ $\frac{1}{12}$ foot (ft)	1 inch = 2.54×10^{-2} m
Liter (L)	1 L = 1 dm^3 = 10^{-3} m^3 (defined)
Pound (lb) ≡ 16 ounces (oz)	1 lb = 0.45359237 kg
Dyne (dyn = g cm s^{-2})	1 dyn = 10^{-5} N
Erg (erg = g cm^2 s^{-2})	1 erg = 10^{-7} J
Thermochemical calorie (cal)	1 cal ≡ 4.184 J (defined)
Liter-atmosphere (L atm)	1 L atm ≡ 101.325 J (defined)
Electron volt (eV)	1 eV = 1.60218×10^{-19} J = 96.4853 kJ mol^{-1}
Wavenumber (cm^{-1}) energy	1 cm^{-1} × hc = 1.98645×10^{-23} J = 11.9627 J mol^{-1}
Bar (bar)	1 bar ≡ 10^5 Pa = 0.986923 atm (defined)
Torr (Torr)	1 Torr ≡ 1/760 atm ≃ 1/750.06 bar
Pounds per square inch (psi)	1 psi = 6.894757×10^3 Pa = 0.06895 bar
Poise (P)	1 P = 10^{-1} Pa s
Stokes (St)	1 St = 10^{-4} m^2 s^{-1}
Celsius temperature t(°C)	t(°C) ≡ T(K) − 273.15 (defined)
Rem ≃ roentgen (r)	1 rem ≃ 0.01 J kg^{-1}
Emu of charge (emu)	1 emu = 10 C
Esu of charge (esu)[c]	1 esu = 10 C/|c| = 3.33564×10^{-10} C
Debye (D)	1 D ≡ 10^{-18} esu cm = 3.33564×10^{-30} C m
Esu polarizability α ("cm^3")	1 cm^3 × $4\pi\varepsilon_0$ = 1.11265×10^{-16} F m^2
Esu polarization P (esu cm^{-2})	4π esu cm^{-2} = 4.19169×10^{-7} C m^{-2}
Gauss (G)	1 G = 10^{-4} T
Oersted (Oe)	1 Oe = 10^3 A m^{-1}
Plane angle (deg = 60 min = 3600 sec)	1 deg = (π/180) rad

3. Energy Conversion Table

Three unusual but convenient "energy" quantities are temperature (K) representing the molecular energy kT at a given T, wavenumber (cm^{-1}) representing the molecular energy $hc\tilde{\nu}$ at a given frequency $\tilde{\nu}$ in cm^{-1} units (where c is the speed of light in cm s^{-1}), and electron volt (eV). All of these molecular energies are changed to molar energies on multiplication by Avogadro's number.

	K	**cm^{-1}**	**kJ mol^{-1}**	**kcal mol^{-1}**	**eV**
1 K =	1	0.69504	8.31451×10^{-3}	1.98722×10^{-3}	8.61739×10^{-5}
1 cm^{-1} =	1.43877	1	$1.19627 - 10^{-2}$	2.85914×10^{-3}	1.23984×10^{-4}
1 kJ mol^{-1} =	1.20272×10^{2}	8.35935×10^{1}	1	0.23901	1.03643×10^{-2}
1 kcal mol^{-1} =	5.03217×10^{2}	3.49755×10^{2}	4.18400	1	4.33641×10^{-2}
1 eV =	1.16044×10^{4}	8.06554×10^{3}	9.64853×10^{1}	2.30605×10^{1}	1

[a] These are "2002 CODATA recommended values"; see *Rev. Mod. Phys.* **77,** 1 (2005). The most recent values of physical constants can be obtained on the National Institute of Standards and Technology (NIST) website (http://physics.nist.gov/constants).

[b] $F\ m^{-1} \equiv C^2\ m^{-1}\ J^{-1} \equiv C\ m^{-1}\ V^{-1}$.

