CHEMISTRY

AN EXPERIMENTAL SCIENCE

Teachers Guide

CHEMICAL EDUCATION MATERIAL STUDY

PERIODIC TABLE

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 See below	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89- See below															
		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
		89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 E (254)	100 Fm (253)	101 Md (256)	102 (254)	103 Lw (257)	

Parenthetical values are mass numbers of the isotopes with longest half lives

TEACHERS GUIDE FOR

CHEMISTRY

AN EXPERIMENTAL SCIENCE

Teachers Guide for

CHEMISTRY

Prepared by

CHEMICAL EDUCATION MATERIAL STUDY

Under a grant from

THE NATIONAL SCIENCE FOUNDATION

Editor: A. L. McCLELLAN, California Research Corporation, Richmond, California

Associate Editors

GEORGE C. PIMENTEL, University of California, Berkeley, California

KEITH MacNAB, Sir Francis Drake High School, San Anselmo, California

An Experimental Science

Contributors

JOSEPH E. DAVIS, JR.
Miramonte High School, Orinda, California

FRED B. DUTTON
Michigan State University, East Lansing, Michigan

SAUL L. GEFFNER
Forest Hills High School, Forest Hills, New York

THEODORE A. GEISSMAN
University of California, Los Angeles, California

CARL GRUHN
South Pasadena High School, South Pasadena, California

ROLFE H. HERBER
Rutgers University, New Brunswick, New Jersey

LAWRENCE D. LYNCH, JR.
Beverly Hills High School, Beverly Hills, California

BRUCE H. MAHAN
University of California, Berkeley, California

LLOYD E. MALM
University of Utah, Salt Lake City, Utah

MARGARET NICHOLSON
Acalanes High School, Lafayette, California

CLYDE E. PARRISH
Cubberley Senior High School, Palo Alto, California

ROBERT W. PARRY
University of Michigan, Ann Arbor, Michigan

EUGENE ROBERTS
Polytechnic High School, San Francisco, California

HARLEY L. SORENSEN
San Ramon Valley Union High School, Danville, California

LUKE E. STEINER
Oberlin College, Oberlin, Ohio

MODDIE D. TAYLOR
Howard University, Washington, D.C.

ROBERT L. TELLEFSEN
Napa High School, Napa, California

Chairman: GLENN T. SEABORG, University of California, Berkeley, California

Director: J. ARTHUR CAMPBELL, Harvey Mudd College, Claremont, California

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PREFACE

This *Teachers Guide* was initially produced by the contributors at a six-week writing session at the University of California, Berkeley, in June 1961. The contributors include high school teachers who tried the CHEM Study *Textbook* and *Laboratory Manual* during 1960–1961, together with professors from universities throughout the United States. The Guide benefited from the constructive criticism our earlier material received and from the comments of those who used it during two years of trial.

The theme of the Guide is support. The support is of a practical, detailed nature for day-to-day use plus background support to help in class and laboratory preparation and in giving a deeper understanding to your talented pupils. In addressing such a varied audience with this dual purpose, an important first decision consists in choosing the level and intensity of approach. We adopted the plan of defining our audience as a lone teacher (isolated from other chemistry teachers) with somewhat less than ideal training, teaching in a poorly equipped school. We realize a majority of readers will not have all these problems, but it is relatively easy for them to skip what is not needed. It is quite difficult for the teacher in the situation described to supply something we omit.

The result of this approach is a voluminous Guide. Three explanatory sections are provided to help you use the Guide most effectively.

Some Introductory Remarks on the CHEM Study Materials discusses the broad arrangement of material; considers how laboratory, films, and problems fit into the course; and presents some remarks on the vocabulary used in the Textbook.

Organization of the Teachers Guide outlines the sections into which we have divided the Guide. Each chapter has been organized in the same order to speed location.

Introductory Guide to the Laboratory Work gives the structure of the guide material for the experiments. It also contains some general information in order to avoid repetition from one guide to another.

The writing effort received extensive support from Harvey Mudd College and the University of California in the forms of facilities and personnel. Our debt of gratitude to the National Science Foundation is also large as a result of their continued support and encouragement.

A. L. MC CLELLAN
Editor, *Teachers Guide*
California Research Corporation

GEORGE C. PIMENTEL
Editor, *Textbook*
University of California

LLOYD E. MALM
Editor, *Laboratory Manual*
University of Utah

J. ARTHUR CAMPBELL
Director, Chemical Education Material Study
Harvey Mudd College

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CONTENTS

SUMMARY OF SUGGESTED SCHEDULE—CHAPTERS 1-17

CHAPTER	DAYS ALLOTTED	TOTAL DAYS
1	8	8
2	10	18
3	6	24
4	7	31
5	10	41
6	7	48
7	7	55
8	8	63
9	8	71
10	5	76
11	9	85
12	9	94
13	6	100
14	6	106
15	7	113
16	8	121
17	8	129

Some Introductory Remarks on the CHEM Study Materials

Before discussing the details of individual chapters, a few general remarks about the course will be made.

Text Arrangement

The Textbook can be considered to consist of four broad sections:

Introduction	(Chapters 1–6)
Principles of Chemical Reactions	(Chapters 7–13)
Principles of Chemical Bonding	(Chapters 14–17)
Application of Chemical Principles to Descriptive Chemistry	(Chapters 18–25)

There is considerable overlap among these sections. Fundamental concepts are introduced in the first section, developed in the second and third, and utilized in the fourth. The first three sections contain much descriptive chemistry, although this subject is not given major emphasis therein. The last section is devoted to descriptive chemistry, but the fundamental concepts are deliberately and pointedly used, again and again. This arrangement has significance for you as the teacher.

Perhaps the most important point is the treatment intended for the Introduction. In general these chapters deal with *ideas that will be taken up in detail later*. Thus a "complete" understanding or mastery is not aimed for in this section. The plan is to give the student a glimpse of a number of concepts, to establish a stock of words and ideas, and to gain the benefit of repeated consideration of the same concept. In short, the students are to gain here a common foundation on which to build.

To achieve these goals most completely, we recommend a fairly quick pace through the Introduction. This will minimize the delay in reaching the more thorough treatment that will answer many of the questions stimulated by the Introduction.

One result of this repeated reference to a given topic is that the topic may come up in an apparently casual way before extensive treatment is intended. An example of a concept that is strengthened through repetition is the pressure-volume relationship of a gas. In Chapter 1 the equation

$$PV = a\ constant$$

is used to demonstrate different ways of communicating information. This use also places before the student the idea that there is only one gas law, *but it is not intended to be pursued at this time*. In Chapters 2 and 4, the same equation is utilized again, along with other aspects of gas behavior. Then in Chapter 5 the discrepancies from the equation at higher pressures are used to introduce liquids. If presented prematurely, a full discussion will upset the argument and require detailed changes in laboratory work. In this instance, the development of vocabulary is predicated upon a reasonable adherence to this sequence.

Exercises

These problems in the body of the Textbook are for the student to do *when he comes to them* during a reading assignment. They are designed to aid the pupil in checking whether he has understood the preceding material. Often the material immediately following assumes that the student has thought about the exercise.

Questions and Problems

A large supply of questions is provided, graded by difficulty and classified by the chapter section to which they apply (see *Schedule and Related Material* for each chapter). Undoubtedly there are more problems than are needed except for accelerated classes. Probably one-half to two-thirds are appropriate for most classes, but you must judge the number and level suitable to your class.

The answers given in this Teachers Guide are generally more complete than most students are likely to give, but they can serve as models for classroom discussion or provide information needed to satisfy the more demanding students. Hints are sometimes given to suggest alternate answers or ways to incorporate student errors into a constructive development of valid conclusions.

Vocabulary

Careful attention has been paid to the development and growth of the vocabulary. Technical terms are introduced deliberately, and, if not explicitly defined, they are juxtaposed with self-explanatory paraphrases. Sentences conveying conceptually difficult ideas are expressed as simply as possible. On the other hand, the growth of vocabulary is encouraged in sentences where the context easily defines the word and where a crucial message is not conveyed.

Laboratory Work

The treatment of laboratory work differs from that employed in many conventional courses. In the CHEM Study course, the student is often sent into the lab to investigate properties of nature before they are treated in class. He gathers some facts—that is, gets an experimental basis for understanding concepts—which the teacher then develops the next day. This technique is superior to sending the student into the lab to verify generalizations made by the Textbook or the teacher.

Most experiments should receive a short prelab discussion on problems of experimental technique and a postlab session devoted to the systematic development of relevant principles. The experiments are described for an ordinary scale of operations. During the trial years, several teachers used a semimicro scale by making certain obvious changes in a few experiments. Since a reduction in sample size might increase errors in weighing, careful consideration should be given to this possibility before reducing the scale of experiments which require weighing.

Films and Demonstrations

Throughout the course, visual substitutes for actual laboratory work are used where appropriate. CHEM Study films are an integral part of the course. The films cover material which the teacher would find very difficult or time-consuming to illustrate by the usual means. The demonstrations are described in detail, and the Textbook assumes they are done when indicated.

Achievement Tests

Two alternate series of exams have been prepared and classroom-tested. Each set consists of 5 tests covering 3 or 4 chapters each, a semester final, and a year final. These are multiple-choice, open-book tests designed to measure whether the student is mastering the course content, that is, whether he understands the major principles well enough to apply them to new or parallel situations. The tests may be ordered from W. H. Freeman and Co., 660 Market St., San Francisco, California, 94104.

Extra Information

The Appendixes (in Textbook and Laboratory Manual) contain quite a bit of extra information. Remind the students of this occasionally. In addition, the index is a handy guide to all the information in the Textbook. Usually, the *first* page reference after each index entry lists a page upon which a definition or defining discussion appears. Encourage the use of these aids by letting students see that you use them often.

Parts of the Textbook are in reduced type to indicate that they are not intended for all classes and can be omitted without serious loss.

Organization of the Teachers Guide

Each chapter has a guide which follows the outline below. In the outline is a short statement of what is to be found in each section.

The first four items provide a quick panorama of the chapter, and could be considered a very short form of guide. The sections headed *Development* and *Answers to Exercises and Problems* give detailed support for the specific textual material. The *Background Discussion* makes available a treatment of the important chemical principles and scientific philosophy. This section is intended to help you give added depth to your presentation, but is not intended directly for the student.

Finally, there is an index of the Teachers Guide for locating specific information. It is only a moderately detailed index.

Intent and Approach

About one page, discussing the overall philosophy.

Outline

Quite brief, with section numbers used to relate ideas to the Textbook.

New Concepts

A short list (5–10 items) of *major* new concepts—the things a student should learn from the chapter.

Schedule and Related Material

A suggested time schedule with proposed assignments. The difficulty and relation of problems to Textbook sections are shown. Attention is focused on time-consuming lab preparations for future experiments.

Development

A section-by-section discussion of the Textbook. Included are typical questions and ideas about how to handle them, additional examples, and suggestions as to what to emphasize and what to skip. Each experiment has an individual guide, described in the *Introductory Guide to the Laboratory Work*, which follows. These are found at the end of the *Development* section (5–15 pp.).

Supplementary Material

Listing of films, monographs, articles and books for student reading and teacher reference.

Background Discussion

Material on chemical principles and scientific philosophy for teacher's benefit. Only incidentally would it appear in the classroom (5–15 pp.).

Answers to Exercises and Problems

Problems (and exercises) are given with full answers. A hoped-for student answer is given, often with a more extensive discussion and with suggested uses for the problem.

Suggested Quiz Questions

More than enough questions for one quiz are given—with answers. The questions are designed for open book use. Questions are supplied for Chapters 1–17. The remaining chapters will likely be treated very differently, as teachers differ in their interests. Accordingly, chapter tests are not included.

Introductory Guide to the Laboratory Work

The following general comments about laboratory matters apply to all experiments. These remarks, plus the individual guides, are to help you plan the laboratory work. The best student results will be obtained when you have prepared well ahead of time.

Notebooks

Keeping a permanent record of observations is a part of scientific training. Furthermore, you need to be in close touch with student progress in the laboratory. Therefore, a carbon copy system is suggested. Collect one copy at the end of each day's work in order that you will know the results achieved without waiting to have calculations or questions completed. This will help you decide which points need additional work.

The student should use his notebook for all work from the laboratory, including calculations and answers to questions in the Laboratory Manual. Keeping one copy allows him to correct it as the material is discussed, even if you have not had time to return the copy he handed in. The student always has his laboratory results available for following experiments, class reference, or study purposes.

In order not to be wasteful of the notebook, the student may need help in planning. Neatness should be emphasized as a desirable achievement, but not to the degree that it interferes with the student's use of the notebook for an original record.

Laboratory Manual

Lab instructions: This section will need frequent reinforcement. It is the teacher's responsibility to emphasize safety, and this should be done repeatedly.

Appendix: This section is for brief explanation, diagnosis, or student review.

Teachers Guide to Individual Experiments

For each experiment the same basic outline is used, although some parts do not occur in all experiments.

PURPOSE

This is stated from the teacher's point of view. Of great importance is the need for the student to plan for his experiments. Detailed instructions have been included for lab experiments to make administration easier for you. Impress the student with your expectation that he will study the procedure before class and be ready to begin work when he comes into the lab. Students should be encouraged to evaluate the procedures given and to suggest extensions of the experiments. They should be encouraged to follow up on these whenever time and interest permit.

PRELAB DISCUSSION

This briefing should be short and devoted largely to experimental or manipulative details. Do not reveal any "element of discovery." In general, the laboratory manual contains sufficient description of purpose.

EQUIPMENT NEEDED

Equipment is listed per student or per pair, except as indicated. Some teachers prefer to have no equipment in the desk at the beginning of the term, and then to issue it as needed. This has the distinct advantage of confronting the student with fewer strange pieces of equipment at one time. Others set out all equipment for each experiment.

A list of chemicals is also included, and directions are given for preparing solutions.

Where the word *concentrated* appears after the name of an acid or ammonia, it means the solution from a freshly opened bottle of commercially available reagent which will normally have the concentration shown in the table.

Average Properties	HCl	HNO_3	H_2SO_4	NH_3 *solution*	CH_3COOH
Specific gravity	1.19	1.42	1.84	0.90	1.06
% Present	37	70	96	29	100
Grams active ingredient/ml	0.426	0.985	1.76	0.527	1.055
Concentration, *M*	11.7	15.6	18.0	15.1	17.6

It is, of course, necessary for the teacher to plan the preparations ahead. To aid in this, experiments for which lengthy or long-range preparation is needed are indicated, in advance, in the *Schedule and Related Material* section.

Convenience in dispensing chemicals and equipment is of great importance to avoid wasted time and boredom from waiting. The best practice is to arrange for enough containers such that students do not consume precious time from an already short period.

TIME REQUIRED

A 50 minute period is used as a standard. Longer periods are desirable, and can be used to advantage in almost every experiment, permitting additional work and open-ended experiments.

PRECAUTIONS

The phrase "Observe the usual lab precautions" is given to suggest the constant dangers of mishandling even common chemicals and equipment. More specific reminders are also listed.

LABORATORY HINTS

Substitutions for apparatus, special problems, and points for teacher background are included in this section.

POSTLAB DISCUSSION

This is the place to make sure the students understand the experiment and the regularities it demonstrates. The questions are to help draw this out. Use a small part of this period to comment on the form of reports.

ANSWER TO QUESTIONS

Questions have been answered in the teacher's vocabulary, in general, although "expected" answers from students have been included in many cases.

SUGGESTED EXPERIMENT REPORT SHEET

Where appropriate, this has been included as a suggestion. You will probably find the material easier to check in summary form than if you were to go over the entire lab report. It is of great importance to discuss the results obtained by the entire class, since students normally do each experiment only once and thus do not have a means of evaluating precision. Whenever possible, results should be posted on a chart of some sort (specific suggestions are given) and the regularity discussed.

One way to use this material is for either you or the students to determine the range of the middle 60% or 70% of the results. This range represents (roughly) plus and minus one standard deviation from the mean. Leaving out the highest and lowest 15–20% eliminates results based on gross errors.

QUESTIONS TO WONDER ABOUT

These questions are to stimulate thinking but are not to be assigned as written work. They vary in scope and difficulty, and some have no specific answers. Discussion of some of these questions will be included soon; and others, later in the Textbook.

EXTENSIONS OF THE EXPERIMENT—EXTRACURRICULAR INVESTIGATIONS

At the end of many experiments is a brief suggestion for further work. This is for *only* the most able students. No procedure is indicated, and certainly no student should be encouraged to continue unless he has some idea of how to go on. For some experiments, suggestions are included in the Teachers Guide.

Use of the Laboratory

In general, it has been assumed that the class is held in a combined laboratory-lecture room. The advantage in this practice lies in the time saved going from lecture room to laboratory. Sometimes the activities described in the Laboratory Manual may be carried on in a regular classroom, but if the laboratory and classroom are separate, a different organization will be required.

Chemical and Equipment Lists; Film Sources

Complete lists of the chemicals and equipment required will be found at the back of the Teachers Guide. Also located at the back of the Guide is a list of all sources from which the CHEM Study films may be ordered.

CHAPTER

1

CHEMISTRY: AN EXPERIMENTAL SCIENCE

Intent and Approach

In the first chapter we treat science as a human activity. We do more than just describe the activities of science; we also hope to give the student a sense of the significance of these activities. For many students, this course may be their first educational experience that deliberately goes beyond: "What are the facts accepted by authority?" and "How are these facts rationalized with other knowledge (that is, how are they explained)?" Perhaps for the first time the student will consider the questions: "Where do the 'facts' come from?" and "What does it *mean* to 'explain' facts?" The answers to the last two questions really constitute the message of this chapter, the most abstract message of the course.

Answering such questions requires introspection—a difficult process for most of us. Yet the ideas in this chapter are probably the most important in the book. This is true both for the science-bound and the science-terminal student. Both types of students need a correct view of the underlying pattern of science and of the meaning, limitations, and purposes of this pattern.

Since the message of this chapter is important and because it is abstract, it has been carefully stated in simple language and couched in familiar metaphor. It has been stripped of the formal trappings that are characteristic of a highly organized system. Thereby the fundamental ideas are placed in sharper focus.

Outline

1. The activities of science (1-1).
    - (a) To accumulate information through observation (1-1.1).
    - (b) To organize this information and to observe regularities in it (1-1.2). Illustrated by "lost child" analogy and Expts. 1 and 2.
    - (c) To wonder why the regularities exist (1-1.3). To search for a model system and use it to explain the results of Expt. 3, on melting point determination.
    - (d) To communicate the findings to others. The merits of various ways are considered in the last quarter of the chapter.
2. Introduction to phases and phase changes (1-1.2).
3. The use of model systems (1-1.3) based upon a "well-understood" process to account for observed behavior. Study of the billiard ball analogy of gas behavior.
4. Uncertainty in science (1-2).
    - (a) Uncertainty in measurement (1-2.1) is shown by the data from Expt. 3.
    - (b) Uncertainty in a sum is shown first, then uncertainty in a product (1-2.2, 1-2.3). Both are illustrated by calculations of the type needed in Expt. 5.
    - (c) Section 1-2.4 states the absence of certainty in science.

   (d) Significant figures are dealt with in Sec. 1-2.5 as one method of indicating uncertainty.
5. Communicating scientific information (1-3). A scientific advance becomes important only when communicated to others. For this reason, the choice of terms and use of language are of prime importance. Several ways of expressing a regularity are indicated.
6. Review (1-4).

New Concepts

1. The scientific approach to problems.
2. Explanations and models.
3. Uncertainty in measurement.
4. Phases, phase changes, and energy involved.

BASIS FOR SCHEDULING

The following expanded schedule is given (only for Chapter 1) to illustrate the method of arriving at the schedule.

Day 1 (50 min)

(*20 min*) Brief introduction: purpose of observation; how to use lab notebook (on lab desk—notebook and candle).
(*15 min*) Candle observation. Distribute Laboratory Manuals.
(*15 min*) Collect notes; discuss observation (including the difference between qualitative and quantitative observation) and interpretation.
Assign further observation and revision of written report.

Day 2 (50 min)

(*10 min*) Conclude discussion of Expt. 1.
Demonstrate sulfur or other unique candle (p. 38).
Lead into Expt. 2.
(*30 min*) Expt. 2.
(*10 min*) Call class together, and compare melting order.
Demonstrate both copper and steel wool in flame.
Assign reading of Expt. 3 and writeup of Expt. 2.

If delays during the first two days make it seem likely that Expt. 3 will not be completed on Day 3, it is suggested that an extra day be used for discussion.

Day 3 (50 min)

(*10 min*) Introduction to Expt. 3.
(*35 min*) Expt. 3. Put Textbooks on students' desks while experiment is in progress.
(*5 min*) Present a few clues about graphing.
Assign graph and report of Expt. 3.
Assign reading of Expt. 4, Secs. 1-1.1 and 1-1.2, and Appendix 1.

