

$$PV = nRT$$

Problems in Chemistry

second edition,
revised and expanded

Henry O. Daley, Jr.
and
Robert F. O'Malley

Problems in Chemistry

**Second Edition,
Revised and Expanded**

Henry O. Daley, Jr.

*Bridgewater State College
Bridgewater, Massachusetts*

Robert F. O'Malley

*Boston College
Chestnut Hill, Massachusetts*

Marcel Dekker, Inc.

New York and Basel

Library of Congress Cataloging in Publication Data

Daley, Henry O., Jr.

Problems in chemistry.

Includes index.

1. Chemistry--Problems, exercises, etc. I. O'Malley, Robert F. II. Title.

QD42.D26 1988 540'.76 87-33165

ISBN 0-8247-7826-X

Copyright ©1988 by MARCEL DEKKER, INC. All Rights Reserved

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Problems in Chemistry

UNDERGRADUATE CHEMISTRY

A Series of Textbooks

edited by

J. J. Lagowski

*Department of Chemistry
The University of Texas at Austin*

- Volume 1:** Modern Inorganic Chemistry, *J. J. Lagowski*
- Volume 2:** Modern Chemical Analysis and Instrumentation,
Harold F. Walton and Jorge Reyes
- Volume 3:** Problems in Chemistry, Second Edition,
Henry O. Daley, Jr. and Robert F. O'Malley
- Volume 4:** Principles of Colloid and Surface Chemistry,
Paul C. Hiemenz
- Volume 5:** Principles of Solution and Solubility, *Kozo Shinoda*,
translated in collaboration with Paul Becher
- Volume 6:** Physical Chemistry: A Step-by-Step Approach,
M. K. Kemp
- Volume 7:** Numerical Methods in Chemistry,
K. Jeffrey Johnson
- Volume 8:** Polymer Chemistry: An Introduction, *Raymond B. Seymour and Charles E. Carraher, Jr.*
- Volume 9:** Principles of Colloid and Surface Chemistry,
Second Edition, Revised and Expanded,
Paul C. Hiemenz
- Volume 10:** Problems in Chemistry, Second Edition, Revised
and Expanded, *Henry O. Daley, Jr. and Robert
F. O'Malley*
- Volume 11:** Polymer Chemistry: An Introduction, Second Edition,
Raymond B. Seymour and Charles E. Carraher, Jr.

TO THE INSTRUCTOR

There have been many changes in the teaching of freshman chemistry since the publication of the last edition of this book—in particular, the full use of the SI system of units, the introduction of the unit factor method of solving problems, the use of the terms *atomic* and *molecular mass* in place of *weight*, and the elimination of the term *gram-atom*. All of these changes are reflected in this new edition.

In addition, approximately 200 new sample problems and supplementary problems have been added to the chapters. The section on the use of the slide rule has been replaced with one on the use of calculators and computers. Included in this section is a discussion of the problems associated with significant figures while using computers and calculators and those problems that can arise in switching between $\ln e$ and the exponent e . A series of useful programs written in general BASIC is included; they can be used on any microcomputer. These programs illustrate the use of computers in solving quadratic equations, approximation methods in solving equations, and nonweighted linear least-squares analysis of data.

As with the first edition, we have chosen our problems with two fundamental concepts in mind: 1) to show students that much of what they learn in freshman chemistry is being used by chemists in their careers, and 2) to encourage students to read the chemical literature. It is important for a student to understand that what is done in the laboratory and what is covered in lectures are related. Whether the course is intended for chemistry, biology, or nonscience majors, students should learn that the knowledge they are acquiring in the lecture part of the course is developed or verified by laboratory experiments.

The interpretation of the results of laboratory experiments involves a chemist in one of the most basic everyday activities associated with chemistry, that is, problem solving. Chemistry is by its very nature a problem-solving-oriented course. All too often, this aspect of chemistry is overlooked by students. Most students require practice in solving problems. Today, students are particularly weak in solving word problems. The more problems a student solves, the more proficient he or she becomes in this aspect of chemistry.

It is the purpose of this book not only to provide the beginning chemistry student with a relatively large number of problems that illustrate chemical principles, but also to facilitate his acquisition of problem-solving skills by helping him see that the skills he acquires even at the introductory level are relevant to the activities of practicing chemists. The hope is that the student will come to see that he is doing what is being done, not that he is merely repeating what has been done. To this end, the problems in the present text are based, wherever possible, on experimental results obtained by chemists, and the corresponding references are cited. The problems and techniques for solving them are intended to reflect the real features of one important aspect of chemistry.