[c] Note that $|c|$ is the *pure number* 29979245800 (i.e., it equals the magnitude of the speed of light in vacuum when it is expressed in cm s^{-1} units).

I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of Science, whatever the matter may be.

Sir William Thomson
(Lord Kelvin)

It is much easier to make measurements than to know exactly what you are measuring.

J. W. N. Sullivan

It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories, instead of theories to suit facts.

Sir Arthur Conan Doyle

It is also a good rule not to put too much confidence in experimental results until they have been confirmed by theory.

Sir Arthur Eddington

Preface

This book is designed for use in a junior-level laboratory course in physical chemistry. It is assumed that the student will be taking concurrently (or has taken previously) a lecture course in physical chemistry. The book contains 48 selected experiments, which have been tested by extensive use.

Three of the experiments are new, and all of these involve optical measurements. One concerns a study of the birefringence of a liquid crystal to determine the evolution of nematic order near the nematic-isotropic phase transition (Exp. 15). The second is a study of the dynamic light scattering from an aqueous dispersion of polystyrene spheres in order to determine their particle size (Exp. 33). The third is a study of the absorption and fluorescence spectra of CdSe nanocrystals with an analysis based on predictions from a quantum model (Exp. 45). To conserve space, three experiments that appeared in the seventh edition have been deleted. These are the binary solid-liquid phase diagram, osmotic pressure, and single-crystal x-ray diffraction. All the other experiments from the seventh edition have been reviewed, and in some cases small changes have been made to either the theory or the experimental procedures. The most extensive of such changes occur in Experiments 1 (gas thermometry) and 4 (viscosity of gases), where the apparatus and procedure have been changed to eliminate the use of mercury. In numerous other experiments, mercury manometers and mercury-in-glass thermometers have been replaced by direct reading pressure gauges and temperature sensors.

Experiments. The 48 experiments provide a balance between traditional and modern topics in physical chemistry, with most of the classical topics in Chapters IV–X (Exps. 1–24) and most of the modern topics in Chapters XI–XV (Exps. 25–48). These experiments are not concerned primarily with "techniques" per se or with the analytical applications of physical chemistry. We believe that an experimental physical chemistry course should serve a dual purpose: (1) to illustrate and test theoretical principles, and (2) to develop a research orientation by providing basic experience with physical measurements that yield quantitative results of important chemical interest.

Each experiment is accompanied by a theoretical development in sufficient detail to provide a clear understanding of the method to be used, the calculations required, and the significance of the final results. The depth of coverage is frequently greater than that which is available in introductory physical chemistry textbooks. Experimental procedures are described in considerable detail as an aid to the efficient use of laboratory time and teaching staff. Emphasis is given to the reasons behind the design and procedure for each experiment, so that the student can learn the general principles of a variety of experimental techniques. Stimulation of individual resourcefulness through the use of special projects or variations on existing experiments is also desirable. We strongly urge that on some occasions the experiments presented here should be used as points of departure for work of a more independent nature.

Introductory and background material. In addition to the experiments themselves, nine chapters contain material of a general nature. These chapters should be useful not only in an undergraduate laboratory course but also in special-project work, thesis research, and a broad range of general research in chemistry.

The first three chapters provide material that is valuable for all experimental work in physical chemistry, and it is recommended that these be read before beginning any laboratory work. Chapter I contains a wide range of introductory material, including advice on the preparation of laboratory reports, and Chapter II covers techniques for data analysis and the assessment of error limits. Chapter III, on the use of computer software and selected aspects of computer interfacing, has been revised and updated. The software aspect emphasizes the application of spreadsheets for the recording, plotting, and least-squares fitting of experimental data. Also discussed, and illustrated with examples, are more sophisticated programs such as Mathcad and Mathematica, along with the program Gaussian, which can be used to obtain molecular structures and properties from ab-initio quantum mechanics. Relevant theoretical calculations using such programs are suggested at the end of a number of experiments.