Day 4 (50 min)

(*25–30 min*) Discuss Expt. 3; show good graph, and discuss smoothing. Reassign graph if warranted.
(*20–25 min*) Conduct Expt. 4.
Assign questions and Secs. 1-1.3–1-2.1 and Expt. 5 for reading plus writeup of Expt. 4.
Mention optional Expt. 4a.

Day 5 (50 min)

(*20 min*) Discuss answers to Expt. 4. Propose challenge concerning "proof."
Demonstrate burning of candle in O_2-CO_2 mixture.
(*20 min*) Discuss text, and assign Secs. 1-2.2–1-2.4.
(*10 min*) *Prelab Discussion* for Expt. 5. Assign preparation of chart.

Schedule and Related Material (See p. 8 for basis of deriving schedule.)

Assignment Prior to Period	Period	Class Work	Ex.	Problems			Topic
				EASY	MEDIUM	HARD	
	1	Expt. 1		None for this chapter			Expt. 1: Scientific observation and description Distribute Laboratory Manual
Rewrite Expt. 1 Read Introduction to Lab Manual and Expt. 2	2	Expt. 2					Demonstrate use of laboratory burner Expt. 2: Behavior of Solids on Warming
Read Expt. 3 Write up Expt. 2	3	Expt. 3					Expt. 3: Melting Temperature of a Pure Substance Distribute Textbook
Read Expt. 4 Write up Expt. 3 S 1-1.1/1-1.2 (pp. 2–5)*	4	Expt. 4†					Expt. 4: Combustion of a Candle
S 1-1.3/1-2.1(pp. 5–9) Write up Expt. 4 Read Expt. 5	5	Discussion					The activities of science Review lab work to date
Prepare chart for Expt. 5 S 1-2.2/1-2.4 (pp. 10–11)	6	Expt. 5**	1, 2				Demonstrate and give practice in use of balance Expt. 5: Heat Effects
Write up Expt. 5 S 1-2.5/1-4.3 (pp. 12–16)	7	Discussion	3. 4				Uncertainty in science
Polish up Expt. 5	8	Review					Review work of Chapter 1 and Expts. 1–5

* This notation means Secs. 1-1.1 through 1-1.2, which include pages 2 to 5.

† Expt. 4 is a teacher-performed experiment.

** Expt. 5 requires advance preparation; see lab hint 3, p. 33.

Day 6 (50 min)

Expt. 5.
Assign Secs. 1-2.5 to 1-4.3 and writeup of Expt. 5.

Day 7 (50 min)

Discuss calculation of uncertainty.

Day 8 (50 min)

Continue previous discussion, and include Expt. 5.
Review.

Development

INTRODUCTION

Before the first day of class, it is important to realize that some of the initial procedures recommended may differ from your normal method of operation. Teachers ordinarily develop routines for the first day or two of school, involving such activities as checking out textbooks, assigning seats, checking out lockers, and other bookkeeping chores. You are asked to postpone as much of this as possible and, on the first day, after a few introductory remarks, to send the student to the lab to begin his own observations. He should then return to the lab on the second and third days—in fact, he should not receive his textbook until the third day. A reaction to this procedure might be, as it was for a number of the teachers who tried it, that, "Yes, this looks good on paper, but it will not work in my situation." If this is your reaction, then be reassured by the fact that these teachers *did* try it and were convinced that it *did* work and that they had never before experienced such a successful beginning to a course.

The work of the first chapter and the related experiments are intended to give the student a feeling for the "activities of science." He is to be made aware that science is based upon observation; that observation must necessarily contain uncertainty; that from observations a search is made for regularities; and that from the regularities arises the third basic activity of science —"wondering why."

The schedule to be followed has been arranged to insure that these concepts become part of the student's experience in an orderly sequence. He begins with his own observation of a burning candle. On the second day, he is led to a search for regularities by investigating the warming of various substances. On the basis of a possible regularity noted during his observations of the previous day he then spends the third day determining the melting point of a pure substance. At this time, he is given the Textbook and his first reading assignment, "Activities of Science." Having engaged in these very activities, he can relate the formal discussion directly to his own experiences. On the fourth day, a class experiment takes up a number of questions related to the burning of the candle. On the fifth day, a class discussion can be devoted to these concepts. The sixth day is spent determining the heat of combustion and heat of fusion of candle wax. The seventh day, after reading the rest of Chapter 1, a discussion is conducted on the topic, *Uncertainty in Science*. Experiences gained in determining melting points and heat of combustion form an experimental basis for the discussion.

THE ACTIVITIES OF SCIENCE (1-1)

Observation and Description (1-1.1)

The content of this section will form the basis for your introductory statements the first day. The student will not have read the material but will review it when the first reading assignment is made. See detailed schedule.

Expt. 1, SCIENTIFIC OBSERVATION AND DESCRIPTION,
fits here. See p. 15 for guide.

The Search for Regularities (1-1.2)

After a scientist has made a series of observations, his next task is to consider: "What regularities appear." Stress that, once regularities have been found, a number of observations can be classed together and used more effectively.

Some of your students may regard the analogy of the "lost child" as too elementary, yet it actually conveys the most sophisticated idea of the course. Observe that this simple example encompasses all of the activities in which scientists are engaged. All of the painstaking years of experimental study, all of the involved mathematical analyses, can be understood in terms of the actions of this child in observing, seeking regularities, generalizing, and testing his generalization. At this point you might want the student to originate analogies of his own.

Emphasize that a generalization is reliable within the bounds defined by the observations and that it may or may not apply beyond these limits. As a direct example of a search for regularity, develop the generalization concerning melting points of solids on the basis of the work of Expt. 2.

Wondering Why (1-1.3)

This activity is explained as the search for a model system that can be used to explain an observed regularity. The model system is framed in terms of a process that *is* well understood and is used to explain a process *not* well understood.

The example, which relates the behavior of balls on a billiard table to the behavior of a gas, is used to indicate what constitutes a "good" explanation. That is, the model system chosen must be well understood, and there must be many and close similarities to the system being studied. Your students may suggest that billiard balls will roll to a stop. If so, observe that this loss of energy is, no doubt, primarily concerned with friction in the continuous rolling process, rather than the relatively infrequent collisions with the cushions. Through questions, the students should be able to volunteer the idea that a particle flying through empty space would not display such a frictional loss of energy.

The behavior of steel wool upon heating is used to show how a generalization concerning one system, melting and burning of wax, might be used in another system, namely, that of burning or melting steel.

Expts. 2–5, BEHAVIOR OF SOLIDS ON WARMING,
THE MELTING TEMPERATURE OF A PURE SUBSTANCE,
COMBUSTION OF A CANDLE,
HEAT EFFECTS,
fit here. See pp. 18, 22, 26, and 32 for guides.

After Expt. 5 has been done, it might be appropriate to assign as outside reading *The Chemical History of the Candle*, Faraday's "Christmas Lectures." (See *Supplementary Material*, p. 39).

UNCERTAINTY IN SCIENCE (1-2)

Uncertainty in a Measurement (1-2.1)

A scientific statement of a measured quantity is well framed if it clearly conveys just what is known and nothing more or less. To illustrate this, ask the student to consider his own measurement of the melting point (Expt. 3) and to think about the limitation inherent in his ability to read a thermometer precisely. Many other examples can be used, such as measuring distance, weighing, and so on.

Uncertainty in a Derived Quantity:
Addition and Subtraction (1-2.2)
Multiplication and Division (1-2.3)

These sections serve two purposes: (1) to illustrate how to express the uncertainty in a derived number and impress the student with the need for such expression and (2) to give some help with the calculations required in Expt. 5. The first is the one to stress. Throughout the course you should show your awareness of the uncertainty in measured and derived quantities. Some typical values for common measurements are given in Appendix 4 of the Laboratory Manual and are repeated here in Table 1-I.

Table 1-I

Uncertainty Found With Typical Laboratory Instruments

Typical Instruments	Typical Uncertainty
Triple-beam (centigram) balance	±0.01 g
Platform balance	±0.5 g
50 ml graduated cylinder	±0.2 ml
10 ml graduated cylinder	±0.1 ml
−10°C to 110°C thermometer	±0.2°C
50 ml buret	±0.02 ml
50 ml gas-measuring tube	±0.02 ml

Make constant and consistent use of this idea in order that the student will feel it is important but not mysterious. The experiments provide a chance to check the understanding achieved by the class.

When he has completed this chapter, the average student should know how to determine uncertainty if only sums and differences are involved. By the end of the first semester, only the better students are expected to know how to determine uncertainty when products and quotients are involved. The calculation of average deviation from the average will be understood by the better student if you perform this operation for the results from several experiments.

The Absence of Certainty in Science (1-2.4)

This is an extremely important concept for the student to get. He should learn that no scientific statement is absolutely certain and should appreciate that the limitation is imposed by the uncertainty of the measurements which support the scientific statement. Chapter 4 will deal further with this idea.

How Uncertainty Is Indicated (1-2.5)

The use of the symbol ± and of significant figures is discussed. Here the important thing is to avoid drilling on significant figures yet to make certain the student realizes the need for some such notation. Repeatedly draw attention to your own correct use of significant figures in the light of the uncertainty. See the background section (p. 48) for further remarks, and see Appendix 4, Laboratory Manual, for rules and examples on handling significant figures.

COMMUNICATING SCIENTIFIC INFORMATION (1-3)

A scientific advance is important only if it is communicated to others. Because of this, the proper choice of terms and use of language are of prime importance.

When a regularity is found, there are several ways by which it might be reported. The choice of methods depends on the set of observations and on the use to which it is put. It can be expressed as a qualitative statement, as a table of data, as a graph, or as a mathematical relationship.

Note that the example $PV = a\ constant$ is *not* a signal to start developing the gas laws. Postpone that topic until Chapter 4. The equation appears here only as an example of a way in which a regularity can be expressed. It is deliberately chosen in order that the same example can be used to introduce the formation and molecular motion of liquids. In addition, its use here helps with the gas laws in Chapter 4.

REVIEW (1-4)

The steps
observe,
organize, and
wonder why
are so important that they should be reviewed in detail. Help the student see that these steps constitute the scientific method *and* that he can perform these steps.

Prediction has been deliberately omitted from this list of steps. A background section (p. 43) discusses various degrees of prediction.

EXPERIMENT 1 SCIENTIFIC OBSERVATION AND DESCRIPTION

PURPOSE. To emphasize the importance and value of careful observations and to illustrate how many observations can be made on a seemingly simple system.

PRELAB DISCUSSION. Give a very short introduction. This experiment illustrates the philosophy of CHEM Study. This is not a course in which the student listens while the teacher talks about science; rather it is one in which the student participates in science. He becomes actively involved in doing what scientists do. He will find out what science is, primarily as a result of his own experiences.

Tell him how to use his lab notebook. Do not give him suggestions as to what to observe, but be certain he knows the assignment: to make and record all his observations on a burning candle.

TIMING. Do this experiment on the first day, before giving anything except the briefest of introductions to the course.

EQUIPMENT NEEDED (PER STUDENT)

candle, mounted on a "drip catcher" (see laboratory hints 2 and 3)
matches
lab notebook

It is desirable to have metric rulers available in the lab.

TIME REQUIRED. About 15–20 minutes.

PRECAUTIONS. A brief comment about not burning noses or hair would be appropriate.

LABORATORY HINTS

1. Experience shows that this exercise in observation engrosses the students sufficiently such that the teacher will be given an excellent opportunity to complete some of the first day's routine. *Laboratory Manuals are needed for directions and are to be given out at the end of the first day.*
2. Be sure candles are not the "dripless" type. Ordinary, inexpensive candles sold under the name "household candles" are satisfactory. A six-inch candle ($\frac{3}{4}$-inch diameter) is fine.
3. Cardboard squares or can lids make good drip catchers. Unless one is provided, the students tend to use the wire gauze with asbestos center, and this causes difficulties later.

POSTLAB DISCUSSION. After the observation period, collect the carbon copy from the notebooks. This is an important step in establishing routine. Make clear to your students that a written description of the burning candle is due the next day. (See the last paragraph in Laboratory Manual *Procedure*.)

Base your discussion of the difference between observation and interpretation upon the "observations" the students make. An observation is simply a record of what is observed. It is devoid of reference to significance, implication, or indirect relation to other observations. An observation coupled with a valid estimate of uncertainty constitutes a "fact," and it is considered to be a statement of a property of nature, unchanging in time.

An interpretation includes reference to significance, implication, or indirect relation to other observations. In essence, interpretation involves an attempt to draw meaning from one or more observations or to establish causal relationships.

Operationally the distinction is simple, though students are not used to keeping the two separate in their minds. A few examples will make clear the distinction. Usually the interpretation is most readily exposed by proposing an alternate meaning or relationship that cannot be discounted with the available information. Here are two examples.

1. *Observation:* Jim and Jane are frequently seen together.
   Interpretation: Jim and Jane are "going steady."
   Possible alternative interpretations: Jim and Jane are brother and sister. They have accidentally become handcuffed together.
2. *Observation:* If you pass your finger through a candle flame, it feels hotter just above the tip of the flame than it does in the middle.
   Interpretation: Heat rises.
   Possible alternate interpretation: Heat is being produced at the tip of the flame, and some is being consumed at the middle (for example, the heat might be used to produce the light emitted by the flame).

Notice that an interpretation "heat rises" might be defended by some student on the basis that it is known from other data. If so, ask him what data he has in mind, and again point out that the remark "heat rises" is an interpretation readily distinguished from the new observation he proposes. Draw attention to the fact that classifying the statement "heat rises" as an interpretation is not a *denial* of the statement, but that it is merely a distinction between what is observed (which does not change) and the significance attributed to the observation (which, experience shows, frequently does change).

Emphasize the difference between qualitative and quantitative observations. This may be brought up during the postlab discussion or it may be delayed until the lab write-up is in. Any observation involving contrasts is, to some extent, quantitative.

For example, the statement "Light is emitted by a candle" is qualitative, whereas the statement "The candle flame appears bright in a normally lighted room" is quantitative, since it provides some basis for judging *how much* light is emitted by the candle. Still more quantitative (and hence more useful) would be the statement: "The candle flame emits about the same amount of light as one square centimeter of iron surface heated to 700 ± 50°C."

When the Textbooks are passed out, the student should be directed to read the observations on a burning candle in Appendix 1. When he compares his observations with those of a profesfesional scientist, the student may be shocked by the number of things he failed to report. This is intended; exploit it. Point out that the professional scientist has years of training and experience behind his ability to observe carefully. It is an important aim of this course to train the student to observe more carefully and more fully.

The student's initial observations are the recording of simple sensory responses. As he becomes acquainted with more sophisticated instruments to augment his senses, the precision with which he is able to make an observation will increase. The accuracy of the observation, however, depends upon the extent to which he actually observes (or measures) what he intends to observe. The degree of uncertainty in an observation depends on both precision and accuracy. Usually the uncertainty due to precision can be learned merely by repeating the experiment many times. The uncertainty due to accuracy is difficult to ascertain. The same quantity must be measured by several methods. When only the uncertainty in precision is known, it is usually called "the uncertainty," though it is understood that accuracy is untested.

Important note: Request each student to bring from home the following items for the next few experiments. Past experience has been that students get a feeling of participation from this request.

1. Tin can lid (*needed the next day*). A lid from a large juice can (see item 2) is good. The diameter should be about four inches.

2. Can to use as a chimney in Expt. 5. This should be a large-size, tall juice can with both ends removed. Instruct the student to punch two or three holes (with a beer can opener) in the side of the can near the bottom. It is easier to punch the holes in the sides *before* the bottom is removed. This size can is marked 1 qt 14 oz, or 1.36 liters. Have a sample to show.
3. Small can for Expt. 5, Part I. This should be a soup or small vegetable (10–17 oz) can with only one end removed.

EXPERIMENT 2 BEHAVIOR OF SOLIDS ON WARMING

PURPOSE. To observe the melting behavior of a number of solids and describe a regularity found in the experiment. The student is to obtain experimental evidence that will confirm or disprove his answer to the question: "What is the colorless liquid in the bowl at the top of the burning candle?"

The "element of discovery" in this experiment lies in noting the characteristic order of melting points. Be sure this aspect comes out in the postlab discussion. The identification of the resolidified candle material as being the same as the original solid candle gives a connection between this experiment and Expt. 1.

PRELAB DISCUSSION. The operation and use of a burner are described in Appendix 1 of the Laboratory Manual. Merely demonstrate lighting it once. Emphasize the desirability of following directions (give a reminder about the general laboratory instructions). Tell the students how to handle the hot ring (and, for a later experiment, the hot lid) and about how to dispose of the used lid and other materials.

TIMING. This experiment should be done during the second day of class, after a brief concluding discussion of Expt. 1 and a demonstration of a "strange" candle made of sulfur or some other substance (see p. 38 for directions).

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

- ring stand, ring, wire gauze
- burner
- candle
- 250 ml beaker or small can
- tool for cutting off piece of candle
- tin can lid (see lab hint 1)
- metric ruler
- small piece each of:
    - sulfur (roll sulfur) (about 0.1 g)
    - lead (see lab hint 2) (about 0.5 g)
    - tin (see lab hint 3) (about 0.5 g)
    - copper (#16 wire, about 1 cm long)
    - steel wool (#00)
    - silver chloride (see lab hint 4) (about 0.1 g)

TIME REQUIRED. This experiment can be done in 25–30 minutes provided the chemicals are placed around the room in such a way that the student need not wait to get them, and provided they are pre-cut in order that the student has to do little more than place each chemical on the lid.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. A quick way to put depressions in the lids is essential. Use a block of soft wood with three nails placed around the circumference of a circle within which the lids will fit. The nails should not be equidistant (see Fig. 1-1). Position the lid with its unlacquered side up. Place the ball of a ball peen hammer about 1 cm inside the edge beside one of the nails. Hit the head (face) with a mallet. Repeat to make indentations beside the other two nails.
2. Cut pieces of sheet lead (about $\frac{1}{2}$ cm square) to produce angular edges in order that melting may be easily detected. Lead shot is not convenient here, both because it rolls around and because its melting is difficult to observe. Narrow, crumpled strips of lead foil (available from X-ray plate wrappings or model shops) are satisfactory, but the student may need to poke at the material with a wooden matchstick to detect melting.
3. Cut pieces from sheet tin as above. If this is very thin, crumple it tightly. Small pieces of mossy tin may also be used.

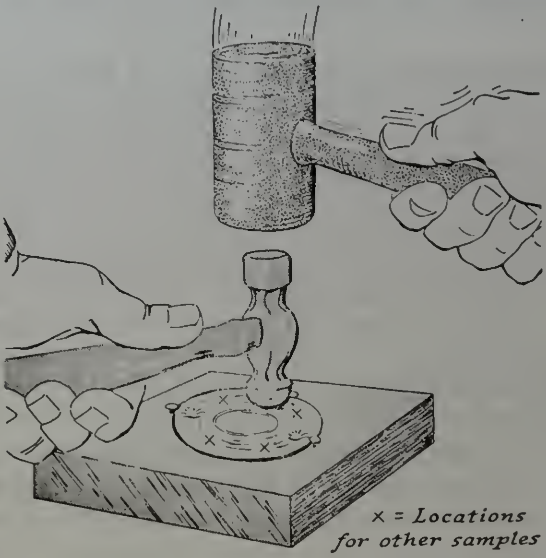


Fig. 1-1. **Preparation of lid.**

4. After a first year use of CHEM Study, you may have saved AgCl from Expt. 8. You may either purchase the AgCl or make it by adding NaCl solution to $AgNO_3$ solution. If you make it, filter the precipitate, wash it thoroughly, dry it in a desiccator or low temperature oven, and store it in brown bottles.
5. The reason for using the candle for the first heating is to be sure that the student heats the lid slowly enough such that the wax and sulfur melt at different times and to show the use of the candle as a heat producer (as a prelude to Expt. 5).

EXPECTED RESULTS

PART I

Order of melting (M.P. is in parentheses):

$$\left.\begin{array}{l}\text{candle wax (about 52–54°C)}\\ \text{sulfur (113°C)}\end{array}\right\}\text{melted by candle}$$

$$\left.\begin{array}{l}\text{tin (232°C)}\\ \text{lead (327°C)}\\ \text{silver chloride (455°C)}\end{array}\right\}\text{melted by burner}$$

$$\left.\begin{array}{l}\text{copper (1083°C)}\\ \text{iron (1535°C)}\end{array}\right\}\text{will not melt in the arrangement used}$$

POSTLAB DISCUSSION. About ten minutes before the end of the period, assemble the class to discuss the observed order of melting. If time permits, continue with the demonstration and discussion below. Assign the reading of Expt. 3.

Make sure that the point of the experiment is clear—solids do melt and do have characteristic melting points, as revealed by the regularity of the order of melting. Ask for an oral presentation of some of the generalizations. The idea that different substances melt at different temperatures is brought out in Part I; the idea that a particular substance always melts at the same temperature is illustrated in Part II.