Besides showing that problem solving even at the introductory level is directly relevant to the practice of chemistry, there are other aims implicit in the general approach taken in this book. One of the most important is to illustrate the use of significant figures in a practical way. It is one thing to learn that significant figures are important because one must learn them in order to pass a test. It is another to learn from example that they are constantly used by chemists and therefore are important for learning chemistry. Consistent citation of references should also provide an indirect introduction to the chemical literature (the instructor, of course, also has the option of using these references to introduce students directly to the literature). Finally, it will be no small gain if the student comes to appreciate that chemical knowledge represents the accumulation of results from the activities of a great many people, each one making a contribution, however small, to the enterprise called chemistry.

A brief word concerning the use of this book. Although it is intended primarily as a self-study supplement and answers to problems are given in an appendix, it can also be used by the instructor as a source of test problems and as a supplementary text. The first 18 chapters contain about 860 problems plus an additional 240 or so example problems with solutions worked out.

The problems at the end of these chapters are divided into two sections to facilitate the choosing of representative problems on the material covered in these chapters. Each section contains a complete selection of problems arranged in the same order as that of the corresponding material in the chapter. An additional 200 problems in Chapter 19 are grouped to correspond to standard organization of the descriptive portion of the introductory course. Since most of the earlier literature did not use the modern metric system of units, the original data are retained in the problems, whereas the answers are given in SI units.

In preparing this new edition, one thing became obvious in the literature, that is, many of the experiments that gave useful data for problems are rarely carried out today. Instrumentation is the keyword for most laboratory experiments of the present. The mass spectrometer is used to determine molecular mass rather than freezing point depression. In addition, even though data such as percent composition may be listed for a new compound, the data used to calculate the percent composition and the method used are rarely given. Despite this, we have found sufficient material to introduce new problems in just about every chapter except Chapter 19. We chose not to add any new additional problems to this chapter. Some new and interesting compounds such as AgF_3 have been prepared and data were available for use in the chapter on empirical formulas.

Although there are many people who have been helpful in developing this second edition, we would like to thank in particular Dr. Vahe Marganian of Bridgewater State College for the many discussions we have had with him. We would also like to thank Rosemary Daley, the wife of one of the authors, for the proof-reading she has done, and the very cooperative and fine editors from Marcel Dekker, including Sandra Beberman, Henry Boehm, and especially Patricia Brecht, without whose help this revision could not have been accomplished.

Henry O. Daley, Jr.
Robert F. O'Malley

TO THE STUDENT

Solving problems by mathematical manipulation is an essential, daily experience of chemists. Students who seek even an elementary knowledge of chemistry must learn to solve a variety of problems. If for no other reason, then, a knowledge of the chemical principles and the mathematical manipulations necessary to solve typical chemical problems is important.

Students almost universally believe that they must *understand* the principles of chemistry before they can apply them to the solution of problems. Many students fail to realize that it is also necessary to *remember* statements of principles, definitions of terms, and many facts of a descriptive nature. The importance of a thorough understanding of the laws and theories of chemistry is not to be underestimated, but the need to *commit* to *memory* a certain body of information is equally important. A student may understand the concepts of an atom, molecule, mole, equivalent mass, and so on as he reads about them in the text, but this understanding is not enough if the student cannot recall the precise definition of the terms when he attempts to apply them to the solution of a problem.

Before trying to solve problems, *study* the relevant sections of the text and class notes. *Memorize* the precise meaning of important terms and statements of principles. The first step toward the successful solution of a problem is to read very carefully the statement of the problem. Next, reflect on the meaning of the terms and *determine exactly what is asked for by the problem*. (This point cannot be overemphasized. Probably the greatest source of confusion in any kind of problem solving stems from the failure to determine what is asked for. Obviously, we need to "understand" the problem. But we often forget that understanding a problem is above all a matter of knowing what kind of

answer we are looking for.) Once you have determined both what the problem asks for and what principles are required to provide the appropriate kind of answer, you can proceed in an orderly fashion to perform the necessary mathematical manipulations.

At this point, the most important advice is the following: *Be neat*. Fewer errors and time saved are the rewards of a neat, orderly approach to the solution of a problem. Write as legibly as you can and leave space between the steps.

Example

A compound containing 5.28% silicon and 94.66% iodine was prepared at M.I.T. Calculate the empirical formula of the compound.

[W. C. Schumb and D. W. Breck, *J. Am. Chem. Soc.*, 74, 1758 (1952)]

$$\begin{aligned}
 \frac{5.28}{28.1} &= 0.188 \text{ mol Si}/100 \text{ g} \\
 \frac{9}{9/\text{mol}} &= \cancel{9} \times \frac{\text{mol}}{\cancel{9}} = \text{mol} \\
 \frac{94.7}{127} &= 0.745 \text{ mol I}/100 \text{ g} \\
 \frac{0.745}{0.188} &= 3.97 \\
 \frac{\text{mol I}}{\text{mol Si}} & \\
 \therefore \text{Si I}_4 &\text{ is the empirical formula.}
 \end{aligned}$$

If the proper procedure for solving the problem does not occur to you, read the pertinent sections in your text and notes again. Reconsider very carefully the definition of terms and the statements of principles. Very often, the difficulty is due to an inexact definition or failure to consider all that is implied in a definition or principle.