Chapters XVI–XX deal with basic experimental methods of broad value in many types of experimental work—electronic measurements, temperature measurement and control, vacuum techniques, diverse instruments that are widely used, and miscellaneous laboratory procedures. These chapters have been revised and updated in various ways. In the case of Chapters XVI and XVIII, the text has also been shortened from that which appeared in the seventh edition. Finally, Chapter XXI presents a thorough discussion of least-squares fitting procedures.

References cited at the end of each experiment and each of the general chapters have been updated. In cases where no new literature source could be found that covers a given topic as well as the source cited in the seventh edition, the original citation has been retained, since most libraries have available copies of older books and monographs.

In the development of the new experiments in this edition, we acknowledge expert advice from Prof. M. Bawendi (MIT), Prof. J. Thoen (Katholieke Universiteit Leuven), and Dr. B. Weiner (Brookhaven Instruments) as well as the assistance of faculty, teaching assistants, and undergraduate students (especially Nicole Baker, Matthew Martin, Colin Shear, Brain Theobald, and Robert Zaworski) at Oregon State University. Helpful comments also have come from a number of reviewers and from those who have used this book at other universities, and for these we are very appreciative. We encourage and welcome feedback from all who use this book, either as students or instructors.

Finally, we wish to acknowledge the suberb proofreading effort of Janelle Pregler, who has made the production of this edition go very smoothly.

Carl W. Garland
Joseph W. Nibler

Contents

I Introduction

Physical chemistry deals with the physical principles underlying the properties of chemical substances. Like other branches of physical science, it contains a body of theory that has stood the test of experiment and is continually growing as a result of new experiments. In order to learn physical chemistry, you must become familiar with the experimental foundations on which the theoretical principles are based. Indeed, in many cases, the ability to apply the principles usefully requires an intimate knowledge of those methods and practical arts that are called "experimental technique."

For this reason, lecture courses in physical chemistry are usually accompanied by a program of laboratory work. Such experimental work should not just demonstrate established principles but should also develop research aptitudes by providing experience with the kind of measurements that can yield important new results. This book attempts to achieve that goal. Its aim is to provide a clear understanding of the principles of important experimental methods, the design of basic apparatus, the planning of experimental procedures, and the significance of the final results. In short, the aim is to help you become a productive research scientist.

Severe limitations of time and equipment must be faced in presenting a set of experiments as the basis of a laboratory course that will provide a reasonably broad coverage of the wide and varied field of physical chemistry. Although high-precision research measurements would require refinements in the methods described here and would often require more sophisticated and more elaborate equipment, each experiment in this book is designed so that meaningful results of reasonable accuracy can be obtained.

In the beginning, you will probably not have the skill and the time to plan detailed experimental procedures. Moreover, the trial-and-error method is not necessarily the best way to learn good experimental technique. Laboratory skills are developed slowly during a sort of apprenticeship. To enable you to make efficient use of available time, both the apparatus and the procedure for these experiments are described in considerable detail. *You should keep in mind the importance of understanding why the experiment is done in the way described.* This understanding is a vital part of the experience necessary for planning special or advanced experiments of a research character. As you become more experienced, it is desirable that there be opportunities to plan more of your own procedure. This can easily be accomplished by introducing variations in the experiments described here. A change in the chemical system to be studied, the use of equipment that purposefully differs from that described, or the choice of a different method for studying the same system will require modifications of the procedure. Finally, at the end of the course, it is recommended that, if possible, you carry out a special project that is completely independent of the experiments described in this book. A brief description of such special projects is given at the end of this chapter.

In addition to a general knowledge of laboratory techniques, creative research work requires the ability to apply two different kinds of theory. Many an experimental method is based on a special phenomenological theory of its own; this must be well understood in order to design the experiment properly and in order to calculate the desired physical property from the observed raw data. Once the desired result has been obtained, it is necessary to understand its significance and its interrelationship with other known facts. This requires a sound knowledge of the fundamental theories of physical chemistry (e.g., thermodynamics, statistical mechanics, quantum mechanics, and kinetics). Considerable emphasis has been placed on both kinds of theory in this book.