When asked why copper and iron did not melt, some will volunteer that these metals did not get hot enough. Demonstrate the melting of copper by holding a short length of #18–24 gauge wire with tongs directly in the burner flame. Then use tongs to hold a loose wad of steel wool (#00, about 10 cm long and 3 or 4 cm wide) directly in the flame. Refer to this behavior as "sparkling," but do not discuss it, since this is explained in the text. If questions arise, or if the students propose that combustion is involved, ask how they know, and require that they propose experiments that might verify the interpretation. The point is to make a clear separation between the observation (The steel wool does not melt quietly; it sparkles.) from the possible interpretation (It is burning.). In this fashion, the steel wool demonstration will support the logical argument present in Sec. 1-1.3 of the Textbook.

You may wish to discuss some of the other observations. The oxide coating on the lead and tin may obscure the melting of these substances. The paraffin and sulfur will probably burn when the change is made to the burner as a source of heat. The AgCl may darken, and some students may miss its melting. If the discussion is held on the day of the experiment, avoid answering the questions at the end of the experiment, but be sure that all students have had an opportunity to make reasonable observations. Be careful to avoid saying that any observation is "wrong" (see postlab of Expt. 1). Suggest that the student consider whether he was observing under the same conditions as were those with whom he disagreed. Encourage a "try it again" attitude.

The wide melting point range for the substances in the experiment should be mentioned. It indicates that solids vary a great deal in their ability to withstand disruption due to heating. This can be discussed as evidence for the variability of crystal stability and can be posed as something to wonder about. It would be inappropriate to discuss melting behavior in terms of structural differences among solids.

One point, however, can and should be stressed: the identical composition of the solid undergoing melting and of the liquid formed on melting. Refer to the substance produced in the bowl of the burning candle and its relation to the candle itself. The student should see that, in a phase change, the solid and its resolidified melt have the same properties. If the resolidified melt had different properties, the change would be called a chemical change.

You might also point out that two or more substances may have practically the same melting point; a difference in the melting point of two substances indicates their difference, but a similarity does not necessarily indicate their identity. For example, ethyl alcohol and hydrogen chloride both melt at $-114.3 \pm 0.2°C$. See Expt. 3 for some other instances.

ANSWERS TO QUESTIONS AND EXERCISES

1. How does your observed order of melting for the substances tested compare with that observed by other members of the class?

   Answer: Most will agree with the order given on p. 19. If the burner is turned up high, the lead and tin may melt so quickly that their order of melting will be uncertain.

2. Make a generalization based on the combined observations.

   Answer: It is hoped that the student will be led to generalize about the consistency in the the *order* of melting. He may state that the various substances seem to have different melting points and that such behavior may be characteristic of the substances. This is a good time to discuss how much evidence is necessary before a regularity is stated and to emphasize the tentative nature of such statements. In this experiment, five examples furnish a reasonable basis for the "characteristic order of melting" gen eralization, but comment that scientists rely on a generalization only after many more facts than this support it.

3. What statement can you make concerning the material in the bowl of the burning candle and the candle wax, based upon your generalization from Exercise 2?

   Answer: Since the resolidified material from the bowl of the candle melted at the same time as the candle material, we can conclude that they are probably the same substance. This does not preclude the possibility that there are two different substances that look alike and have the same melting behavior. Additional similarities in other physical tests would lower the probability of such a chance occurrence.

A QUESTION TO WONDER ABOUT

Why did the substances tested on the lid begin to melt at different temperatures?

Answer: It is not intended that class discussion be devoted to the *Questions to Wonder About.* If this comes up through student questions, solicit volunteer answers, and keep channeling discussion to force some decision on what sort of data are needed to decide. Point out that information leading to an answer will be accumulated during the course.

EXPERIMENT 3 THE MELTING TEMPERATURE OF A PURE SUBSTANCE

PURPOSE. To provide a quantitative experiment on the phase change treated qualitatively in Expt. 2. A real "element of discovery" awaits the student in noting the occurrence of the flat portion of the curves and in identifying the melting and freezing point.

PRELAB DISCUSSION. Since this will immediately follow the postlab discussion of Expt. 2, the introduction should be very brief. To save time in getting started and in finishing, see especially lab hint 4. You will need to mention the heating of the tube for Part I (precautions and lab hint 1) and how to read a thermometer (lab hint 3).

Early in the course, students will need assistance in organizing their notebooks and planning their use of time. Make it clear to the student that he is expected to study the lab procedure and to prepare blank tables before class in order that he can use his lab time for the experiment. However, since this is only the third day, some students will not have done this. Be sure that each pair realizes that while one of the partners is getting the beaker of water and melting the *para*dichlorobenzene, the other should prepare the data sheet, using two carbons in order that both student and teacher may have copies.

TIMING. This experiment is to be done on the third day, following the brief discussion of Expt. 2. Hand out the Textbooks while students are working on this experiment.

EQUIPMENT NEEDED (PER PAIR OF STUDENTS)

15 g *para*dichlorobenzene in an 18 × 150 mm pyrex test tube (see lab hint 2)
2 thermometers (−10°C to 110°C range)
ring stand, ring, wire gauze
burner
clock or watch with sweep second hand
400 ml beaker
clamp (see lab hint 1)

TIME REQUIRED. A 30–35 minute period includes time for pairs to organize their work—a step often necessary at the beginning of a year. Part I takes about 15 minutes (possible stopping point here). Part II takes about 10–15 minutes if the water is prewarmed.

PRECAUTIONS. Warn students to be careful when heating the solid to 70°C in part (c). They should move the tube in the burner flame, not heat it at a single spot—especially not at the bottom—and should not "aim" it toward themselves or others (see lab hint 1).

LABORATORY HINTS

1. The clamp should be used as a test tube holder for Part I in order that the tube of *para*dichlorobenzene may be moved about in the flame while it is being melted and then quickly clamped in place. If heating is done in the clamped position, the student is too likely to overheat the base of the tube. Since the temperature rises rapidly once the solid has melted, the heating *must* be done gradually.
2. Tubes containing *para*dichlorobenzene (10–15 g) should be supplied to the students. To prepare these, melt the solid in a beaker, and pour it into the test tubes. The proper height for the tubes you use can be determined by melting 12.5 g of the moth repellent crystals in one tube.
3. Students will need instruction in reading a thermometer, especially on the necessity of reading it with their eyes at the same level as the top of the mercury column.
4. For Part II about 300 ml of hot water (70°C) is needed for each pair of students. Hot tap

water is most convenient, but if it is not available, start heating some while Part I is being done.

5. Many students will need help with the graphical presentation of the data. If the class finishes early, some description may be given at the end of the lab period, but more than likely it will have to wait until the next day. Such discussion might be more meaningful after the students have attempted the graph (see postlab discussion).

DISCUSSION OF PROCEDURE. For the cooling curve the temperature of the water is not too critical, but if it is much below 25°C, the moth repellent will cool too quickly along the sides. The temperature and amount of hot water have been selected such that the water will have enough heat content to melt the solid easily. This is a critical point in getting satisfactory results. The beaker must be $\frac{3}{4}$ full and the water temperature 68 ± 3°C when the tube is inserted. If warmer, the flat portion will be lost; if cooler, there will be too little heat to complete the melting.

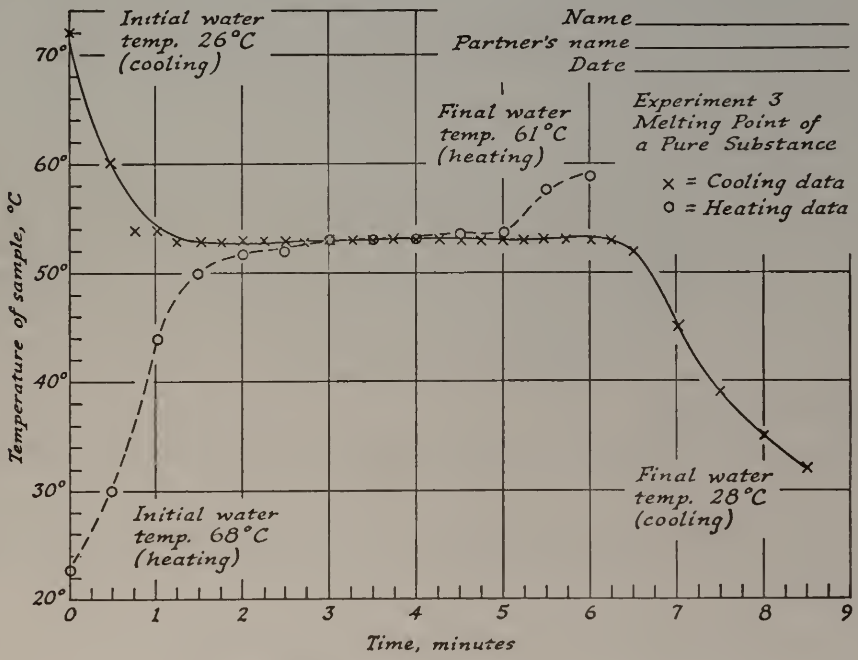
EXPECTED RESULTS. Figure 1-2 shows some student data.

POSTLAB DISCUSSION. If possible give a few pointers about graphing at the end of the experiment period. Refer students to the Laboratory Manual, Appendix 5.

On the next day, discuss the experiment briefly. Students will note the plateaus (lines of constant temperature) as well as the fact that the two plateaus occur at the same temperature. These are the important points to be "discovered." Make sure all students realize that these are generally observed for many substances. You might also comment on changes in the rate of heating or cooling at the ends of the graph.

Show the class some good graphs made by students. If there are no good graphs, prepare a

Fig. 1-2. **Cooling and heating curves** *for paradichlorobenzene.*



sample using data collected in class. Be sure it is understood that plotting and reading graphs are skills they are expected to develop and use. Discuss criteria used in selecting a suitable scale. Give an explanation about smoothing the curve. It will probably be necessary for many students to prepare a second graph to correct errors in their first trial.

Discussion of the summary report and questions may be delayed if necessary to allow class time for Expt. 4. Later you may wish to post the best reports or, perhaps, duplicate an excellent one.

In your discussion mention the possibility of determining the melting point by this procedure. The student does not yet have background for interpreting the energy relationships, but he will certainly have an opportunity to *think*. He can see that he had a source of heat and that, as heat was added to the test tube, the temperature kept rising rather rapidly until melting started; and then did not rise again until melting was complete. He may come up with the correct conclusion that the energy was used in the melting process instead of for heating. How he expresses this will depend on his sophistication in science.

Discuss the sources of error and difficulty in this experiment and possible improvements for eliminating them. When discussing the reports, emphasize the "wondering why" aspect; then, later in the course, refer the student back to these observations for further interpretation.

ANSWERS TO QUESTIONS

1. What effect would increasing the amount of *para*dichlorobenzene have on the shape of the melting or cooling curves?

   Answer: Increasing the amount of substance would change neither the fundamental shape of the curve nor the melting temperature provided there is a large enough heat supply. The slope of the curve, however, would be more gradual, both above and below the plateau, since more time would be required for a given temperature change; and the plateau itself would be extended, since more heat would be gained or lost and hence a longer time required for all the material to change phase.

2. Based on your data, what is the melting temperature of the *para*dichlorobenzene?

3. Based on your data, what is the freezing temperature of the *para*dichlorobenzene?

   Answer to 2 and 3: The answer to both is the same: 53°C. Any answer between 51–55°C is good for the conditions of this experiment. There is a tendency for students to obtain higher readings from the cooling curve than from the heating curve. This is probably due to the poor heat conductivity of *para*dichlorobenzene. A discussion of sources of error should be delayed until uncertainty of measurement is discussed. The amount of smoothing needed and the difference between the temperatures established from each curve indicate the uncertainty of the answer.

A QUESTION TO WONDER ABOUT

Why do the heating curve and the cooling curve have the characteristic shape shown by your graph?

ADDITIONAL INVESTIGATIONS. Very few entire classes will have time—and it is not suggested that any extra time be allowed—but if individual students are interested in additional work, here are two suggestions.

1. Devise an experiment in which you can obtain data to plot a heating curve for the evaporation of a liquid substance. If you use a liquid which does not mix with water, you can investigate

the behavior of a liquid as it evaporates in a similar manner to that you used for a melting solid in Part II of Experiment 3.

2. Determine the cooling and warming behavior for another solid substance. Acceptable materials are:

*para*chlorobenzaldehyde, M.P. 48°C
octadecanol, M.P. 58.5°C
cetyl alcohol, M.P. 49°C
diphenylamine, M.P. 53°C
glyceryl tripalmitate, M.P. 55°C
lauric acid (dodecanoic acid), M.P. 44°C
maleic anhydride, M.P. 53°C
palmitic acid, M.P. 65°C
thymol, M.P. 50°C
urethane, M.P. 50°C
dimethyl oxalate, M.P. 54°C

It may be interesting to use a solid from which you have made the unique candle that the student will see you demonstrate (do not use sulfur for the melting curve: the fumes are too noxious).

EXPERIMENT 4 COMBUSTION OF A CANDLE *A class experiment*

PURPOSE. To become acquainted with some of the chemical processes involved in the combustion of a candle and to identify some of the products of combustion. This experiment was designed as a class experiment in which the teacher plays the role of "manipulator" and the students the role of recorders. Care must be taken that the individual considers himself a participant and that this does not become a "lecture-demonstration."

PRELAB DISCUSSION. Direct the students to record observations in their notebooks, just as they would while working at their lab desks. The questions are to be answered later. Avoid interpretation and discussion.

TIMING. This experiment should be done on the fourth day, following the discussion of Expt. 3.

EQUIPMENT NEEDED (PER PERIOD)

candle (about 3 inches long)
2 pieces cobalt chloride paper (see lab hint 1; paper must be prepared ahead of time)
150 ml lime water, $Ca(OH)_2$, saturated (10 g/liter)
wide-mouth quart jar (or 1000 ml beaker) } (see lab hint 2)
wide-mouth pint jar (or 500 ml beaker) } (see lab hint 2)
3 250 ml flasks or pint or half-pint jars (see lab hint 2)
blow pipe (homemade; see Figure 4-3 in the Laboratory Manual)

TIME REQUIRED. About 15–20 minutes.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. The cobalt chloride paper must be dry (blue in color). It is wise to store it in a desiccator, such as a closed jar containing anhydrous calcium chloride or Drierite (anhydrous calcium sulfate). If cobalt chloride paper is not available, copper sulfate may be dehydrated by careful heating. Sprinkle a little of the anhydrous powder onto the film of moisture.

   Cobalt chloride paper may be made a few days ahead of time by dipping absorbent paper (filter paper or cleansing tissue) in a saturated $CoCl_2$ solution and then drying it in a low temperature oven.
2. In Part II (a) and (b) either beakers or wide mouth jars are satisfactory. When two flasks are used, the illustration is not as satisfactory, since doubling the volume does not double the time unless the sides of the container are parallel (probably because of convection effects).

OBSERVATIONS

PART I. Cobalt chloride paper turns pale pink in both trials.

PART II. In a 1000 ml beaker the candle burns for about 35 seconds; in a 500 ml beaker, about 18 seconds.

PART III

(a) The candle burns with a smaller, less luminous flame. It seems more "concentrated" in space, and the wax melts more rapidly.

(b) The lime water becomes cloudy when swirled in the flask in which the candle was burned and does not become cloudy in the "control" flask. As the breath is bubbled through, the lime water becomes cloudy.

ANSWERS TO QUESTIONS

PART I

1. What conclusion can be drawn from this experiment?

   Answer: The most obvious conclusion is that water is a product of the burning of a candle.

2. Does the evidence you have gathered eliminate the possibility that something other than water caused the observed changes? Explain your answer.

   Answer: The intent of this question is to bring up a consideration of what constitutes proof. The evidence certainly indicates that the product could be water but does not eliminate the possibility that something other than water may cause the paper to become pink. In order to be sure of this, additional experiments would be needed.

3. If the liquid film is water, where does it come from?

   Answer: It comes from the condensation of a combustion product of the candle (see also discussion of question 1).

4. Would you expect water to be produced if an electric heater were used in place of the candle under the beaker? Explain your answer.

   Answer: No, since there is no chemical reaction and thus no products other than heat when an electric heater is used.

PART II

5. How does the time required to extinguish the candle flame using the quart jar or liter beaker compare to the time using the pint jar or 500 ml beaker?

   Answer: The candle burns about twice as long in the larger container.

PART III

6. Explain how these experiments offer a basis for preference between the two answers postulated in Part II for the following question: "What causes the candle flame to be extinguished when confined for a short time in a flask?"

   Answer: The students will probably suggest the second postulated answer, since their previous experience leads them in this direction (see postlab discussion).

7. Name some possible products of combustion for candle material as indicated by these experiments.

   Answer: Water and carbon dioxide are "indicated" by the experiments. Heat and carbon (soot) may also be mentioned.

POSTLAB DISCUSSION. On the next day, ask for answers to question 2. Discuss the nature of proof (see answer to question 2). Discuss the indications that CO_2 is also a product. Ask for explanations for the burning behavior noted for Part III (a). Be sure the students understand that, although CO_2 is present in exhaled air and that this helped identify lime water as a possible "test" for the production of CO_2, there is much unused oxygen. In normal breathing the exhaled air contains only 4% CO_2. Thus, the blow pipe demonstration showed the effect of adding air to the flame. At this time you may wish to force a little O_2 through a tube into a candle flame, perhaps using the hollow wick candle described on p. 38.

Finally, challenge the students in connection with question 6. Almost certainly most of them will have selected choice number 2. If you can get suggestions as to how to obtain more evidence, follow up on these. At any rate, the following should be demonstrated.

Fill a beaker or pint jar with oxygen and invert this over a burning candle. Fill a beaker or pint jar with $\frac{1}{5}$ oxygen and $\frac{4}{5}$ CO_2. Cap the jar, and allow time for mixing (10 minutes at least), and then invert the jar over a burning candle. Compare the length of burning time in each with that in a container of air.

Warning: Do not use an Erlenmeyer flask for this purpose. In such a flask, even with adequate time for thorough mixing of the two gases, the candle usually goes out. The CO_2 tends to accumulate in the neck of the inverted flask and extinguishes the flame on its way through. Unless the candle is long enough to reach to the very top and the inverting is done very rapidly, the results will lead to a spurious conclusion.

EXPERIMENT 4a FURTHER INVESTIGATIONS OF A BURNING CANDLE

(OPTIONAL)

PURPOSE. To give an opportunity for more experiments with the candle than the usual class time permits and to encourage students to continue their observations at home.

PRELAB DISCUSSION. Mention the presence of this experiment in Appendix 6 following the discussion of Expt. 4. Do not use class time to prepare for this experiment.

TIMING. This experiment fits after Expt. 4.

PRECAUTIONS. Remind the student to pick an appropriate work area and to be careful with fire, glass, and hot objects.

EQUIPMENT NEEDED (PER STUDENT)

You may wish to supply the student with the items that he is unlikely to have at home:

8 cm length of glass tubing (8 mm in diameter)
30 cm length of copper wire (#16 gauge)

Probably he will have the following:

candle
white cardboard (3 × 5 inch file card)
clothespin
aluminum foil
wick materials of various sorts
medicine dropper

PROCEDURE AND RESULTS

(a) If the student tries a few different positions, he should be able to conduct the unburned gas up and out of the tube, where it can be lighted.
(b) Since little or no unburned gas is present, the tube will not light, in contrast to (a).
(c) A few trials will surely give successful relighting of the candle, since the hot vapor will continue to rise for a short time after the flame is blown out. With practice it is possible to relight the candle by holding the match as far as 5 cm away from the wick.
(d) A ring-shaped pattern will show on the cardboard. The central part of the flame is not hot enough to scorch the cardboard.
(e) Results will depend on the ingenuity of the experimenter. An occasional student may recall that if paraffin is hot enough it will burn without a wick (Expt. 2). Among the properties of a good wick, which the student should note, are: a degree of flammability and, most important, capillarity.
(f) The movement of the tiny carbon particles shows flowing currents in the melted wax and may help the student realize that the liquid is flowing up the wick.
(g) This involves a rather delicate balance between the size of the wick, the ease with which the wax is melted, and whether the coil is effective in drawing away the heat fast enough to put out the flame. Observations may vary with different coils.
(h) Student experience. The aluminum probably reflects enough heat such that the melted wax solidifies, cutting off the supply of wax.
(i) Same as (h).
(j) Since the water cools the melted paraffin and blocks its movement up the wick, this is an effective way to put out the candle.

POSTLAB DISCUSSION. None—although you will want to comment individually to students who turn in reports. You may also sometimes refer to findings of this experiment if you know that some of your students have done it.

QUESTIONS AND EXERCISES

1. Will a candle of larger diameter produce a larger flame? How can you construct a candle so that it will produce a larger flame? Test your hypothesis by experiment.

   Answer: It will not unless the wick also is larger. It is possible to construct a hollow wick candle that produces a larger flame. Multiple wicks may be used.

2. List as many of the necessary properties of a good wick material as you can.

   Answer: A good wick material must be easily "wet" by the melted candle material and must be combustible so as to burn away as the candle is used up.