Although students study to acquire knowledge of a subject for many different reasons, they must all face the practical requirements of passing examinations. To prepare for examinations

they must *learn* or memorize definitions and principles, and they must *practice* the application of what they have learned by answering questions and solving problems similar to those that appear on examinations. This book is intended to assist the student in his *active preparation* for examinations in chemistry.

CONTENTS

To the Instructor	iii
To the Student	vii
Chapter 1 Properties and Their Measurements	1
1-1 Properties	1
1-2 Extensive and Intensive Properties	1
1-3 Units of Measurement	1
1-4 The Metric System	2
1-5 Density and Specific Gravity	3
1-6 Accuracy and Precision	5
1-7 Significant Figures	5
1-8 Significant Figures in Calculations	6
1-9 Addition and Subtraction	7
1-10 Multiplication and Division	8
1-11 Units in Calculations	8
1-12 Conversion of Units	10
1-13 Temperature	11
1-14 Conversion of Temperatures	12
1-15 Specific Heat	13
Problems	15
Supplementary Problems	19
Chapter 2 Elements, Atoms, and Molecules	23
2-1 Atoms	23
2-2 Atomic Mass	23
2-3 Molecules	24
2-4 Molecular Mass	24
2-5 The Mole	24
2-6 Symbols	26
2-7 Determination of Atomic Masses	27

2-8	Law of Definite Proportions	28
2-9	Atomic Masses from Combining Ratios	30
	Problems	32
Chapter 3	Percent Composition, Empirical and Molecular Formulas	37
3-1	Molecular Masses	37
3-2	The Mole	37
3-3	Formulas	39
3-4	Determination of Formula	40
3-5	Composition from Formulas	40
3-6	Formulas from Composition	42
	Problems	45
	Supplementary Problems	48
Chapter 4	Chemical Equations	55
4-1	Equations	55
4-2	Balancing Equations	56
4-3	Types of Chemical Equations	57
4-4	Rules for Balancing Simple Equations	58
4-5	Balancing Redox Equations	59
4-6	Oxidation Number Method	59
4-7	Quantitative Aspects of Chemical Reactions	62
4-8	Theoretical Yield or Calculated Yield	62
4-9	Actual Yield, Percent Yield	67
4-10	Limiting Reactant	68
	Problems	69
	Supplementary Problems	76
Chapter 5	Gases	83
5-1	Boyle's Law	83
5-2	Gay-Lussac's Law (Charles' Law)	84
5-3	Equation of State	86
5-4	Quantity of a Gas	88
5-5	Evaluation of the Gas Constant	88
5-6	Molecular Masses of Gases	89
5-7	Gas Density and Ideal-Gas Equation	91
5-8	Dalton's Law of Partial Pressures	92
5-9	Gay-Lussac's Law of Combining Volumes	93
5-10	Molar Volume	93
5-11	Graham's Law of Diffusion (Effusion)	94
5-12	Behavior of Real Gases	96
5-13	Equations of State for Real Gases	96
	Problems	97
	Supplementary Problems	102

Chapter 6	Chemical Bonds	109
6-1	Classification of Compounds	109
6-2	The Ionic Bond	109
6-3	The Covalent Bond	110
6-4	Lewis Structures	110
6-5	Rules for Writing Lewis Structures	110
6-6	Multiple Bonds	113
6-7	Coordinate Covalent Bonds	113
6-8	Departures from the Octet Rule	114
6-9	Resonance	116
6-10	Formal Charges	117
6-11	The Shape of Molecules	118
6-12	Electron-Pair Repulsion Theory	118
6-13	Deviations from Regular Shapes	119
6-14	Molecules Containing Multiple Bonds	124
6-15	An Alternate Representation of Types of Structures	125
6-16	Bonding Orbital Types	125
	Problems	126
Chapter 7	Solutions	131
7-1	Expressing Concentrations of Solutions	131
7-2	Molar Solutions	133
7-3	Calculation of Quantity of Solute	135
7-4	Dilution	138
7-5	Molal Solutions	139
7-6	Mole Fraction	141
	Problems	142
	Supplementary Problems	145
Chapter 8	Colligative Properties	149
8-1	Colligative Properties	149
8-2	Vapor-Pressure Lowering	149
8-3	Boiling-Point Elevation	151
8-4	Freezing-Point Depression	152
8-5	Osmotic Pressure	154
8-6	Determination of Molecular Masses	155
8-7	Ideal Solution	157
	Problems	158
	Supplementary Problems	161
Chapter 9	Thermochemistry	165
9-1	Heat Capacity	165
9-2	Heat Content, or Enthalpy	167
9-3	First Law of Thermodynamics	167