In the final analysis, however, research ability cannot be learned merely by performing experiments described in a textbook; it has to be acquired through contact with inspired teachers and through the accumulation of considerable experience. The goal of this book is to provide a solid frame of reference for future growth.

ORGANIZATION OF THE BOOK

Before undertaking any experiments, you should become familiar with the overall structure of this book. The material is divided into three blocks: essential introductory material is given in Chapters I–III, the experiments are given in Chapters IV–XV, and extensive reference material is given in Chapters XVI–XXI. The heart of the book is the collection of experiments, which are designed to provide significant "hands-on" laboratory experience. The general chapters present basic background information of value both for undergraduate laboratory courses and for independent research work.

INTRODUCTORY ESSENTIALS

Chapter I provides a general introduction to experimental work in physical chemistry. This includes advice on how to prepare for and carry out an experiment, how to record data in a laboratory notebook, and how to report results. Chapter II describes mathematical procedures for analyzing data. Part A of this chapter deals with calculations and the presentation of numerical results, and Part B is concerned with the quantitative assessment of random errors and their effect on the uncertainty in the final result. Chapter III deals with several types of computer hardware and software commonly used in physical chemistry. Commercial products for digital measurement of temperature, voltage, and pressure are now readily available, and the need for machine-level programming has been greatly reduced. Examples of some data collection systems are briefly described. Emphasis is placed on the use of spreadsheets, since these are very convenient for data handling, analysis, and presentation in both tabular and graphic forms. All three chapters should be read at the very beginning, since they provide general information of value for all experiments in physical chemistry.

It is important to mention briefly the issues of notation and units. A glossary of frequently used symbols is given in Appendix A. Note that the definition of thermodynamic work used here is the work done *on* a system (e.g., $dw = -p\,dV$). As a result, the first law of thermodynamics has the form $dE = dq + dw$. Note also that E is used for the thermodynamic internal energy and U for the potential energy instead of the IUPAC choices of

U and V respectively. Système International (SI) units, described in Appendix B, are used extensively but not slavishly. Chemically convenient quantities such as the gram (g), cubic centimeter (cm^3), and liter ($L \equiv dm^3 = 10^3\ cm^3$) are still used where useful—densities in $g\ cm^{-3}$, concentrations in $mol\ L^{-1}$, molar masses in g. Conversions of such quantities into their SI equivalents is trivially easy. The situation with pressure is not so simple, since the SI pascal is a very awkward unit. Throughout the text, both bar and atmosphere are used. Generally bar ($\equiv 10^5$ Pa) is used when a precisely measured pressure is involved, and atmosphere ($\equiv 760$ Torr $\equiv 1.01325 \times 10^5$ Pa) is used to describe casually the ambient air pressure, which is usually closer to 1 atm than to 1 bar. Standard states for all chemical substances are officially defined at a pressure of 1 bar; normal boiling points for liquids are still understood to refer to 1-atm values. The conversion factors given inside the front cover will help in coping with non-SI pressures.

EXPERIMENTS

Chapters IV–XV contain the descriptions of the experiments, which are numbered 1 to 48. In addition, Chapters V and VI each contain some separate introductory material that is pertinent to all the experiments in the given chapter. Each figure, equation, and table in a given experiment is identified by a single number: e.g., Fig. 1, Eq. (8), Table 2. For cross references, double numbering is used: e.g., Fig. 38-1 refers to Fig. 1 in Exp. 38 and Eq. (V-8) refers to Eq. (8) in the introductory part of Chapter V.