3. Write a paragraph describing *what you think* is taking place within the candle flame. Justify your arguments with experimental evidence. Propose "answers" to as many of the introductory questions as you can.

   Answer: When a candle is lighted, the burning match supplies enough heat to cause the candle material to melt and wet the wick. The melted substance is further heated by the match and vaporized into a gas. The gaseous candle material is mixed with air and, upon reaching the kindling temperature, ignites. A chemical reaction between the candle wax and the oxygen in the air then begins, releasing heat and producing warm carbon dioxide and water vapor. The hot gases produced rise upward, and cooler air is drawn in from the bottom. The air mixes with more vaporized candle material, which is then heated to the kindling temperature. As these gases are heated and partially burned, carbon particles are produced and heated to incandescence, causing the yellow, luminous portion of the flame. These incandescent particles slowly "burn" to form carbon dioxide.

   The size of the flame depends upon the melting point of the wax and upon the amount of fuel available per unit of time, which in turn depends upon the properties of the wick. The larger the wick, the larger the flame.

A QUESTION TO WONDER ABOUT

How is the solid wax, which is composed of carbon and hydrogen, transformed into the products of combustion?

Answer: Let the students wonder for a while. The following discussion contains the answer.

DISCUSSION. (This material is available for your use in discussion. Probably not all of it would be used with all classes.) The common paraffin candle is made of a white, wax-like substance consisting of a mixture of hydrocarbons that melt between 45°C and 65°C. This material is derived from the oil fraction during the fractionation of petroleum, and consists of straight chain hydrocarbons from about C_{20} to C_{35}. The chain may also contain methyl branches. To initiate the burning of the candle, a wick made of cotton fibers is embedded in the wax. The wick ignites first, and in turn melts some wax at the top of the candle. Capillary action then draws the melted wax up the wick. As the liquid rises, it becomes heated sufficiently to vaporize. Thus, it is the paraffin vapor that is actually burning.

A candle flame is considerably more complex than is apparent from superficial examination. When combustible vapors or gases reach their kindling temperatures, a flame results. The luminosity of this particular flame depends upon the solid particles that reach incandescence and glow. Whether a hydrocarbon flame will be luminous depends upon the extent of combustion. Flames generally consist of a number of zones, the colors of which provide a clue to the degree of oxidation.

There are three distinct zones in the candle flame. The innermost zone is dark in color and consists largely of unburned hydrocarbons. In a part of Expt. 4a, the student draws off some of this unburned gas and ignites it. The middle zone is generally yellow in color and consists of solid carbon particles produced by incomplete combustion of the hydrocarbons. When these solid particles are heated to high temperatures, they glow, radiating yellow light. It is fairly simple to show the presence of carbon in this yellow zone by condensing it on a cold, light-colored object. The outermost zone of the candle flame is pale blue. The abundance of oxygen in this zone permits almost complete combustion of the hydrocarbons, to form water and carbon dioxide. This zone is the hottest, reaching about 1400°C. The temperature in the luminous region is 1100–1300°C; in the dark zone, 700–1100°C, being coolest near the wick.

It has already been pointed out that the function of the wick is to provide a steady supply of liquid paraffin. The wick's fibrous structure permits the melted paraffin to be drawn upward by capillary action. The student should not fail to observe the liquid in the bowl of the candle. When this liquid is identified, he will appreciate this point.

It has been shown that in the candle flame, a series of phase changes occurs in a chain-like fashion. Solid paraffin is melted to a liquid, which in turn vaporizes and burns. The extent of combustion (color of the flame) depends on the oxygen supply. Any condition which breaks the chain will cause the candle flame to go out. It is commonly thought that blowing puts out a candle flame because the area around the flame is cooled below the kindling temperature of the flame. If this were so, candles would not burn in very cold regions. It is more likely that blowing upsets the fine balance of conditions necessary for the flame to function.

EXPERIMENT 5 HEAT EFFECTS

PURPOSE. To contrast the energy involved in a phase change and a chemical change. To provide experience in a quantitative investigation.

PRELAB DISCUSSION (10 MINUTES; ON THE DAY BEFORE LAB)

Exhibit the laboratory setup for both parts of the experiment. Demonstrate the proper use of both the platform and centigram balances. Be sure to point out:

(a) Proper care of balances.
(b) Proper weighing technique. The balance arm should always swing free when making a reading. Note that the swing of the pointer with and without load should be the same. The rest point should be near zero.
(c) The reason for numbering the balances. No two balances are identical.

One possible exercise the students could use at the beginning of the laboratory period, before starting the experiment, is the following (to be used only if enough balances are available such that time will not be wasted. The first two weighings have to be done as part of the experiment):

(a) Weigh the candle and lid on a centigram balance, and record the weight to the nearest 0.01 g.
(b) Weigh the can on the platform balance, and record the weight to the nearest gram.
(c) Weigh the candle, lid, and can on the platform balance, and compare this weight to the sum of the individual weighings. This gives a check on gross errors.

These students doing Part II should weigh the test tube containing wax and the empty 250 ml beaker. Avoid any discussion of uncertainty in measurement and in derived quantities until the postlab discussion. Caution students to avoid getting soot on clothes.

TIMING. This experiment should come after Expt. 4.

EQUIPMENT NEEDED (PER STUDENT; HALF OF THE CLASS WILL DO PART I; HALF WILL DO PART II)

PART I

candle mounted on a lid
balance (±0.01 g)
balance (±0.1 g)
ring stand, ring
thermometer, −10°C to 110°C
2 or 3 ice cubes
6 mm glass rod, 15–20 cm long

PART II

18 × 150 mm test tube containing 10 g of wax
18 × 150 mm test tube (tare)
balance (±0.01 g)
balance (±0.1 g)
ring stand, ring, wire gauze
burner
2 250 ml beakers
test tube holder

From home, bring:

1. A large fruit juice can with openings for air around the base and both ends removed, as illustrated in Expt. 5, Figure 5-3. See lab hint 1.
2. A small can (10–17 oz) with two holes at opposite sides, just below the rim of the open end (illustrated in Expt. 5, Figure 5-2). See lab hint 1.

TIME REQUIRED. A full 45 to 50 minute period. With each student doing just one part, some may have time to repeat the experiment.

PART I

About 20 minutes are needed to change the temperature of 350 g of water about 30°, as described in procedure (f), Part I.

PART II

About 5–10 minutes are needed to melt the wax, if the water bath is heated from room temperature. After the slightly cloudy wax is placed in the water bath, about 5 minutes are needed before the highest water temperature is obtained. Best procedure is to start water heating (part e) first, then do weighings, etc.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. Make the assignment to bring cans from home several days in advance of experiment day. One class set of cans may be used for all classes. Punch holes in the soup cans before class in order to save time and to avoid accidents. Use an ice pick to start the hole, and enlarge it with the end of a file. Instruct the students to punch holes in the large juice cans with a beer can opener before removing the bottom of the can. An alternate method for obtaining a draft through the "chimney" is to elevate the can by placing it on three rubber stoppers.
2. If the cold water from the tap is 10 or 15°C below room temperature, ice will not be needed in procedure (e), Part I.
3. Select "matched sets" of 18 × 150 mm test tubes from the same "lot." Then put about 10 grams of wax chips into one of the tubes, and melt it. Mark the other tube for use as a tare. On the day of the experiment, supply each student with a matched pair of test tubes, and warn him to take care of the sets because subsequent classes will use the same sets. This procedure is recommended in order that large numbers of test tubes will not be "dirtied" with wax.
4. In procedure (e), Part II, tin cans may be used for the hot water bath if beakers are not available.
5. Half-pint jars or cans may be substituted for the 250 ml beakers used as calorimeters in Part II, procedure (c).

POSTLAB DISCUSSION. This experiment provides an excellent opportunity to discuss uncertainty both in measurements and in calculated quantities. Begin the discussion by calling for the student values for calculated heat of combustion and heat of solidification. Ask the students about the uncertainty involved in the calculated value. Why is the heat of combustion known only to about ±300 cal/g, and the heat of solidification only to about ±10 cal/g?

To answer this question, first develop the idea of uncertainty in a measured quantity, as discussed in Chapter 1 of the Textbook and by referring to the table in Appendix 4. Using student data from the experiment, go through the sample calculations as follows:

SAMPLE CALCULATIONS. PART I

A. WEIGHT OF CANDLE BURNED

Weight of candle before	32.48 ± 0.01 g
Minus weight of candle after	31.23 ± 0.01 g
Weight of candle burned =	1.25 ± 0.02 g

Illustrate this calculation by using the extremes to determine the uncertainty.

$$\begin{array}{lrlr} \text{maximum} & 32.49\text{ g} & \text{minimum} & 32.47\text{ g} \\ & \underline{-31.22\text{ g}} & & \underline{-31.24\text{ g}} \\ & 1.27\text{ g} & & 1.23\text{ g} \end{array}$$

These extremes give an average value of 1.25 ± 0.02 g.

B. WEIGHT OF WATER HEATED

$$\begin{array}{lrl} \text{Weight of can plus water} & 401 \pm 1\text{ g} & \text{(using uncertainty specified in Experiment)} \\ \text{Minus weight of can} & \underline{80 \pm 1\text{ g}} & \\ \qquad \text{Weight of water heated} = & 321 \pm 2\text{ g} & \end{array}$$

$$\begin{array}{lrlr} \text{maximum} & 402\text{ g} & \text{minimum} & 400\text{ g} \\ & \underline{-79\text{ g}} & & \underline{-81\text{ g}} \\ & 323\text{ g} & & 319\text{ g} \end{array}$$

These extremes give an average value of 321 ± 2 g.

C. TEMPERATURE CHANGE OF WATER, Δt

$$\begin{array}{lr} \text{Temperature of water after} & 40.2 \pm 0.2°\text{C} \\ \text{Minus temperature of water before} & \underline{10.2 \pm 0.2°\text{C}} \\ \Delta t = & 30.0 \pm 0.4°\text{C} \end{array}$$

$$\begin{array}{lrlr} \text{maximum} & 40.4°\text{C} & \text{minimum} & 40.0°\text{C} \\ & \underline{-10.0°\text{C}} & & \underline{-10.4°\text{C}} \\ & 30.4°\text{C} & & 29.6°\text{C} \end{array}$$

These extremes give an average value of 30.0 ± 0.4°C.

D. QUANTITY OF HEAT REQUIRED TO WARM THE WATER

This is given by

$$(\text{weight of water}) \times \Delta t$$

Again using extremes from (B) and (C) we obtain:

$$\begin{array}{ll} \text{maximum} & 323 \times 30.4 = 9819\text{ cal} \\ \text{minimum} & 319 \times 29.6 = 9442\text{ cal} \\ \text{average} & (321 \pm 2\text{ g})(30.0 \pm 0.4°\text{C}) = 9631 \pm 189\text{ cal} \end{array}$$

E. HEAT OF COMBUSTION PER GRAM OF WAX

This is given by

$$\frac{\text{quantity of heat from combustion}}{\text{weight of candle burned}}$$

We obtain

$$\begin{array}{ll} \text{maximum} & \dfrac{9800\text{ cal}}{1.23\text{ g}} = 7970\text{ cal/g} \\[2ex] \text{minimum} & \dfrac{9400\text{ cal}}{1.27\text{ g}} = 7400\text{ cal/g} \\[2ex] \text{average} & \qquad\qquad 7685 \pm 285\text{ cal/g} \end{array}$$

Since the uncertainty is in the hundreds place, the 6 (and the 8 and the 5) is uncertain in the value 7685. Therefore, the calculated value and the uncertainty are rounded off to 7700 ± 300 cal/g.

SAMPLE CALCULATIONS. PART I[1]

A. WEIGHT OF WAX

Weight of test tube plus wax 28.6 ± 0.1 g (using uncertainty specified in Experiment)
Minus weight of test tube 18.5 ± 0.1 g
Weight of wax = 10.1 ± 0.2 g

	maximum		minimum
	28.7 g		28.5 g
	−18.4 g		−18.6 g
	10.3 g		9.9 g

B. WEIGHT OF WATER

Weight of beaker plus water 247 ± 1 g
Minus weight of beaker 89 ± 1 g
Weight of water = 158 ± 2 g

	maximum		minimum
	248 g		246 g
	−88 g		−90 g
	160 g		156 g

These extremes give an average value of 158 ± 2 g.

C. TEMPERATURE CHANGE OF WATER, Δt

Temperature of water after 24.6 ± 0.2°C
Minus temperature of water before 22.0 ± 0.2°C
$\Delta t =$ 2.6 ± 0.4°C

D. QUANTITY OF HEAT REQUIRED TO WARM THE WATER

This is given by

$$(\text{weight of water}) \times \Delta t \times (\text{heat to change 1 g by 1°C})$$

Using values obtained before, we find

maximum $160\text{ g} \times 3.0°\text{C} \times 1\text{ cal/g°C} = 480\text{ cal}$
minimum $156\text{ g} \times 2.2°\text{C} \times 1\text{ cal/g°C} = 343\text{ cal}$

thus

$$(158 \pm 2\text{ g})\,(2.6 \pm 0.4°\text{C})\,(1\text{ cal/g°C}) = 412 \pm 69\text{ cal}$$

Since the uncertainty goes as far as the number of tens involved, the rounded off number is 410 ± 70 cal.

E. HEAT OF SOLIDIFICATION OF THE WAX

This is given by

$$\frac{\text{quantity of heat given up by solidifying wax}}{\text{weight of wax}}$$

Using values from previous calculations, we have

maximum $\dfrac{480\text{ cal}}{9.9\text{ g}} = 48\text{ cal/g}$

minimum $\frac{340 \text{ cal}}{10.3 \text{ g}} = 33 \text{ cal/g}$

thus

$$\frac{410 \pm 70 \text{ cal}}{10.1 \pm 0.2 \text{ g}} = 41 \pm 8 \text{ cal/g}$$

After this detailed discussion of uncertainty, assign the reading on uncertainty in the Textbook and in Appendix 4 of the Laboratory Manual. Encourage the students to recalculate their values for Expt. 5 using uncertainty. Do not expect all students to become expert in the use of uncertainty after this brief exposure. Adequate experience will be provided in subsequent quantitative experiments.

Call attention to the ratio combustion heat/melting heat. Ask the students to wonder about this ratio.

Table 1-II. **Comparison of Combustion and Melting Heats**

Substance	Heat of Combustion (cal/g)	Heat of Melting (cal/g)	Ratio
Ethyl alcohol *(l)*	7,200	25	290
Benzoic acid *(s)*	6,900	34	200
Methyl alcohol *(l)*	5,300	16	330
Phenol *(s)*	8,100	29	280
Stearic acid *(s)*	9,500	48	200
Paraffin *(s)*	~10,000	35	290

Table 1-II reveals that the heat of combustion is always larger than the heat of melting and that the range is considerable. The difference between these energies makes it profitable to identify two kinds of change: chemical changes and phase changes. It is important that the student realize why we differentiate chemical and phase changes: because the energy effects are extremely different. It is logically incorrect to say that the energy effect is larger in combustion than in melting *because* one is a chemical change and the other is a phase change. Although there are other properties which make it useful to differentiate chemical and phase changes, the most important is the energy effect.

Later, in Chapter 2, and then in detail in Chapter 16, the energy difference is shown to provide the basis for identifying chemical bonds. Molecules consist of a fixed number and arrangement of atoms held in position by chemical bonds. The rupture of these bonds requires high energy, which is characteristic of the chemical change. Again we have the same logical connection. We differentiate chemical bonds from weaker van der Waals attractions because the energy required to overcome the two types is so different.

QUESTIONS FOR EITHER PART I OR PART II

1. Considering the assumptions made in either the "heat of solidification" or "heat of combustion" calculations, would you expect your results to be lower than or higher than the accepted value? Explain.

Answer:

Heat of combustion.

Since we assumed all the heat from the burning candle was used to heat only the water, when actually some was used to heat the cans and some was lost to the air, the calculated heat of combustion should be lower than the accepted value.

Heat of solidification.

A small amount of heat was required to raise the temperature of the beaker. Neglecting this factor made the calculated amount of heat slightly less than the actual value. The solid wax and the test tube gave up some heat in cooling from the solidifying temperature to the final temperature when removed from the bath. Since this small amount of heat was neglected in the calculations, the value found for the heat of solidification was slightly higher than it should be. Since one factor tended to make the heat of solidification less than the accepted value, and since the other factor tended to make it more, we are unable to say in which direction the net result would be without further calculation.

2. Compare the class averages for heat of combustion and heat of solidification. How much larger is one than the other?

   Answer: If we use the sample data for comparison, the heat of combustion is about 190 times larger than the heat of solidification.

A QUESTION TO WONDER ABOUT

Why is the heat of combustion so different from the heat accompanying the phase change?

Note to teacher: The student is not ready for a detailed discussion of this question at this time. Reference will be made back to the question later in the course, when the student's background will give him more of a basis for understanding.

ADDITIONAL INVESTIGATIONS

1. Devise an experiment to measure the heat effect for the phase change—gas to liquid or liquid to gas—for some suitable substance.

   A procedure is often included in physics lab manuals. Water is the simplest (and safest) liquid to study. Allow steam to condense in a known weight of water and measure Δt. Find the weight of steam condensed by weighing the apparatus with the condensed steam.

2. Devise suitable refinements in Part I of Expt. 5 to eliminate the major sources of error you encountered. Determine the heat of combustion of a pure substance, such as stearic acid, and compare your results with data found in the literature.

   Loss of heat to the surroundings is probably the major error. It can be lessened by insulation (dead air space, asbestos, etc.) and by cutting down on liquid evaporation. For pure substances to be tested, the materials suggested for unique candles (see next page) are good.

ADDITIONAL NOTES

The use of a wall chart as suggested in the Introductory Guide to the Laboratory Manual (p. 5) is very important for this experiment, since by observing the results of a number of determinations of the heat of combustion and heat of solidification of the candle wax the student will get a better understanding of this experiment. Such compilations give a basis for discussing both the accuracy and the precision of measurement possible in this case.

HOW TO MAKE A CANDLE

It is desirable to have some unique candles for a demonstration with the postlab discussion of Expt. 2, with Expt. 4, and as an extension of Expt. 5. Many substances may be used, but the following are recommended for the reasons listed.

1. Naphthalene or benzoic acid—burns with a very smoky flame;
2. Dimethyloxalate—almost colorless flame;
3. Octadecanol, cetyl alcohol (C_{16}) or other such alcohol—burns with a bright flame and almost no liquid "drip."

You may purchase wick material from hobby shops, or you may use wicks from discarded candles. Weight the wick with a small piece of lead, and adjust it to hang in the center of a small tube. The wick may either be suspended from a test tube rack, held in place by a clothespin, or tied to a wood splint resting on the top of the mold.

Small vials make good molds. Discarded glass medicine containers are good, as are the plastic ones if their melting point is above that of the substance being used for the candle. Glass tubing tightly closed with a cork also works. The wick can be fastened to the cork.

Pour the melt into the tube. Hardening may be speeded by placing the tube in cold water or in a refrigerator. Since most liquids contract when solidifying, plan to add more liquid after partial cooling. To free the candle, dip the mold in hot water.

These pure substances are likely to crumble as they crystallize, and in some cases sublime. To limit these undesirable effects, the candle may be dipped in a fairly high-melting paraffin to coat the outside.

A hollow wick is interesting in both the paraffin and naphthalene or benzoic acid candles in that air can be blown through it to show the effect of an abundant air supply. Most cotton shoestrings are tubular. To make a candle with a hollow wick, slide a piece of shoestring around a small glass rod; place this in the mold; and pour the liquid into the mold. When the candle has hardened, remove the glass rod.

Supplementary Material

Books

1. THE CHEMICAL HISTORY OF A CANDLE, M. Faraday, Viking, New York, 1960.

   This pocket book reproduces Faraday's famous series of "Christmas lectures" on the candle. It is suitable for all students.

2. INTRODUCTORY QUANTITATIVE ANALYSIS, A. R. Olson, C. W. Koch, and G. C. Pimentel, Freeman, San Francisco, 1956, Chapter 5.

   QUANTITATIVE ANALYSIS, Pierce, Haenisch, and Sawyer, Wiley, New York, 1958, Chapter 6.

   Each chapter deals with uncertainty and how to express it. Significant figures, rounding, propagation of error, accuracy, and precision are other topics. The better student can read these with profit.

3. SCIENCE AND HUMAN VALUES, J. Bronowski, Harper (Torchbook, Science Library TB505), New York, 1959.

   A philosophical essay about science and its basic tenets. Good for teachers and a few of the best students.

4. EXPERIMENTATION AND MEASUREMENT, W. J. Youden, National Science Teachers Association, Scholastic Book Services, *Vistas of Science* 2, New York, 1962.

   A simple explanation of the treatment of data through the use of examples from student experiments. Valuable for the teacher and for any student interested in the subject. Not highly mathematical.

PROGRAMMED SEQUENCES

There are two skills that are very helpful to students of science. These skills are not properly part of chemistry, hence we do not recommend they be taught in the CHEM Study course; but since they often give trouble, we have prepared some help for the student needing it.