9-4	Heat Changes Accompanying Changes in State	168
9-5	Heat of Reaction	170
9-6	Heat of Combustion	170
9-7	Standard Enthalpy of Formation	171
9-8	Hess' Law	171
9-9	Calorimetry	174
9-10	Bond Energies	176
	Problems	178
	Supplementary Problems	184
Chapter 10	Solutions of Electrolytes	191
10-1	Colligative Properties	191
10-2	Concentration of Ions	194
10-3	Analytical Concentration	195
10-4	pH and pOH	196
	Problems	198
Chapter 11	Chemical Equilibrium, I	203
11-1	Reversible Reactions—Equilibrium	203
11-2	The Equilibrium Constant	203
11-3	The Dynamic Nature of Chemical Equilibria	204
11-4	Homogeneous and Heterogeneous Equilibria	205
11-5	K_c and K_p	205
11-6	Calculation of Equilibrium Constants	206
11-7	Calculation of Concentrations from Equilibrium Constants	209
	Problems	212
	Supplementary Problems	217
Chapter 12	Chemical Equilibrium, II	223
12-1	Weak Acids and Bases	223
12-2	Calculation of Dissociation Constants	224
12-3	Calculations from Dissociation Constants	225
12-4	The Ion Product of Water	228
12-5	pK_w	229
12-6	The Common-Ion Effect	229
12-7	Buffer Solutions	231
12-8	The Henderson-Hasselbalch Equation	232
12-9	Polyprotic Acids	233

12-10	Additional Types of Calculations Involving Dissociation Constants Problems Supplementary Problems	235 237 240
Chapter 13	Chemical Equilibrium, III	243
13-1	The Solubility Product	243
13-2	Calculation of K_s from Solubility	243
13-3	Calculation of Solubilities from K_s	247
13-4	Common-Ion Effect Applied to Solubility	249
13-5	Complex Ions	251
13-6	Dissociation Constant	251
13-7	Hydrolysis	253
13-8	Sodium Acetate	254
13-9	Ammonium Chloride	255
13-10	Ammonium Acetate Problems Supplementary Problems	257 258 261
Chapter 14	Oxidation-Reduction	265
14-1	Oxidation Numbers	265
14-2	Assignment of Oxidation Numbers	265
14-3	Oxidation-Reduction Reactions in Solution	267
14-4	Balancing Oxidation-Reduction Reactions by the Ion-Electron Method	267
14-5	Stoichiometry of Oxidation-Reduction Reactions Problems	272 274
Chapter 15	Electrochemistry	279
15-1	Electrolysis	279
15-2	Faraday's Laws of Electrolysis	279
15-3	Determination of the Faraday	280
15-4	Galvanic Cells	281
15-5	Standard Potentials: Measurement	283
15-6	Standard Potentials: Table	284
15-7	Use of Standard Electrode Potentials	284
15-8	The Effect of Concentration on the emf of Cells	290

15-9	Calculation of Equilibrium Constants	292
	Problems	293
	Supplementary Problems	297
Chapter 16	Entropy and Free Energy	303
16-1	Entropy	303
16-2	Entropy Changes Accompanying Changes in State	303
16-3	Entropy Changes at Constant Temperature	304
16-4	Irreversible Changes	305
16-5	Entropy of the Universe	306
16-6	Boltzmann Equation	307
16-7	Absolute Entropies	308
16-8	Gibbs Free Energy	310
16-9	Standard Free Energy of Formation	310
16-10	Free Energy and the Equilibrium Constant	313
16-11	Free Energy and Spontaneous Reactions	314
16-12	Calculation of Free Energy Changes from Cell emf's	315
	Problems	316
	Supplementary Problems	320
Chapter 17	Chemical Kinetics	325
17-1	Introduction	325
17-2	Rate of Reaction	325
17-3	Rate Equation	325
17-4	Determination of n and k	328
17-5	Half-Life	331
17-6	Other Integrated Equations for First-Order Reactions	332
17-7	Higher-Order Reactions	333
17-8	Second-Order Reactions	335
17-9	Half-Life of Second-Order Reactions	337
17-10	Zero-Order Reactions	337
17-11	Initial Rate Method	338
17-12	Arrhenius Activation Energy	341
	Problems	342
	Supplementary Problems	350
Chapter 18	Coordination Compounds	357
18-1	Introduction	357