Every attempt has been made to write each experiment in sufficient detail that it can be intelligently performed without the necessity of extensive outside reading. However, it is assumed that the student will refer frequently to a standard textbook in physical chemistry for any necessary review of elementary theory. Literature sources are cited explicitly for those topics that are beyond the scope of a typical undergraduate textbook, and these numbered references are listed together at the end of each experiment. In addition, a selected list of reading pertinent to the general topic of each experiment is given under the heading General Reading. It is hoped that you will do some reading in these books and journal articles, since this is an excellent way to broaden your scientific background.

A complete and very detailed list of equipment and chemicals is given at the end of each experiment.[1] The list is divided into two sections: Those items listed in the first paragraph are required for the exclusive use of a single team; those in the second paragraph are available for the common use of several teams. It is assumed that standardized stock solutions will be made up in advance and will be available for the students' use. The quantities indicated in parentheses† are for the use of the instructor and do *not* indicate the amounts of each chemical to be taken by a single team. In addition to the items included in these apparatus lists, it is assumed that the laboratory is equipped with analytical balances, a supply of distilled or deionized water, and a barometer as well as gas, water, and 110-V ac power lines. Also desirable, but not absolutely necessary, are gas-handling lines and a rough vacuum line.

BASIC REFERENCE MATERIAL

Chapters XVI–XX contain a variety of information on experimental procedures and devices. This includes the theory and practice of many types of electrical measurements,

†On the basis of the authors' experience, it is necessary to make available these amounts for each team that will do the experiment. They are scaled up from the amounts stated in the experiment to provide for possible wastage and to give a generous safety factor. It is hoped that they will be useful as a rough guide the first time an experiment is given.

the principles and devices used in measurement and control of temperature, vacuum techniques, detailed descriptions of frequently used instruments, and a description of many miscellaneous procedures such as gas handling and the construction of equipment.

Chapter XXI provides an introduction to least-squares fitting procedures and a discussion of how to assess the magnitude of random errors and how to judge the quality of any given fit to a set of data points.

PREPARATION FOR AN EXPERIMENT

Although most of the experiments in this book can be performed by a single person, they have been written under the assumption that a pair of students will work together as a team. Such teamwork is advantageous, since it provides an opportunity for valuable discussion of the experiment between partners. The amount of experimental work to be assigned will be based on the amount of laboratory time available for each experiment. Many of the experiments can be completed in full during a single 4-hour laboratory period. Many others are designed for 6 to 8 hours of laboratory work but may be abridged so that meaningful results can be obtained in a single 4-hour period. Some of the experiments require at least 6 hours and should not be attempted in a shorter time (in particular, Exps. 22, 24, 26, 28).

Before you arrive in the laboratory to perform a given experiment, it is essential that you study the experiment carefully, with special emphasis on the method, the apparatus design, and the procedure. It will usually be necessary to make changes in the procedure whenever the apparatus to be used or the system to be studied differs from that described in this book. Planning such changes or even successfully carrying out the experiment as described requires a clear understanding of the experimental method.

Experimental work in physical chemistry requires many complex and expensive pieces of apparatus; many of these have been constructed specially and cannot readily be replaced. Each team should accept responsibility for its equipment and should *check it over carefully before starting an experiment.*

EXECUTION OF AN EXPERIMENT

Making experimental measurements is like playing the piano or singing a song. You need some natural ability—bright students with no innate experimental skills often end up as theorists—but most people can learn to execute an experiment and have a lot of fun doing it. Like playing the piano and singing, you get better with practice. It is also useful to start with something reasonably simple and build up experience with a variety of techniques before taking on a really tough experiment.

GENERAL ADVICE

Some of the practice involved in developing experimental skills occurs within a single experiment and some occurs as the superposition of many experiments. In carrying out any given experiment, it may be necessary to make several "runs", i.e., sets of measurements. On some occasions, it is worthwhile to carry out a practice run as a warmup test of the apparatus and your own skills. Such a practice run can be made with a known standard material or standard set of conditions, or it can be a first try at a real set of measurements to get a feel for the operation of the equipment.