These skills are expressing and manipulating numbers using powers of ten and using a slide rule. The first is used in the Textbook, and some explanation is given, along with a few exercises, in Laboratory Manual Appendix 5. The use of a slide rule does not come up explicitly, but of course it is a great help in doing the problems.

We have prepared some programmed sequences to help the *student teach himself* these topics. This technique (which you may have heard described as "machine teaching"—though our sequences require no machines) uses a series of questions, each a very small extension of the student's knowledge. After answering, the pupil checks the correct answer in the right margin and then moves to the next item. In theory, the quick affirmation of his answer (usually correct because of the small "steps") raises his confidence and reinforces his learning.

The intended procedure is that you determine by observation which students need help, then lend them the appropriate sequence for home study. Since the sequences themselves are not marked by the students, they can be reused as required. The sequences are:

Exponential Notation
- Powers of ten and exponential notation of numbers
- Shifting the decimal point
- Multiplication and division
- Extraction of square roots
- Addition and subtraction

The Slide Rule
- Reading the scales
- Multiplication
- Division
- Extraction of square roots

These programmed sequences may be ordered from W. H. Freeman and Co., 660 Market Street, San Francisco, California, 94104.

Background Discussion

THE ESSENCE OF SCIENCE

On page 7 of this guide, the essence of science is discussed and used to establish the tone for Chapter 1. In spite of all your efforts some students may give this chapter only superficial consideration, regarding it as too elementary. Any student who feels this chapter is too elementary has missed its message. His interest can probably be awakened by asking him such questions as the following:

1. According to Chapter 1, why is man curious? Why are you curious?
2. According to Chapter 1, an explanation reveals a hidden likeness to something alalready known. Can you think of explanations where this hidden likeness can be pointed out? Can you think of explanations where this definition of an explanation is not correct?
3. According to Chapter 1, there is uncertainty in *every* scientific statement about the environment. Can you think of a nontrivial statement about the environment in which there is absolute certainty? (A trivial statement might be, "On warming, a solid either melts or it does not.")
4. Some philosophers believe in the existence of scientific ideas that are surely true without the slightest bit of supporting evidence. Chapter 1 indicates that *every* statement of regularity is a paraphrase of experimental facts. Can you think of any scientific idea that you believe can be shown to be true without using any experimental facts. (Eliminate, without discussion, any proposal of a religious flavor.)
5. Can you think of a more sophisticated fable?

THE FABLE

Science actually moves forward in exactly the way the child developed his regularities regarding combustion. The fable contains some important notions set in a transparent example, in order that the reader can see every false step as it occurs. If a student feels the example is too elementary, ask him to think of a more sophisticated fable, and then examine his offering for the following ideas.

1. A theory or law need not be correct in every context to be useful in a limited context. (For example, in the woods, the rule "cylindrical objects burn" would be useful, since few nonflammable cylindrical objects are found in the woods.)
2. There is no assurance that a law established within a certain range of experience applies outside of this experience.
3. Implications of a law (predictions) lead to experiments outside the range of experience upon which the law was based.
4. Laws in agreement with presently known information may, nevertheless, be changed or abandoned in the future as additional experiments increase our knowledge.

Stress the idea that scientific advance does *not* involve a special process that is incomprehensible to most people. Though some people are better at the game than others, the process is understandable to all. Avoid giving science an air of mysticism through historical eulogies that emphasize the "stroke-of-genius" cliché. Instead, make it clear that the recognized genius is merely better at actions that we all can do. Imply that "Everyone can apply the scientific method; you may have to work a little harder, but why not try?"

Finally, stress that science is constantly changing as our knowledge increases. Science is not a completed structure but a growing one. Let the student see how exciting the future of science is to you, the teacher; make him aware that he can contribute to this future.

REGULARITIES: RULE, LAW, THEORY

The simple skeleton of scientific activity—observe; find regularity; find explanations (hidden regularities)—could be elaborated at great length.

Don't do this. Avoid encumbering this simple view. Let the student begin his study of science with a feeling of confidence that he will understand what he is doing.

To give an example, no semantic distinction is offered between a rule, a law, and a theory. They are all presented as expressions of regularity. Useful argument can be made in favor of a semantic distinction. The more abstract expressions of regularity are usually called "theories."

However, the likenesses among these statements of regularity are more important to an understanding of science than are their differences. Compare the *Law* of Conservation of Energy and the Atomic *Theory*. Why is one a law and the other a theory? Energy is a derived quantity, not a measured one. Temperature is measured, not heat. Velocity and mass are measured, not kinetic energy. Chemical energy is *never* measured—its existence is implied by the model that states that if heat is expended in bringing on a chemical change, some other, unseen form of energy must have been stored. In beta decay, energy is indeed lost, but we "saved" the Law of Conservation of Energy by inventing an undetected particle, the neutrino. Thus the Law of Conservation of Energy is a model. It has great value because it aids us in correlating a wide variety of measurements: position, velocity, temperature, voltage, current, chemical composition. This is just the language we would apply to the Atomic Theory. It, too, is a model. It, too, has great value because it aids us in correlating a wide variety of measurements: *PVT* measurements, composition of substances, mass relations in reactions, crystal structures. We see that there is great likeness here.

In a real sense, even laws which seem to relate directly to measurements are models. Consider Boyle's Law. The rule $PV = a\ constant$ doesn't really fit any gas perfectly. Deviations from this behavior are small but measurable at normal conditions. At higher pressures, the deviations become large (see Chapter 4). Near its critical conditions, a gas doesn't follow Boyle's Law at all. Neither NO_2 nor H_2O follows the law even under normal conditions (we "explain" this by saying that association occurs). The law $PV = a\ constant$ really applies, then, to a model gas (an "ideal" gas). This model has great value, because it aids us in correlating pressure-volume measurements on many real gases over a wide temperature range.

We see that these laws and theories have a common function: they correlate results of measurements and, in so doing, aid us in dealing with the knowledge given us by these measurements. If the student comprehends the nature of this common function, he will have no difficulty realizing for himself that this correlation can be carried out at different levels of abstraction.

CHEMISTRY UNDEFINED

Chapter 1 concludes with a definition of science (see Textbook, p. 15), that clearly includes chemistry. An explicit definition of chemistry is omitted, though it is defined, by implication, under the heading *Review* (Textbook, p. 15) as "what chemists do."

How do other authors define chemistry? They usually begin with words of caution about the danger of trying to convey the scope of chemistry in a definition. Then the definition may be offered that chemistry is the science concerned with structure, properties, reactions, and energy effects associated with substances. There are two quite different problems raised by this definition. The first is that some of the words in the definition are rather meaningless to a person who has studied no chemistry (for example, consider the word *substance*). Why give the definition at this time if it is unintelligible? The second problem is that the definition can be construed to include all of science.

Mature scientists can do better in defining chemistry because they have more vocabulary to aid them. Since we accept the nuclear atom, we can see that a chemist is generally concerned with the behavior of matter associated with the electrons surrounding the nucleus. He is, furthermore, generally concerned with relatively pure substances. With this general background, he may attack any problem on which he can make progress. These problems, then, become part of chemistry.

For example, as chemical knowledge has increased, it has become possible to apply standard methods of chemistry to biological systems. There is no longer any question that the same principles that govern all chemical systems are operative in living systems. A substantial part of biology is now taken to be chemistry; it is called biochemistry. Another example is provided by nuclear chemistry. The determination of the fate of a nucleus on bombardment or decay is frequently a problem requiring a deep knowledge of chemistry. This being so, chemists are better equipped to solve some problems concerned with the structure of the nucleus than are physicists. Hence a substantial part of nuclear physics is now within the purview of chemists; it is called nuclear chemistry.

Thus chemistry *is* "what chemists do," and it is a changing thing. What is outside of today's definition of chemistry may be within chemistry by the time today's student is a practicing chemist. We can say for certain, however, that chemistry will always remain within the definition given in Chapter 1: "· · · man's systematic investigation of his environment."

EXPERIMENT AND THEORY

All scientific knowledge is based upon our knowledge of the environment as derived from experimental observations. Hence this course places great emphasis on the experimental aspects of chemistry. A valid picture of chemistry must include direct laboratory experience. Furthermore, this laboratory work must be carefully integrated into the course to show the relationship between laboratory results and the increased understanding that stems from them. There is distinct loss if the timing of experimental work is governed by the expediency of laboratory availability. The timing should aim to furnish the student with *prior*, relevant experience that he can bring to mind when a given principle is presented. He must be given the opportunity to experiment without having a firm expectation of the outcome; he should have the opportunity to discover principles himself, through his own laboratory work. Through prior participation in appropriate experiments, a student will fully realize how principles are derived and why they are retained. For these reasons the student is placed in the laboratory on the first day of the course.

PREDICTION

One of the most appealing rewards of scientific activity is the development of predictive power. Let us examine the various kinds we can attempt: repetition, interpolation, and extrapolation.

Repetition of an experiment is expected to yield the same result obtained earlier. Consequently, repetitious experiments offer the most elementary opportunity for prediction. In fact, science is built upon the assumption (and the corroborating experience) that a scientist can predict with confidence the result of an experiment that duplicates an earlier set of operations. If the important conditions are known and properly controlled, then this result should be close to the earlier result. If a large difference is found, then some important (but perhaps unknown) condition is not being allowed for. As the experiment is repeated many times, the likelihood decreases that such an important condition will go undiscovered.

Interpolation is a higher form of prediction. A succession of two or more experiments in which one condition is varied systematically provides a basis for interpolation within the range of the variation. There always remains a possibility that an unsuspected behavior occurs at intermediate values of the variable condition. The likelihood that this will happen decreases as we increase the number of measurements used to establish the trend. Of course the same limitations mentioned for repetitious experiments apply here, too. The probability of a surprise decreases as the explanation of the trend gains support by fitting a wider range of data.

Extrapolation represents the true realm of prediction. What can a scientist predict with confidence that is outside his range of experience? The term "with confidence" is the key expression here. The answer is that the further he goes beyond his range of experience, the less confidence he can enjoy. The confidence that an extrapolation deserves is fixed by the weight of the experimental support for the basis of extrapolation and by the distance of the extrapolation. This is true whether one is predicting the *PV* behavior of ammonia at high pressure from measurements made at lower pressures or predicting a quantum-mechanical result for the nucleus on the assumption that quantum mechanics holds for nuclei because it holds for atoms. A theory which is used for prediction without *any* experimental basis deserves no confidence whatsoever.

Examples are legion. Consider Table 1-III, which shows the *PV* behavior of a mole of ammonia between 0.1000 and 0.6000 atmosphere. The regularity $PV = 22.37 \pm 0.05$ permits one kind of prediction: interpolation over the range 0.1–0.6 atmosphere pressure with uncertainty near ±0.05, or 0.25%. It also provides a basis for extrapolation: at 1.000 atmosphere, the volume is expected to be 22.37/1.000 = 22.37 liters; at 2.000 atmospheres, it is expected to be 11.18 liters; at 4.000 atmospheres, it is expected to be 5.592 liters, and at 5.000 atmospheres, it is expected to be 4.474 liters. Do all of these expectations deserve the same confidence? By no means. The further we depart from the area of our experience, the less confidence we can enjoy. To show that this is so, consider Table 1-IV, which contrasts our extrapolated expectations with very accurate experimental results. The experiments up to 4.000 atmospheres do show a growing deviation from our expectations. In retrospect, all we can say is that we should not feel chagrin that this is so—after all, we made an excursion from the range in which $PV = 22.37 \pm 0.05$ is known to hold. Outside this range of experience we were relying upon hope alone. But, more important, observe what happened to the prediction at 5 atmospheres! There is no connection at all between the expected volume, based on $PV = 22.37 \pm 0.05$, and the actual volume of the liquid that has formed. From gas measurements alone, this behavior could not be anticipated. Furthermore, the ornate model that explains so well the behavior of gases (the kinetic theory) provides no basis for expecting the discontinuity of behavior. In fact, the model gives us a false confidence in extrapolation.

Table 1-III

PV Behavior of 17.0 g of Ammonia Between 0.2000 and 0.6000 Atmosphere at 0°C

P (atm)	*V* (liters)	*PV*
0.1000	224.4	22.44
0.2000	111.6	22.32
0.4000	56.02	22.41
0.6000	37.20	22.32
	Average	22.37 ± 0.05

Table 1-IV

Contrast of Extrapolations (from Table 1-III) with Experimental Values for 17.0 g Ammonia at 0°C.

P (atm)	V_{calc} (from $PV = 22.37$)	V_{expt}	% Error in Prediction
1.000	22.37	22.264	0.5
2.000	11.18	11.051	1.2
4.000	5.592	5.4520	2.6
5.000	4.472	0.02	catastrophically large

There are many such familiar examples—behaviors observed so often before that we are no longer surprised by them. For example, if asked to extrapolate the density of a newly discovered solid substance to a temperature above the explored range, you would undoubtedly qualify your answer by saying "provided it hasn't melted already." You are used to this discontinuity in the behavior of a solid. Would you have the same doubts about extrapolating this *downward* in temperature? You should have. Many solids change crystal forms as temperature is lowered. Electrical conductivities of metals provide an even more dramatic example.

High-temperature measurements of electrical conductivities give no basis whatsoever for expecting the complete and sudden loss of all resistance by the superconducting metals. One of the most advertised erroneous extrapolations was the assumption that the classical laws of physics held on the molecular level. Progress in elucidating the behavior of matter on the atomic level had to await Bohr's courage in recognizing that extrapolating classical physics to the microscopic domain need not be correct.

Despite all this, we are continually hearing of successful predictions by theory. These do occur, and they represent the "special reward" we have associated with the discovery of a "hidden likeness." With the aid of a model, it may become apparent that two types of behavior imply a third type. Then we may say that we can predict the third type. In a real sense, however, we see that the model (or theory) has aided us in interpolating—that is, in filling in as yet unexplored areas which are within the bounds implied by previous experiments.

An elementary example would be the prediction of *PT* behavior of a gas from a study of the *PV* and *VT* behavior. A more abstract example would be the prediction of acoustic properties of a gas from the kinetic theory established on the basis of observed *PVT* behavior of a gas.

HOW THEORY LEADS TO EXPERIMENT

The foregoing discussion is concerned with the limited ability of a theory to predict outside of the area in which it is known to agree with experiment. It should not, however, becloud the value of a well-substantiated theory. Several times in the Textbook the student is reminded that science could not advance if our overwhelming mass of knowledge were not ordered with the aid of theories. Our power in dealing with the environment must be attributed to the principles that give coherence to different types of information.

His ability to recognize and to use the operative principles distinguishes the scientist from the inventor. An inventor is a person who proceeds on an empirical basis, relying mainly on his own experience. A scientist, on the other hand, proceeds in his search for and application of new knowledge with cognizance of the broad generalizations of the fundamental principles of science. In so doing, he brings to his own use all of the accumulated knowledge that lies behind these principles. In effect, he multiplies his own ability by the number of scientists who have preceded him.

Thus the scientist is continually guided and aided by his theories. As a result, he avoids conducting fruitless experiments; instead he proceeds quickly to crucial experiments extending beyond the firm expectations that can be based on earlier studies.

THE EVALUATION OF DATA

To evaluate and interpret data in an intelligent way, a student must have a clear understanding of uncertainty in measurements. He must realize that measurements are never exact. The reliability of data is fixed by the nature of the equipment used, the method, and the skill of the experimenter. Under any set of conditions, though, there is some limit beyond which finer measurements cannot be made.

At the start of your discussion of data, it is a good idea to distinguish between two terms which are used in science with a clear-cut differentiation—precision and accuracy. Precision refers to the extent that a measurement deviates from the average of many measurements; it measures reproducibility. Accuracy refers to the extent that a measurement agrees with a true, known value. These two terms have familiar counterparts in educational testing: reliability and validity. The degree to which a set of test questions correlate with each other in identifying a group of students (for example, according to ability, achievement, and so on), measures the reliability of the test. This is a matter that can be clarified by rather straightforward statistical methods. It is quite another matter, however, to determine the validity with which the test identifies the student group actually desired.

In the same way, an experimental technique designed to furnish, say, the molecular weight of a gas will have some precision limitations fixed by the actual manipulations required. These precision limitations determine the degree to which successive measurements reproduce each other. As is true of test reliability, such limitations can be estimated readily by performing a sufficient number of experiments. Furthermore, the effect on the uncertainty can be reduced by improving technique and, usually, by averaging the results of many experiments. In addition, however, there remains the quite separate question of whether the method, whatever its reproducibility, measures the quantity actually desired (in this example, the molecular weight). Thus, if a gas density measurement is made, it may be quite reproducible if conditions are carefully controlled, but if the gas is not a perfect gas, Avogadro's Hypothesis is not perfectly applicable! Then there is an inherent error in the method, and this error fixes the *accuracy* of the measurement.

For this example (a gas density molecular weight) experience with many gases furnishes a basis for estimating the extent to which gas imperfections are liable to cause deviations from Avogadro's Hypothesis. Most gases under normal conditions are in accord with Avogadro's Hypothesis within 1%. Hence any given molecular weight determination must be assigned an uncertainty of about 1% because of *accuracy* uncertainty. In addition, there is an uncertainty due to reproducibility that depends upon the balance used, the accuracy of the volume measurement, the technique of flushing the container, and other experimental details. If several successive measurements fluctuate about 5% above and below the average, then the principal uncertainty arises from precision limitations. If, however, all of the operations are so much improved that the reproducibility uncertainty has been reduced to 0.1%, then the principal uncertainty must be due to the accuracy limitation arising from the assumption made regarding Avogadro's Hypothesis.

In general, the types of errors that arise from measurements can be segregated into two groups: those that affect precision and those that affect accuracy. The errors that affect precision are called *random* or *indeterminate errors*. These errors are due to poor equipment and to carelessness in making proper observations. They as often give a result that is too high as they do one that is too low. From the nature of these errors, it should be clear how they can be minimized: by greater care, by experience and practice, by improved apparatus, and so on. The errors that limit accuracy are called *systematic* or *determinate errors*. This type of error always affects the measurement in the same way, no matter how many times the measurement is made. Thus the error is reproduced with each determination. For example, if the zero-degree position on a thermometer is marked incorrectly, the use of this thermometer would introduce a reproducible error. The results obtained in a determination involving the use of such a thermometer could be extremely precise but not very accurate.

Repeating a measurement many times reveals the magnitude of the random errors. The average of many measurements tends to eliminate uncertainty due to random errors. On the other hand, repetitions of the same measurement neither reveal nor remove error caused by systematic errors. Only changes of the method of measurement will provide a clue to the probable accuracy. *A measurement with high precision does not necessarily have high accuracy.*

Usually reproducibility is measured, and as a result the uncertainty associated with precision can be stated. The uncertainty due to accuracy is less readily learned and is often unknown. In such a case, the uncertainty due to reproducibility is used to estimate the uncertainty quoted, *and it is identified as the precision.* Thus a molecular weight measurement might be stated to be 101 ± 3, accompanied by the explanation that "the results have a precision of 3%." The ± factor can be calculated as the average deviation from the average (as we have done in the examples) or as the standard deviation. Each of these clearly indicates that the uncertainty quoted is that associated with reproducibility. *It should not be inferred that doubt about the accuracy contributes nothing to uncertainty just because it is not mentioned.*

Sections 1-2.1–1-2.5 in this chapter show how to express uncertainty using significant figures or the symbol (±). Significant figures must be used with attention to the limitations listed hereafter. Students will have difficulties with the propagation of uncertainty through algebraic operations. Don't expect too much—instead, build their understanding through your repeated use of uncertainty calculations during the semester. Frequently remind the student of the meaning of significant figures—the number of significant figures shows all the digits that are certainly fixed by the numbers that were combined plus one more digit that is uncertain.

PROPAGATION OF UNCERTAINTIES IN A DERIVED QUANTITY

The Textbook treats the accumulation of uncertainty, as data are combined, in terms of the *maximum* possible uncertainty. The *probable* uncertainty has deeper significance. The probable uncertainty is smaller than the maximum possible uncertainty because only an unlikely coincidence will cause every error to reinforce. The maximum uncertainty, however, is more easily understood and is more simply estimated. Furthermore, it contains the conceptually important idea we wish to convey: *uncertainty in a derived quantity is fixed by the combined uncertainties of the components.*

The manner in which uncertainties propagate and combine depends upon the mathematical manipulations used. The examples that follow are given to display this dependence.

Addition and Subtraction

Suppose we are interested in z, the sum of two measurements $x \pm \Delta x$ and $y \pm \Delta y$.* The maximum possible error in z is obtained when the uncertainties Δx and Δy happen to reinforce.

The estimated value is

$$z = x + y$$

Thus the maximum possible value is

$$\begin{aligned} z + \Delta z &= (x + \Delta x) + (y + \Delta y) \\ &= (x + y) + (\Delta x + \Delta y) \\ \text{max. } \Delta z &= (\Delta x + \Delta y) \end{aligned}$$

Thus the *absolute uncertainty* in the sum z is simply the sum of the absolute uncertainties in the quantities added. (The probable value of uncertainty Δz would be given by $\sqrt{\Delta x^2 + \Delta y^2}$.)

Multiplication and Division

Suppose we are interested in the product, z, of two measurements $x \pm \Delta x$ and $y \pm \Delta y$.† The maximum possible error in the product is obtained when the uncertainties Δx and Δy reinforce.

The estimated value is

$$z = (x)(y)$$

Thus the maximum possible value is

$$\begin{aligned} z + \Delta z &= (x + \Delta x)(y + \Delta y) \\ &= \left[x\left(1 + \frac{\Delta x}{x}\right)\right]\left[y\left(1 + \frac{\Delta y}{y}\right)\right] \\ &= xy\left[\left(1 + \frac{\Delta x}{x}\right)\left(1 + \frac{\Delta y}{y}\right)\right] \\ &= xy\left[1 + \frac{\Delta x}{x} + \frac{\Delta y}{y} + \frac{\Delta x\,\Delta y}{xy}\right] \end{aligned}$$

For small relative uncertainties, both $\Delta x/x$ and $\Delta y/y$ are small, hence their product (the last term) can be neglected,

$$z + \Delta z = xy + xy\left(\frac{\Delta x}{x} + \frac{\Delta y}{y}\right)$$

Subtracting the estimated value $z = xy$ from each side, we obtain

$$\Delta z = xy\left(\frac{\Delta x}{x} + \frac{\Delta y}{y}\right)$$

or

$$\frac{\Delta z}{z} = \frac{\Delta x}{x} + \frac{\Delta y}{y}$$

We see that in multiplication the *relative uncertainty* in the product $\Delta z/z$ equals the sum of the relative uncertainties in the quantities multiplied. The probable value of relative uncertainty $\Delta z/z$ would be given by

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* All of the discussion of addition is applicable to subtraction.

† All of the discussion of multiplication is applicable to division.

$$\left(\sqrt{\frac{\Delta x^2}{x} + \frac{\Delta y^2}{y}}\right)$$

Other Mathematical Operations

Other mathematical relations, such as logarithms, exponentials, and trigonometric functions, require individual consideration. To illustrate this, consider the uncertainty cast into a function $z = e^x$ if x has an uncertainty Δx.

The estimated value is

$$z = e^x$$

Hence the maximum possible value is

$$z + \Delta z = (e^{x+\Delta x}) = (e^{\Delta x})(e^x) = (e^{\Delta x})(z)$$
$$\Delta z = (e^{\Delta x})(z) - z = z(e^{\Delta x} - 1)$$

or

$$\frac{\Delta z}{z} = e^{\Delta x} - 1$$

Thus we see that the *relative uncertainty* in z depends on the *absolute uncertainty* in x.

Summarizing, we see that uncertainty propagates through mathematical manipulations in a variety of ways:

In addition and subtraction, the *absolute* uncertainty in a sum is fixed by the *absolute* uncertainties in the components.

In multiplication and division, the *relative* uncertainty in a product is fixed by the *relative* uncertainties in the components.

In an exponential relationship, the *relative* uncertainty in the exponential is fixed by the *absolute* uncertainty in the exponent.

THE ADVANTAGES AND DISADVANTAGES OF SIGNIFICANT FIGURES

There are real advantages to the development of good habits in reference to significant figures. It is surely true that scientists generally use the appropriate number of significant figures, as determined by the criterion stated on Textbook p. 12, "The digits that are certain and one more· · ·." It is not true, however, that scientists generally use the number of significant figures either as a definitive statement about the uncertainty in a number or as a mechanism for estimating the propagation of uncertainty through mathematical manipulations. Instead, a quantitative statement is almost always accompanied by an explicit statement of the probable uncertainty computed from the uncertainties in the input data and taking due account of mathematical manipulations.

We can cite two specific advantages of the significant figure designation of uncertainty.

1. It provides an easy introduction to the existence of uncertainty.
2. It provides an easy basis for making a crude estimate of the uncertainty propagated through multiplication and division.

These advantages must be weighed against four disadvantages.

1. *Significant figures furnish only a rough estimate of uncertainty.* For example, consider the three numbers 0.50 ± 0.01, 0.90 ± 0.03, and 1.10 ± 0.07. In terms of significant figures, these would be written 0.50, 0.90, and 1.10, a notation that hides the fact that the uncertainties these numbers cast into a product would be, respectively, 2%, 3%, and 6%. Not only do the numbers expressed as significant figures fail to reveal that the uncertainty in 1.10 is three times that in 0.50; but they suggest that 1.10 is *less* uncertain.
2. *Significant figures omit reference to the accumulation of uncertainty as data are combined.* For example, the sum of 14 and 15 would be 29. All these numbers have two significant figures. However, if the addends are uncertain by ±1, the sum will be unknown to ±2. This absolute increase is not indicated at all by the answer 29.
3. *The rules concerning significant figures used for multiplication are not applicable to other manipulations, notably addition and subtraction.* In addition and subtraction, the number of significant figures is *not* fixed by the number of figures known for the least precise datum. For example, consider the addition of two weights,

$$w_1 = 1.10 \pm 0.01 \text{ g}$$

and

$$w_2 = 1000.0 \pm 0.1 \text{ g}$$

The sum,

$$w_1 + w_2 = 1001.1 \text{ g}$$

has five significant figures, and the number of significant figures is determined by w_2, though it has the larger number of significant figures. Contrast the subtraction of the weight of an empty flask, $w_1 = 160.02 \pm 0.01$ g, from the weight of the flask containing a sample, $w_2 = 160.83 \pm 0.01$ g. The difference, $w_2 - w_1 = 0.81 \pm 0.02$ g, has but two significant figures, not the same as either individual weight, w_1 or w_2.

4. *Even in multiplication, the usual rules of significant figures can give erroneous indications of uncertainty.* Consider the two examples

$$(0.90 \pm 0.01)(1.15 \pm 0.01) = 1.04 \pm 0.02$$

and

$$(1.01 \pm 0.01)(1.03 \pm 0.01) = 1.04 \pm 0.02$$

In these two products, the uncertainties are the same, but the rules for significant figures, rigorously applied, would require that we round off the first answer to two significant figures and retain three figures in the second.

Despite these limitations we feel that good habits in the use of significant figures should be encouraged. As often as feasible, the student should be encouraged to express uncertainty explicitly (by adding ± to each measurement) and to estimate uncertainty in sums and differences, always using an appropriate number of significant figures. In referring to the use of significant figures as a basis for estimating the propagation of uncertainty, it must be emphasized that the method is applicable only in a general sense to multiplication and division, and is decidedly not applicable to addition, subtraction, or other mathematical manipulations.

Remind the student that if he gives too many significant figures, he is making an erroneous scientific statement—he is saying more than he knows to be true, possibly misleading himself and others. Thus, the matter of expressing uncertainty is much more than a formal set of rules; it is as important a part of the result of measurement as the result itself.

Some question may arise about the use of slide rules and logarithms as computational tools. Point out that inexpensive slide rules give a precision of about 2–3 parts per 1000, whereas four-place logarithms provide a precision of about one part per 1000. The use of such tools limits the number of significant figures. Although students should not be forced to use computational tools, they should be encouraged wherever possible.

SOME OMISSIONS

Perhaps some omissions in the earliest chapters will seem unusual. They are omitted deliberately and with purpose.

1. Memorization of symbols: this, we feel, is tedious and should not be stressed. With the aid of the chart of names and symbols to remind him, the student will quickly learn the symbols which he commonly uses. Furthermore, the text systematically connects names and symbols.
2. History: we have placed emphasis on the contemporary aspects of chemistry. It is important to make the student keenly aware that he is preparing himself to deal with the scientific problems of today, not those of Dalton's time.
3. Eulogy: emphasis upon the "stroke of genius" tends to obscure the way in which science advances. It tends to exclude the student who feels no pretensions to genius. Emphasize instead that the great advances of chemistry made by the greatest of scientists can be understood by everyone, at least in retrospect. These great advances almost always are preceded by intensive, deliberate, and prolonged study.
4. Answers to some questions: some questions are raised and left unanswered in this chapter to make the student realize that there is a point to further study.

Answers to Exercises and Problems

Ex. 1-1. In Expt. 5, the weight of a sample of water is determined by subtracting the weight of the empty can from the weight of the can containing the water.

(wt water) = (wt can + water) − (wt empty can)

Suppose the weight of the can is 61 ± 1 grams and the weight of the can plus water is 406 ± 1 grams. Calculate the weight of the water and the maximum uncertainty in the weight caused by the uncertainties in each of the two weighings.

Answer

	Max.	Min.
406 ± 1 g	407	405
61 ± 1 g	60	62
345 ± 2 g water	347	343

Ex. 1-2. Calculate the uncertainty in the product $w \times \Delta t$ caused by the temperature measurement alone (assuming that the uncertainty in the 345 gram weight of water has been made negligible by more careful weighings). Calculate the uncertainty caused by the ±2 gram weighing uncertainty alone (assuming the uncertainty in the temperature change, 29.2°C, has been made negligible by use of a more sensitive thermometer). Compare these two contributions to the total uncertainty, about 200 calories.

Answer

Uncertainty caused by ±0.4 in Δt

$$345\,(0.4) = 138 \text{ cal}$$

Uncertainty caused by ±2 in w

$$29.2\,(2) = 58.4 \text{ cal}$$

About three-fourths of the uncertainty is caused by variation in Δt and one-fourth by variation in w. The relative uncertainties are in the same ratio.

Ex. 1-3. In Section 1-2.3 we multiplied 345 × 29.2 to obtain 10,074.0 calories.

(a) How many significant figures are there in the factor 345? In the factor 29.2?

(b) How many significant figures should be retained in the product, 10,074.0?

(c) Six figures are specified in the number 10,074.0—more than are warranted. "Round off" this number in accordance with your answer to (b). Compare your answer with the final result derived in Section 1-2.3, q = 10,100 ± 200 calories.

Answer

(a) Three, three.

(b) Three.

(c) 10,100—the same as obtained on Textbook p. 11.

Ex. 1-4

(a) Add the six values of $P \times V$ in Table 1-II and divide by 6 to obtain the average, $(PV)_{av}$.

(b) Now add a fourth column to Table 1-II showing the deviation of each $P \times V$ product from $(PV)_{av}$. Head this column with the word "Deviation," and calculate each entry by subtracting $(PV)_{av}$ from the measured value. For example, the second entry will be −0.6 (since 21.8 − 22.4 = −0.6

(c) When you have completed the column of deviations, add the column (disregarding algebraic signs) and divide by 6 to obtain an average deviation.

(d) Compare your calculations in (a) and (c) with the result given in Textbook Table 1-II,

Average = 22.4 ± 0.6.

Answer

(a) Sum = 134.2;

$$\frac{134.2}{6} = 22.366, \text{ or } 22.4.$$

(b)

$P \times V$	Deviation
22.4	0
21.8	−0.6
24.0	1.6
21.4	−1.0
22.2	−0.2
22.4	0

(c) The sum of the deviations (ignoring minus signs) is 3.4;

$$\frac{3.4}{6} = 0.566 \text{ or } 0.6$$

(d) Parts (a) and (c) give 22.4 ± 0.6.

ANSWERS TO QUESTIONS IN APPENDIX 4 OF THE LABORATORY MANUAL

Calculate the maximum uncertainty in each of the following.

1.
$$\begin{array}{r} 40.2 \pm 0.2^\circ\text{C} \\ -10.2 \pm 0.2^\circ\text{C} \\ \hline 30.0 \pm 0.4^\circ\text{C} \end{array}$$

2.
$$\begin{array}{r} 1500 \pm 10\ \text{cm} \\ 1500 \pm 10\ \text{cm} \\ 481 \pm 1\ \text{cm} \\ 481 \pm 1\ \text{cm} \\ \hline 3962 \pm 22\ \text{cm} \end{array}$$

3.
$$\begin{array}{r} 103.24 \pm 0.01\ \text{g} \\ -98.13 \pm 0.01\ \text{g} \\ \hline 5.11 \pm 0.02\ \text{g} \end{array}$$

4.
$$\begin{array}{r} 5.18 \pm 0.02\ \text{g} \\ +1.76 \pm 0.02\ \text{g} \\ \hline 6.94 \pm 0.04\ \text{g} \end{array}$$

5. How many significant figures are there in each of the calculated quantities of Exercises 1–4?

Answer: Three in each case.

6. Find the area of a rectangle measured to be 10.0 ± 0.1 cm by 2.5 ± 0.1 cm and calculate the uncertainty by each method (by using significant figures and by summing percent uncertainty). Make a drawing of the rectangle, shading in the area of uncertainty. Calculate the area of the shaded part. Compare this to the calculated uncertainty.

Answer

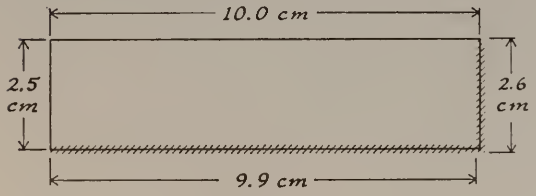
Area of rectangle:

% uncertainty

$$(10.0\ \text{cm} \pm 1\%)(2.5\ \text{cm} \pm 4\%)$$
$$= 25.0\ \text{cm}^2 \pm 5\% = 25.0 \pm 1.25\ \text{cm}^2$$

Significant figures

$$(10.0\ \text{cm})(2.5\ \text{cm}) = 25\ \text{cm}^2$$



Area of shaded part

$$\begin{array}{rr} \text{at bottom } (9.9\ \text{cm})(0.2\ \text{cm}) = & 1.98\ \text{cm}^2 \\ \text{at right } (2.6\ \text{cm})(0.2\ \text{cm}) = & \underline{0.52\ \text{cm}^2} \\ & 2.50\ \text{cm}^2 \end{array}$$

This answer is in rough agreement with ±1.25 cm² and with ±1 cm², the implied uncertainty in 25 cm² by the significant figure method. The use of highest and lowest value yields the same answer as % uncertainty.

$$\begin{array}{rl} 2.6 \times 10.1 = & 26.26\ \text{cm}^2 \\ 2.4 \times 9.9 = & \underline{23.76} \\ \text{As found before:} & 2.50\ \text{cm}^2 \end{array}$$

7. Find the heat absorbed if 200 g ± 0.5 g of water is heated 5.0 ± 0.2°C.

Answer

200 g ± 0.5 g is 200 g ± 0.25%

5.0°C ± 0.2°C is 5.0°C ± 4%

(200 g ± 0.25%)(5.0°C ± 4%)

× 1 calorie/degree/gram

× 1 calorie/degree/gram

= 1000 calories ± 4.25%

or 1.00×10^3 calories ± 4%

Using significant figures, the least well known number has two (5.0°C) so the answer should have two, giving 1.0×10^3.

8. Find the heat of combustion (calories per gram) for a substance if 9800 ± 200 calories are liberated when 1.23 ± 0.02 g of it burns. Express your answer to the correct number of significant figures. Uncertainty need not be reported.

Answer

$$\frac{9.8 \times 10^3\ \text{cal}}{1.23\ \text{g}} = 7.967 = 8.0 \times 10^3\ \text{cal/g}$$

(Note: Two significant figures.)

9. Calculate the heat of solidification for the above substance if 210 ± 70 calories of heat are liberated as 10.3 ± 0.2 g of it solidifies. Express your answer to the correct number of significant figures.

Answer

$$\frac{2.0 \times 10^2\ \text{cal}}{10.3\ \text{g}} = 19.4 = 2.0 \times 10\ \text{cal/g}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Observation is made solely by examining a burning candle.

1. Which of the following is an interpretation rather than an observation?
   (1) The candle gives off light and heat as it burns.
   (2) The wick is made of three strands of string braided together.
   (3) The burning candle makes little or no sound.
   (4) The candle burns to produce carbon dioxide and water.
   (5) The top of the candle becomes wet with a colorless liquid, and the top becomes bowl-shaped.

   Answer: 4.

2. Which of the above can be considered *quantitative* descriptions?

   Answer: 2 and 3.

3. Which of the above can be considered *qualitative* descriptions?

   Answer: 1 and 5.

In a group of students, each was directed to measure the temperature of a beaker of boiling water and that of a beaker of ice plus water, both to the nearest 0.2°C. Each was to use his own thermometer and record the readings at the board. The following data were obtained.

Student	Boiling Water Temp. °C	Ice-water Temp. °C
1	98.8	−0.4
2	99.0	0.0
3	98.6	0.2
4	98.4	−0.2
5	99.2	0.0
6	98.8	0.0
7	98.8	0.4

4. Using all of the data given, express the boiling water temperature using the form ______ ± ______°C.

   Answer: 98.8 ± 0.2°C.

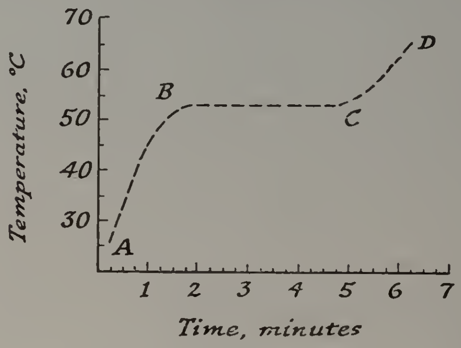
5. What is the uncertainty in the measurement for the ice-water temperature? ± ______°C.

   Answer: ±0.2°C.

6. What is the uncertainty in the difference between the boiling temperature and the melting temperature? ± ______°C.

   Answer: ±0.4°C.

Consider a typical graph for the melting of *para*dichlorobenzene obtained in Expt. 3, Part I.



7. The portion of the graph between ______ represents the melting temperature of *para*dichlorobenzene. Two phases are present, solid and liquid.

   Answer: BC.

8. The portion of the graph between ______ represents the warming of the liquid *para*dichlorobenzene.

   Answer: CD.

9. A possible explanation for the BC portion of the curve being flat is ______________.

   Answer
   Heat is required to change the *para*dichlorobenzene from a solid to a liquid.

As long as there is any solid remaining, and provided the heat is supplied at a slow even rate, the heat is used up in changing the compound from solid to liquid.

Listed below are the melting point and boiling point for some common substances.

Substance	M.P. °C	B.P. °C
Copper	1083	2582
Silver	961	2193
Iron	1535	2800
Moth balls	53	174
Sugar	112	—
Wax	53–55	282

10. What regularity seems to exist for the six melting points?

Answer
The high melting points belong to metallic substances.

11. Does this same regularity hold for the boiling points listed?

Answer: Yes.

12. List two questions that are suggested to you as a result of "wondering why" about these data.

Answer
Student response, such as (1) Do all metals have high melting points and high boiling points? (2) Do all nonmetals have low melting points and low boiling points?

CHAPTER

2

A SCIENTIFIC MODEL: THE ATOMIC THEORY

Intent and Approach

In Chapter 2 the development of atomic theory does not follow a historical path but relies heavily on combining volume data instead of combining weight data. The logic of this approach is easier for the student and makes use of experimental data within his grasp at this time. The background section (pp. 75–84) details the argument and our reasons for preferring the method presented. That section should be read carefully.

The purpose of this chapter is twofold: to show a theory growing and to introduce molecules via Avogadro's Hypothesis. Chapter 1 set the stage for the first goal through its particulate explanation of gases. Here the theme will be to show the scientific method in action. This is done by a few turns around the cycle of questions that asks what is implied; what experiment will give the needed data; what the results are; what change in theory is required; what this change implies; and so on.

The second goal is approached by showing that gases other than oxygen also give $PV = constant$. After finding that different weights are needed to give the same numerical constant, we wonder why. This leads us to look at some properties of gases, from which we can propose that molecules of different gases are different, and that their difference is due to variation in the atoms contained. From here it is a natural step to wondering about the weight of a molecule. By using combining volumes of gases together with Avogadro's Hypothesis we can provide an answer to this and also settle the diatomicity of O_2, H_2, and other gases. Symbols and formulas follow naturally.

The chosen arrangement permits each major concept to be preceded by experimental evidence; some obtained directly by the student, and some shown in the film on gases or given in the Textbook.

Outline

1. Scientific models are explained, and a model of gas behavior (2-1) is used to correlate pressure-volume data for a gas (2-1.1).
2. Other gases are studied (2-1.2) each of which is found to give $PV = constant$. Samples of different weight are needed to get the same numerical constant.
3. A series of properties (color, water solubility, action toward litmus, reaction with air) is used to establish that the particles in each gas are different (2-1.3).
4. The production of new substances means new arrangements must occur. Thus the particles (molecules) must have subunits (atoms) (2-2). The molecular model has grown to accommodate new information.
5. Section 2-2.1 asks why different weights of gas are required for $PV = 22.4$ and sets up two possible answers.
6. To get data on combining volumes, a film and Sec. 2-2.2 discuss the reaction of ammonia with hydrogen chloride. Avogadro's

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Problems*				*Topic*
			EX.	EASY	MEDIUM	HARD	
Read Expt. 6	1	Expt. 6					Weight of Gases
Write up Expt. 6 S 2-1 (pp. 18–21)	2	S 2-1	1	1, 2			*PV* Behavior of Gases
S 2-2/2-2.2 (pp. 21–25)	3	S 2-2/2-2.2 Show film: GASES AND HOW THEY COMBINE		3			Molecules, Atoms, Combining Volumes
S 2-2.3/2-2.5 (pp. 25–29)	4	S 2-2.3/2-2.5	2	4	5	6	Relative Weight of a Molecule, Diatomicity
S 2-3/2-3.1 (pp. 29–30)	5	S 2-3/2-3.1	3	7, 8			Atoms in Liquids, and Solids; Elements, Compounds
Read Expt. 7	6	Start Expt. 7 (20–30 min.)					Conservation of Mass
S 2-3.2/2-3.3 (pp. 30–33)	7	Cont. Expt. 7 (20–30 min.) S 2-3.2/2-3.3	4	9–13, 15, 20	14, 16–19, 22, 24	**21**,* 25	Formulas, The Mole
Read Part I, Expt. 8 S 2-3.4/2-4 (pp. 33–34)	8	Finish Expt. 7, and start Expt. 8 (15 min.) S 2-3.4/2-4	5-9	23	**26**, 27	28-31	Atomic, Molecular Weights
Write up Expt. 7	9	Problems, Misc.; Discuss Expt. 7					
	10	Review, Quiz					

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* Boldface indicates problems whose answers are given in the Textbook.

Hypothesis is shown to give the simplest explanation for the fact that the combining volume ratio is an integer.

7. Relative weights of gas molecules (2-2.3) and the number of atoms per molecule (2-2.4) follow easily.
8. The particulate theory is generalized to solids and liquids, as well as to gases (2-2.5).
9. Element and compound are defined in terms of the number of kinds of atoms (2-3). Symbols are introduced (2-3.1).
10. Formulas and models of molecules are mentioned in Sec. 2-3.2.
11. The mole as a unit (2-3.3) is described and used to fix molecular weight (2-3.4).

New Concepts

1. The presence of subunits—atoms—in the molecules of gas.
2. Avogadro's Hypothesis.
3. Relative weight of molecules.
4. The mole.
5. Models of molecules.
6. Symbols and formulas.

Development

Expt. 6, THE WEIGHTS OF EQUAL VOLUMES OF GASES,
fits here. See p. 63 for guide.

IMPLICATIONS AND GROWTH OF A SCIENTIFIC MODEL (2-1)

This section uses the particle model of gases from Chapter 1 as a starting point for wondering about *PV* behavior. Make this and following sections serve as examples of the steps given on p. 2 of the Textbook. Notice the care that is taken to avoid the words "molecule" and "atom" and the symbols (or formulas) for the gases until these terms and symbols are logically needed in Sec. 2-2. There is distinct pedagogic advantage in waiting till the student sees the need for the word and gets a clear, operational picture of why atoms are needed (as subunits of molecules).

You should make an opportunity to tell the student clearly what is happening during this chapter. We are going through the typical growth of a model. It is at first devised to explain a particular property in a specified range of conditions. As other aspects of behavior or wider ranges of conditions are considered, the model is modified (sometimes replaced, but not in this instance). In practice (but not in this chapter) this process of revision is continued until all the behavior is adequately (usually not perfectly) described or until the model is shown to be of so little value that it is discarded and a new one tried.

You may use ping pong balls in a screened cage to illustrate the motion of gas particles. The apparatus could be a bird cage containing a wire mesh floor. When air is blown in the bottom by an electric fan, the motion of the balls as they strike the walls of the cage will be analogous to the invisible air particles pushing against the walls of the balloon.

A quick demonstration of the kinetic model can be made with a book and a pencil. Establish the book as part of the container wall and the eraser end of the pencil as a molecule. Then tip the book slightly, and tap it lightly but rapidly. It will be held up by the colliding molecules. More frequent or stronger taps will hold the book more upright, illustrating increased pressure. A fairly heavy book works best. If the book is too light you will find it troublesome trying to avoid knocking it over.

These models supply indirect evidence from which the model of gas particles in motion derives support. It is often helpful to remind the student that models for unknowns are not new to him. They are a common item in conversation. Ask a sports fan or a high school coach, "How do you play rugby?" He will probably answer, "It's like football." The answer suggests a *model* —a well-known example which has certain similarities to the unknown one. The next part of the explanation about rugby might very well be "But you are not allowed to block or run ahead of the ball carrier." The difference between model and unknown is explored. We did this same thing in the gas model. We specified "small," or even "tiny," balls.

The next step in deriving implications is less frequently heard in everyday usage. But let us pursue the rugby-football example. The person hearing that no player can run ahead of the ball carrier nor block for him might think a moment and then say: "Well, there must not be a forward pass play (correct), and the runner must have a rough time of it (not necessarily)." The last, partially wrong, implication does not allow for the lateral or backward pass—a very common play in rugby.

As another example, suppose a music teacher is asked "How do you play a harp?" The first response might be, "It's like a piano (setting up the known as a model), but the strings are plucked instead of struck by hammers (differences are brought out)." The answer shows that the teacher expects to make use of the student's background in reading music, understanding chording, and so on.

Bring out and emphasize that a model permits predictions, which may or may not be correct, *and* that there is a real difference between model and system—rugby is *not* football; a harp is *not* a piano; the moving billiard balls are *not* gas molecules.

The Pressure-Volume Behavior of Oxygen Gas (2-1.1)

A good approach to use in explaining the gaseous phase consists in applying the model to an inner tube. All students know that tires require air for support. Take a deflated tube, and show how easy it is to press the walls together. You say, "It contains no air? Let us see." Remove the valve core, attach a piece of rubber tubing, and suck on the tubing or press on the inner tube while the end of the tubing is held under water.

The air left in the tube is at the same pressure as that outside. A "flat tire" is full of air, but the air is not at a high enough pressure to support a car or bicycle.

Insert the valve core, and pump air into the tube. Try pressing the tube against the table. You will notice that something inside the tube resists compression. Referring to your previous models, ask the students if they can see a relationship between the forces demonstrated in the models and the resisting force in the tube. Many relationships of gases can be used here, such as pressure varying with the number of particles, the number of collisions between particles, or the energy of motion for particles.

In Sec. 2-1.1 we *assume* that the "push" of each collision is the same. You know, and the student may have observed from the demonstrations, that this is not so, and we will return to the point later. At this stage, however, it is a convenient assumption.

Note: This is not the time to start a discussion of gas laws (Chapter 4) or molecular structure (Chapters 15–17).

The Pressure-Volume Behavior of Other Gases (2-1.2)

The purpose of this section is to initiate the idea that the particles of different gases are different. The *PV* data are used to show that the most general regularity is found when different weights of gases are tested. *Remember:* the student is not yet aware of molecular weight; these numbers are just those needed to make the same regularity fit each gas. From the different sample weights we are led to wonder about the weights of individual particles.

Some Properties of Gases (2-1.3)

Throughout these pages your aim should be to give simple data to convince the student that the gas particles are different. Solubility in water, gas color, and reactions with litmus and oxygen are all used to supply this data. Some simple demonstrations of these will be seen in the film on gases. Keep in mind that the student is not ready for any reactions or other "explanations" of what occurs. Lead him to see that different properties of the samples imply different kinds of particles, which are called molecules.

The gases brought up here are chosen to fit with the film on combining volumes (see Sec. 2-2.2), the first equation the student will see (Chapter 3), and the example used to introduce equilibrium (Chapter 9). It is best not to change these for other gases which will not be exploited later.

MOLECULES AND ATOMS (2-2)

You can see that we do not suggest a rigid definition of the words *atom*, *element*, *molecule*, and *compound*. Most students will come to your course knowing these words. Their use in this section will serve as an operational definition (see background to Chapter 1).

Now that the student knows there are different kinds of molecules, he can appreciate Figure 2-3 (Textbook), which shows some models. The caption makes an important point, and you should channel interest toward making sure the class grasps this point. You can assure the student that we will devote plenty of time toward understanding how the size, shape, and arrangement of atoms in molecules are learned and on the benefits of such knowledge. *This is not the time to develop this knowledge.* Chapters 15 and 16 will give details, although there is much reference to models before these chapters. There will be considerable interest in these models.

Construction of Molecular Models
There is a discussion of model construction on p. 82.

The Weights of Molecules (2-2.1)

This section, the next section, and Expt. 6 seek to establish Avogadro's Hypothesis as a reasonable, simple explanation of a number of facts about gases. Emphasize the recurring method of approach. Our wondering why about $PV = k$ leads to some new explanations (A and B, p. 22). These in turn suggest new experiments which help make one explanation seem more probable than the other. The pattern of self-consistency defined by such "probabilities" found many times by different methods constitutes *scientific proof*. Chapter 14 will go into detail about scientific proof.

Mixtures of Ammonia and Hydrogen Chloride (2-2.2)

Film, GASES AND HOW THEY COMBINE, fits here. See p. 73 for summary.

You will recognize the law of combining volumes, but let the film and text make the point. Notice also that the groundwork is being laid for reactions and equation balancing. Nevertheless, keep the focus of attention on the logic through which Avogadro's Hypothesis is implied by the integer volume ratios *without* reference to the actual reaction taking place. In fact, the argument becomes circular if it is predicated upon a knowledge of the chemical formulas, for these formulas are deduced from the hypothesis. Leave the development of chemical equations for Chapter 3, after symbols and formulas have been introduced.

The Relative Weights of Molecules (2-2.3)

It may be difficult to avoid saying "molecular weight" in connection with this section. Bu look at the advantages of waiting until Sec. 2-3.4, after molecules have been further defined, the mole introduced, and the terms element and compound made clearer.

Point out that any gas *could* be taken for the standard (as oxygen was in the text). This matter of an arbitrary standard comes up repeatedly (ΔH in Chapter 7, and $E°$ in Chapter 12).

The Number of Atoms in a Molecule (2-2.4)

Students are often confused by the diatomic gases. "How do you know?" is a common question. The example shows the logic used on oxygen, and Exercise 2-2 also helps. Some of the problems (5, 6, 28, 31) are also designed to teach which gases are diatomic. It is probably worthwhile bringing up all the common diatomic gases (H_2, O_2, N_2, F_2, Cl_2, Br_2, I_2) if only to make the student familiar with them.

Atoms in Liquids and Solids (2-2.5)

This section provides a basis for proposing the presence of atoms in all matter. Its main use will come in Expt. 7 and in Chapter 3, but this is the place for introduction. The third paragraph of the Textbook holds the key—simplicity. The presence of atoms in liquids and solids is the simplest model. The "proof" of the atomic theory is for Chapter 14. Emphasize here that the value of the theory will depend upon its success in helping us explain and understand facts of chemistry. At this point, the atomic theory should be regarded as a working hypothesis to be used, questioned, and criticized.

SUBSTANCES: ELEMENTS AND COMPOUNDS (2-3)

It is probably best not to try for an extremely precise definition of the words *atom*, *element*, *molecule*, and *compound*. Your use of these terms and the stress on particles in Chapters 1 and 2 will suffice. Take copper, for instance. Ask for its properties (color, electrical conduction, heat conduction, density, malleability, etc.). The students will know these in a qualitative way. Show some less common elements from your stockroom, such as P, Na, Br_2, Zn, and others. Emphasize that these are called elements because experiments show that they contain only one kind of atom.

Compounds are somewhat more difficult. Although almost everything we see is made of compounds rather than elements, many of the objects are mixtures, polymers, minerals, and natural products of complex (often unknown) structure. But these do not make good examples. The traditional ones are water, salt, and sugar. Others the student might know are alcohol (rubbing), baking soda ($NaHCO_3$), "hypo" ($Na_2S_2O_3 \cdot 5H_2O$, sodium thiosulfate), epsom salts ($MgSO_4 \cdot 7H_2O$, magnesium sulfate), and milk of magnesia [$Mg(OH)_2$, magnesium hydroxide]. Just show the compounds, and name them; don't give formulas yet.

Stress the changes which compounds undergo to give different products that lead us to conclude that compounds contain more than one kind of atom. The Textbook treats water and sugar. You might demonstrate burning alcohol (to give water and CO_2) or put vinegar and baking soda together to give CO_2. This will provide background material to be drawn upon in Chapter 3 when chemical reactions are introduced.

The Elements (2-3.1)

To a beginning student, chemical names and symbols are quite foreign. They should be treated as items of convenience. Encourage the students to learn the symbols, but don't tell them to memorize a list. Make their use seem so easy and important that the student feels he must learn them.

Expt. 7, THE BEHAVIOR OF SOLID COPPER IMMERSED IN A WATER SOLUTION OF THE COMPOUND SILVER NITRATE, fits here. See. p. 68 for guide.

Chemical Formulas (2-3.2)

The same treatment given elemental symbols should be used for formulas. Be sure to tie the written formula H_2O to the more pictorial drawings as well as to the stick and styrofoam models. Prepare the students for different ways of representing formulas. Structural formulas come up specifically in this section. Molecular formulas appear on p. 31. Empirical formulas will be defined in Chapter 5.

The Mole (2-3.3)

See the background section (p. 79) for reasons why we stress the mole. We have used the basic definition of a mole as a weight of material and have commented on this use in the actual measurement of a mole. On the other hand, we have stressed the significance of the number of molecules in a mole and have extended the concept to any particle. Thus, a mole is 6.02×10^{23} particles of any kind—for example, atoms, ions, electrons, molecules, or even people, dollars, or calories.

This use provides several advantages that teachers have found quite important:

(a) The idea of a mole goes over very easily.
(b) The mole method of working problems fits, in a helpfully obvious way, with balancing equations.
(c) Special units (equivalents, formula weights, combining weights) are not needed and should not be introduced.

The student should learn that the choice of the first atomic weight is arbitrary. After that first choice, the others are fixed experimentally, and Avogadro's number is also fixed. This point can be made in terms of alternate scales, as discussed in the background, only convenience dictating which is used.

Questions may be asked about methods of determining Avogadro's number. The background discussion treats this point, indicating that chemists had no need to know N until the last three or four decades, when the details of the molecular model began to be explored. For the student, an answer based on Millikan's experiment (Chapter 14) and Faraday's Laws (Chapter 14) is most easily understood and closely tied with what he will study. The optimum explanation follows this line of logic: Later, you will study two sets of experiments. One determines the charge of a single electron; the other measures how much total charge is needed to cause one mole of silver atoms to plate out of solution as metal (a change which takes one electron per atom). By dividing as follows, we see that

$$\frac{\text{total charge/mole}}{\text{charge/electron}} = \frac{\text{number of electrons}}{\text{mole}} = \frac{\text{number of atoms}}{\text{mole}} = \text{Avogadro's number}$$

You may want to just list some of the other methods—X-ray diffraction, radioactive decay, Brownian motion—but discussion is not profitable, because the student lacks the proper background.

Atomic and Molecular Weights (2-3.4)

A portion of the background material (p. 79) discusses ways to determine molecular weight, but it is not intended that this be discussed in class. If a question does arise, stress the gas density method based on Avogadro's Hypothesis. The student will do (in Expt. 7) an experiment of the type that is used in determining many atomic weights. Of course, in Expt. 6 he determined the molecular weight of a gas, although that point could not be brought out then. Exercise 2-6 does show this method for finding molecular weight.

EXPERIMENT 6 THE WEIGHTS OF EQUAL VOLUMES OF GASES

PURPOSE. To give experimental evidence that equal volumes of gases do not have equal weights (at the same *T* and *P*) and later, after a discussion of Avogadro's Hypothesis, to enable the student to calculate a molecular weight from laboratory measurements. Exercises 2-5 and 2-6 in the Textbook use the data of this experiment and form an essential part of its calculations.

PRELAB DISCUSSION. On the day before this experiment is to be done, have a plastic bag fastened to a stopper as described in the directions. Press out all the air, weigh the bag, and fill it with air. To avoid excess moisture, use a hand pump if compressed air is not convenient. Equalize the pressure, put the cap in place, and weigh the bag full of air. When the students have observed the identity (± the uncertainty of the measurement) of these two weights, ask: "Would this be true regardless of the gas used to fill the bag?" Do not discuss the answer, but assign the reading of the experiment. If this seems too little for one night, give some questions for review of Chapter 1. The answer to the problem posed in the experiment comes early in the chapter (Sec. 2-1.2); for this reason, delay assigning reading in Chapter 2.

TIMING. This experiment should precede any reading assignment in Chapter 2.

EQUIPMENT NEEDED (FOR EACH STUDENT OR PAIR)

one quart-size plastic bag (frozen food type)
#5 or #6 one-hole rubber stopper
  (see lab hint 1)
rubber band
medicine dropper
balance (±0.01 g)
pneumatic trough or other water container
half-gallon jar (or $2\frac{1}{2}$ liter acid bottle)
  plus stopper to fit
rubber delivery tube, 50–60 cm long
thermometer, −10°C to 110°C
large graduate (see lab hint 2)
source of O_2, CO_2, and possibly another gas
  (see lab hint 3)

TIME REQUIRED. This experiment requires one period for all students to get the weight of O_2, the weight of CO_2, and the volume of the bag. Some will have extra time for getting additional weights, either of the same gases or of others.

PRECAUTIONS. Observe the usual lab precautions plus special care if noxious gases are used.

LABORATORY HINTS

1. A sharp knife, lubricated with water, is a simple tool for cutting grooves in stoppers. Rubber stoppers resist filing, but the grooves can be cut quite quickly. The rubber band should fit tightly in the groove to prevent leaks. Expel the gas gently to avoid leaks around the band.
2. The directions call for a large graduated container. If there is a shortage of graduates, have some calibrated containers such as liter flasks or quart jars available. Mark such containers with their volume and the uncertainty of the calibration. The level of water inside the large collecting bottle should be close to that in the trough, but need not be exactly the same. A 10 cm difference of level makes only a 1% change in pressure.

3. (a) OXYGEN

When a supply of compressed oxygen is not available in the lab, the most convenient source for most schools is to borrow a tank from the auto shop or maintenance department. The small "lecture" bottles hold so little that they are not really very satisfactory. However, two cubic feet—the volume in the usual lecture bottle carried by most supply companies—will be enough for one class (2 cubic feet O_2 is about 56 liters and costs about $1.50 if you already own the cylinder and order directly from the manufacturer). Anchor the cylinders securely.

If bottled oxygen is not available, it can be generated by using stabilized 30% H_2O_2. **(Caution:** 30% H_2O_2 burns flesh. Use safety glasses and gloves. In case of accident, wash it off with plenty of water.) Set up a generator by inserting a dropping funnel into a 2 hole rubber stopper equipped with a delivery tube. The stopper assembly is placed in a 250 ml flask containing a gram or two of MnO_2 powder. Using distilled water, dilute 50 ml of 30% H_2O_2 to 100 ml. Add the diluted H_2O_2 via the dropping funnel as needed to release a steady flow of oxygen. Use a drying tube containing anhydrous $CaCl_2$ or $CaSO_4$. This amount of H_2O_2 will give about 5½ liters of oxygen at room temperature and pressure. For student use, supply H_2O_2 which has already been diluted. A 5% solution reacts rapidly enough and is safer to use. It is also satisfactory to use Na_2O_2 in a flask into which water may be introduced. A mixture of $KClO_3$ and MnO_2 is *not recommended.* Many serious accidents have occurred with this combination. Certainly it should not be used by students. If you decide to use it, be sure that both the MnO_2 and the $KClO_3$ have been heated strongly in evaporating dishes (*separately*) and that each is known to be free of any organic or other oxidizing material. Be sure that none of the mixture gets on the rubber stopper of the generator.

(b) CARBON DIOXIDE

An inexpensive way to obtain CO_2 gas is from dry ice. One hundred students will require 2–4 lbs. Place chunks of it in water (the evolution of gas is not fast enough unless warmed by water), and use a long delivery tube from the generator to allow the gas to warm to room temperature. If dry ice is not readily available, set up a CO_2 generator using $CaCO_3$ and HCl. Use a drying tube in either method. Use a 250 ml flask with a long-stem funnel and a delivery tube. Add about 25 grams of $CaCO_3$ and about 100 ml of 6 M HCl. This will produce about 6 liters of CO_2 at 25°C and 1 atmosphere. Carbon dioxide is also available in lecture bottles. These contain 4 cubic feet of the gas, which costs $1.50 excluding cost of the cylinder. While in use, clamp the cylinder in an upright position.

(c) OTHER GASES

Since it is desirable to have a gas lighter than air, ammonia is probably the best choice, but adequate ventilation is essential. Lecture cylinders holding 8 cubic feet cost about $1.50 excluding the cost of the cylinder. Clamp these vertically also. Another way to obtain ammonia is by warming a dry mixture of NH_4Cl and $Ca(OH)_2$. About 100 grams of each will produce enough NH_3 for one class (about 50 liters).

Methane may also be purchased in cylinders. Natural gas is not satisfactory for the molecular weight determination of methane, since natural gas is a mixture. (See extension at end of experiment.)

OBTAINING THE VOLUME OF THE BAG. Delay obtaining the bag volume until all gases have been collected and weighed, then empty the bag, and fill it with air. Repeat a time or two to be sure that air is essentially the only "gas" in the bag. Then obtain the volume by water displacement. This sequence will avoid getting the bag wet before all the weights are taken. Discourage students from weighing the bag when full of air. The molecular weight of the mixture (containing water and CO_2 if they blow to fill it) is not meaningful. A second determination of the bag volume by the faster working students will give them better understanding of the uncertainty of that measurement.

CALCULATIONS. Avoid a long presentation about buoyancy. The following may be adequate. A block of wood falling through air is stopped when it hits the water in a swimming pool. Why? Must not the water provide an upward force to counterbalance the force supplied by gravity? The wood sinks until the upward force equals the downward force. In a similar way, a balance gives the net effect resulting from all the forces acting on the weighed object. The two most important are the attraction of the earth (gravity), pulling the object down, and the upward push due to the displaced material.

Air, like water, is a fluid which imposes an upward force on objects immersed in it. A plastic bag full of oxygen gas experiences an upward force when it is weighed in air. The weight of the oxygen, as determined in air, is then a weight which has been reduced by this upward force. To determine the amount of material contained in the bag, its weight in air will have to be increased to allow for the upward force supplied by the air. This is also true when a person is weighed in air, but the upward force or buoyancy is so much less than the gravitational force that the buoyancy can be ignored.

SAMPLE DATA AND CALCULATIONS (AT 20°C, 1 ATM)

Weight of bag assembly	22.53 ± 0.01 g
Weight of bag assembly + O_2	22.68 ± 0.01 g
Weight of bag assembly + CO_2	23.31 ± 0.01 g
Weight of bag assembly + NH_3	21.93 ± 0.01 g

Volume of bag (1.200 ± 0.025) liters.

The precision of the volume measurement will be quite variable depending, in part, on the size of the volumetric equipment available. Assuming 12 measurements are made with a 100 ml graduate, it could be ±6 ml. But since the level in the large container cannot be marked exactly, a ±25 ml estimate has been used.

CALCULATED RESULTS

1. What is the apparent weight of oxygen in the bag? (Subtract the weight of the empty bag from the weight of the bag full of oxygen.)

   Answer: From the data above, we have

$$\begin{array}{r} 22.68 \pm 0.01\ \text{g} \\ \underline{-22.53 \pm 0.01\ \text{g}} \\ 0.15 \pm 0.02\ \text{g} \end{array}$$

2. Calculate the weight of the air displaced by the bag filled with gas. Indicate the uncertainty in this derived result. (Refer to Appendix 4.)

   Answer: From the data above and from the table, we find

$$(1.20\ \text{liters} \pm 2\%) \times (1.21\ \text{g} \pm 1\%)/\text{liter} = 1.45\ \text{g} \pm 3\%$$

   Since 3% of 1.45 g is 0.04 g, we have 1.45 ± 0.04 g.

3. What is the actual weight of oxygen in the bag? (Add the weight of the air displaced to the apparent weight recorded from the balance.)

   Answer:

$$(1.45 \pm 0.04\ \text{g}) + (0.15 \pm 0.02\ \text{g}) = 1.60 \pm 0.06\ \text{g}$$

   or

$$1.60\ \text{g} \pm 4\%$$

4. In a similar way, determine the weight of carbon dioxide gas in the bag and the weight of any other gas used.

Answer: For carbon dioxide:

Apparent weight

$$\begin{array}{r} 23.31 \pm 0.01\text{ g} \\ -22.53 \pm 0.01\text{ g} \\ \hline 0.78 \pm 0.02\text{ g} \end{array}$$

Actual weight of CO_2

$$(1.45 \pm 0.04\text{ g}) + (0.78 \pm 0.02\text{ g}) = 2.23 \pm 0.06\text{ g, or } 2.23\text{ g} \pm 2\%$$

For ammonia:

Apparent weight

$$\begin{array}{r} 21.93 \pm 0.01\text{ g} \\ -22.53 \pm 0.01\text{ g} \\ \hline -0.60 \pm 0.02\text{ g} \end{array}$$

Actual weight of ammonia

$$(1.45 \pm 0.04\text{ g}) + (-0.60 \pm 0.02\text{ g}) = 0.85 \pm 0.06\text{ g, or } 0.85\text{ g} \pm 7\%$$

5. Compare the weight of each gas measured to that of oxygen by dividing each weight by the weight of the comparable volume of oxygen. Express each ratio as a decimal fraction. Include the uncertainty in this derived result.

Answer:

Weight of CO_2 to O_2 $$\frac{2.23\text{ g} \pm 2\%}{1.60\text{ g} \pm 4\%} = 1.39 \pm 6\% \text{ or } 1.39 \pm 0.08\text{ g}$$

Weight of NH_3 to O_2 $$\frac{0.85\text{ g} \pm 7\%}{1.60\text{ g} \pm 4\%} = 0.53 \pm 11\% \text{ or } 0.53 \pm 0.06\text{ g}$$

A QUESTION TO WONDER ABOUT. Is there any relation between the comparative weights of equal volumes of gases and the relative weight of molecules?

After Sec. 2-2.3 has been assigned in the Textbook, remind the students of this question. Exercises 2-5 and 2-6 are based directly on this experiment.

POSTLAB DISCUSSION. On the day after the experiment (next day), record individual weight ratios of CO_2, and other gases used, to O_2, and discuss the range of these. It is to be expected that about two-thirds of the ratios will be well within the uncertainty of the measurements. Be sure students have an opportunity to compare their results with those of other students. If time permits, you may wish to calculate the weight of one liter of each gas. This was not asked for in the written questions, since it involves more complicated calculation of uncertainty and is not essential to the discussion of the experiment in the Textbook.

ADDITIONAL INVESTIGATIONS—*to be undertaken as extracurricular experiments. Consult your teacher before proceeding.*

1. How do the weights (of equal volumes) of gases at atmospheric pressure, but at higher than ordinary temperatures, compare with those at room temperature?

   Let the exceptional student who decides to tackle this problem suggest something first. One possibility is to drill a hole in the base of a balance (±0.01 g) that may be placed on top of the drying oven. Remove the pan and pan support and, after proper counterbalancing, suspend a plastic bag from the hook by a thread extending through the hole in the support and into the oven. The bag may be filled with oxygen and later with CO_2 or other gases and fitted with a cap such as the one used in Expt. 6, except that a hole should be made in it with a hot needle in order that the pressure may be equalized as the gas is warmed. A graph of the changes in weight during the warming of each gas should make an interesting record. When a constant weight is reached at a given temperature, you may assume that the gas is at the same temperature and pressure as the oven.

2. The burner gas in the laboratory is ordinarily natural gas, which is mostly methane, CH_4, but contains some ethane, C_2H_6, and small amounts of other compounds. Weigh a sample of burner gas and calculate the percentage of methane and of ethane, assuming that they are the only gases present.

It is assumed that the student will not get to this immediately after the completion of the experiment and that he will have read all of Secs. 2-3.3 and 2-3.4 by the time he considers this problem. The weight ratio of natural gas to oxygen usually is about 0.58 to 1, which gives a "molecular weight" of about 19 and a molar composition of 80% methane and 20% ethane.

Let X = mole % of methane. Then $100 - X$ = mole % ethane.

$$\frac{16X}{100} + \frac{30(100 - X)}{100} = 19$$

$$16X + 3000 - 30X = 1900$$

$$-14X = -1100$$

$$X = \frac{1100}{14} = 78 \text{ mole \% methane}$$

EXPERIMENT 7 THE BEHAVIOR OF SOLID COPPER IMMERSED IN A WATER SOLUTION OF THE COMPOUND SILVER NITRATE

PURPOSE. To provide an experimental determination of the molar relationship between silver and copper; to emphasize the mole concept and, later, to furnish a basis for writing equations.

PRELAB DISCUSSION. Little discussion is needed. Since the students have already learned to use the balance, they can start on their own. A check (or test) on weighing procedure can be used here with no time loss. The diameter of copper wire is uniform, and you can measure lengths carefully enough to be quite sure of the weight of each. If you do this, have the student tell you the weight of the wire before continuing the experiment in order that mistakes may be corrected.

Note that the words "reaction" and "equation" are not used. These have not been introduced in the Textbook so only a statement in words is used in the questions.

TIMING. This experiment should come near the end of Chapter 2, after Sec. 2-3.3.

EQUIPMENT NEEDED (PER INDIVIDUAL OR PAIR)

about 30 cm of copper wire, #16 gauge, bare (unlacquered)
vial with 3–5 g $AgNO_3$ (fine crystals)
balance (±0.01 g)
250 ml beaker (see lab hint 1)
glass stirring rod
wash bottle (see lab hint 2)
watch glass
drying oven (for other arrangement see lab hint 3)
5 ml 0.2 *M* $AgNO_3$ (34 g/liter)

TIME REQUIRED. Thirty minutes the first class period and about 20 minutes from each of two subsequent periods. The first thirty minutes are used to weigh the copper wire, beaker, and silver nitrate, and to place the wire in the solution. [A stopping point occurs after (e).]

Later, twenty minutes are used to prepare the Ag sample for drying. [A stopping point occurs after the first part of (i).]

The final twenty minutes allow the student to weigh the dried sample. Experiment 8 may be started as soon as this is weighed.

PRECAUTIONS. Warn the students about getting $AgNO_3$ solution on their hands and clothing. If $AgNO_3$ is spilled on hands or clothing, the immediate use of a sodium thiosulfate (hypo) solution may prevent staining. Wash the hypo off the clothing with water.

LABORATORY HINTS

1. If desired, 100 ml beakers may be used. If they are used, it is best to have 2.5–3 grams of $AgNO_3$ in the vials and to fill the beaker about one-half full when the solution is prepared.
2. The wash bottle is most conveniently a plastic bottle of about 300 ml capacity. This may be a discard from home, such as a plastic container for detergent, adhesive, or food, or it may be one purchased for the purpose.
3. Drying can be conveniently and quickly accomplished by using a drying oven or two or three infrared heat lamps mounted in a fume hood. A sand bath may be constructed from a 1-lb coffee can, about one-fourth full of sand, heated with a burner. But since this requires frequent checking to avoid spattering, it is the poorest method.
4. If balances are limited in number, an alternate activity should be provided while the copper wire, silver nitrate, and beakers are being weighed. This could be work on problems assigned in connection with this part of the chapter.

POSTLAB DISCUSSION. Sources of difficulty in the calculations for this experiment are few. Most of the errors made by students in trial groups were made in measurement rather than in calculation.

It is interesting to have the students record both the weights of Ag and Cu and the ratio of moles of Ag to moles of Cu on a class chart, since this shows clearly how different numbers (the weights) yield closely similar numbers (the ratios).

Since the weight of silver is obtained by subtracting the weight of the beaker from that of the beaker plus silver, weighed on balances with a precision of ±0.01 g, the final weight of about 2.50 g is known to ±0.02, or 1%. The weight of copper is less precise, having an uncertainty of ±0.02 in 0.80 g, or 2½%. The number of moles of Ag may be expressed as 0.0250; the number of moles of Cu as 0.0125; and the ratio calculated to two or even three significant figures.

Be sure to collect class data (see question 6) and plot moles of Ag on one axis against moles of Cu on the other. The resulting scattergram should show the two to one relationship. It should also indicate the uncertainty. This is an excellent experiment from which to discuss the increase in certainty obtained when conclusions are based on many measurements rather than upon a single one.

EXPECTED RESULTS. The theoretical ratio is 2.00/1.00. A mean ratio of about 1.9 was obtained during a trial year, with 67% of the results being in the range 2.0 ± 0.2. In one summer institute, 87% of the participants found 1.95 ± 0.05.

SAMPLE DATA

Weight of:	copper before immersion	2.72 ± 0.01 g
	copper at close of expt.	1.96 ± 0.01 g
	copper	0.76 ± 0.02 g
	vial plus silver nitrate	16.36 ± 0.01 g
	vial	12.31 ± 0.01 g
	silver nitrate	4.05 ± 0.02 g
	beaker plus silver	75.16 ± 0.01 g
	beaker	72.60 ± 0.01 g
	silver	2.56 ± 0.02 g

CALCULATIONS

1. Calculate the number of moles of copper which reacted.

$$\text{Grams of copper} \times \frac{1\text{ mole}}{\text{g copper}} = \text{moles of copper}$$

$$(0.76\text{ g} \pm 2.6\%) \times \frac{1}{63.5} = 1.20 \times 10^{-2}\text{ mole} \pm 2.6\%$$

The uncertainty of atomic weights is so low (generally 0.01% or less) that it can be ignored.

2. Calculate the number of moles of silver obtained.

$$\text{Grams silver} \times \frac{1\text{ mole}}{\text{g silver}} = \text{moles silver}$$

$$(2.56\text{ g} \pm 0.8\%) \times \frac{1}{108} = 2.37 \times 10^{-2}\text{ mole} \pm 0.8\%$$

3. Determine the ratio of moles of silver to moles of copper involved in this reaction.

$$\frac{2.37 \times 10^{-2} \pm 0.8\%}{1.20 \times 10^{-2} \pm 2.6\%} = 1.99 \pm 3.4\%$$

QUESTIONS AND ANSWERS

1. What you have observed can be described by the following statement: One mole of copper (solid) + ______ mole(s) of silver nitrate (in water) ⟶ ______ mole(s) of silver (solid) + ______ mole(s) of copper nitrate (in water). Using the results obtained in this experiment, write the proper whole-number coefficients in the above statement when 1 mole of copper is used up.

   Answer: The student will fill in 2 moles of silver nitrate, 2 moles of silver, and 1 mole of copper nitrate. No attempt is to be made to write the formulas, and the mention of ions is purposely avoided. Ions will be taken up in the Textbook before long (Chapter 5), and this experiment can be referred to then. Some students may suggest 2 moles of copper nitrate on the basis of 2 moles of nitrate from $AgNO_3$. Ask them how this could be, with only one mole of copper atoms available. The students may propose $Cu(NO_3)_2$ or $CuNO_3 + NO_3$. Stop at this point, since this experiment does not give enough information to decide. Verification is not easy, because anhydrous $Cu(NO_3)_2$ is difficult to obtain.

2. How many atoms of solid copper were involved in *your* experiment? See Sec. 2-3.3 in the Textbook.

   Answer: From the sample data, 1.20×10^{-2} mole of copper was used.

   $$6.02 \times 10^{23} \text{ atoms/mole} \times 1.20 \times 10^{-2} \text{ mole} = 7.21 \times 10^{21} \text{ atoms copper}$$

3. How many atoms of solid silver were involved in *your* experiment?

   Answer: From the sample data 2.37×10^{-2} mole of silver was found.

   $$6.02 \times 10^{23} \text{ atoms/mole} \times 2.37 \times 10^{-2} \text{ mole} = 14.3 \times 10^{21} \text{ atoms of silver}$$

4. What is the relationship between the number of atoms of silver and the number of atoms of copper calculated in questions 2 and 3?

   Answer:

   $$\frac{14.3 \times 10^{21} \text{ atoms silver}}{7.21 \times 10^{21} \text{ atoms copper}} = 1.99 \frac{\text{atoms silver}}{\text{atoms copper}}$$

5. In order to evaluate the results of this experiment, your teacher will collect the data obtained by other members of your class. Make a graph, plotting the number of individuals obtaining a given silver/copper ratio along the vertical axis. Plot the Ag/Cu ratios along the horizontal axis. These should be rounded off so that each division on the graph will represent values of ±0.05. For example, values from 1.85 up to but not including 1.95 should be plotted as 1.9.

   Answer: Figure 2-1 shows data from 186 individual students. A bar graph is actually more suitable for these data, but has not been presented to the student in this course.

6. Considering only the middle two-thirds of the data plotted, what is the range of values obtained? How does this compare with the uncertainty you considered justifiable from your measurements?

   Answer: The middle 67% of the data covers a range of 1.7–2.1, or 1.9 ± 0.2. From the uncertainty of the measurements, we considered 1.9 ± 0.07 as justifiable. The actual results then show more variation than the precision would indicate. Moreover, the average is low (1.9 rather than 2.0). A discussion of systematic rather than random errors may be helpful to the students.

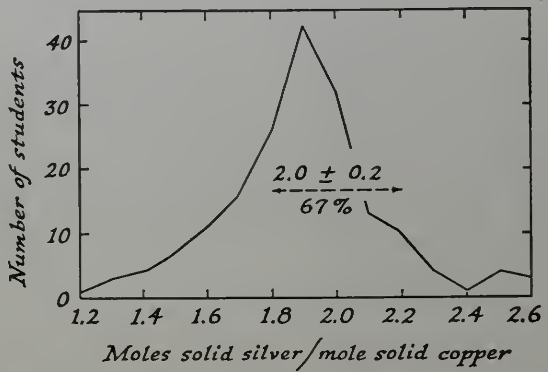

Fig. 2-1. **Distribution of student results** *for reacting molar ratio (silver/copper).*

QUESTIONS TO WONDER ABOUT (NOT TO BE ASSIGNED FOR WRITTEN WORK. DISCUSSED LATER.)

1. What causes the color in the solution after the reaction is completed?

   Answer: Some of the students will deduce or guess that the color is due to copper in water solution. It would be a good idea to make available an aqueous solution of cupric nitrate for comparison by interested students.

2. What is the nature of particles in aqueous solution?

   Answer: The student is not expected to have any background on which to base an answer to this question at this time. It is presented merely to cause him to "wonder." Ions in aqueous solution will be studied later in Chapter 5.

ADDITIONAL INVESTIGATIONS. Divide the "blue solution" obtained in step (h) into two approximately equal portions so you can make the following investigations.

1. Carefully evaporate the solution to dryness and observe the product.
2. Place a piece of a metallic substance into the blue solution. Observe any changes which occur immediately and after a day or so.

Although some students will be interested enough to undertake this extra work, they should not be encouraged to try quantitative work. For example, in Part 1 the $Cu(NO_3)_2 \cdot 3H_2O$ decomposes if heated strongly, and in Part 2 the solution is acid enough to give other reactions in addition to the plating of copper.

Supplementary Material

Books

L. E. Steiner and J. A. Campbell, GENERAL CHEMISTRY, Macmillan, New York (1955). Chapter 9 gives a good overview to the behavior of gases with considerable emphasis on experiments that led to our present understanding of the gas phase.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

GASES AND HOW THEY COMBINE

A CHEM Study film

Running Time: 22 minutes

This film was produced in collaboration with Dr. G. C. Pimentel and fits quite closely with the Textbook, for which several figures are taken directly from the film.

The purpose of this film is to provide experimental evidence that can be used in the development of the atomic theory. The film presumes that the description of a gas as a collection of particles has been established. The first portion of the film shows the great differences among gases: color, solubility in water, and combustibility are shown for NH_3, Cl_2, H_2, HCl, NO, NO_2, and O_2. These observations furnish the basis for the conclusion that the particles (molecules) of different gases must be different.

The remainder of the experimental part of the film demonstrates the integer combining volume relations for the following reactions:

$$NH_3 + HCl = NH_4Cl(s)$$
$$O_2 + 2H_2 = 2H_2O(l)$$
$$2NO + O_2 = 2NO_2\ \textit{(dissolved in water)}$$
$$H_2 + Cl_2 = 2HCl\ \textit{(dissolved in water)}$$

Having developed this evidence on combining volumes, the film narration is arranged in order that the film can be stopped as an "open-ended" presentation. Then you can develop Avogadro's Hypothesis through classroom discussion if you desire. On the other hand, the last section of the film draws the conclusion—Avogadro's Hypothesis—through additional narration. Show this part if you prefer, or else use it as a climax to the classroom discussion. Thus the film provides experimental support for Avogadro's Hypothesis.

Background Discussion

This section comprises discussions of the following topics.

"Modern" Evidence for Atoms
Chemical Evidence for the Existence of Atoms
Origin of the Atomic Hypothesis
Interpretation of Combining Volume Data
What Is a Molecule?
Molecular Weight Determination
The Mole
Avogadro's Number (determination)
The Atomic Weight Scales
The Naming of Chemical Elements
Construction of Molecular Models
(with directions for making)

In Chapter 1, the particulate model of a gas is offered as an intuitively acceptable explanation of experimental facts known to the student. We are, quite frankly, building upon the student's readiness to accept the atomic theory on the basis of previous contact with the idea—through earlier science courses and through various communication media (even including the funny papers). Then in Chapter 2, the particulate model is developed on the experimental base provided by the combining volumes of gases. The experiments are described in the Textbook and are actually shown in the film entitled GASES AND HOW THEY COMBINE.

This introduction to the atomic description of matter ignores historical chronology and differs from traditional treatments in which combining weights play a dominant role. This presentation, evolved during the two-year field trial period of CHEM Study, was initially based upon a prolonged deliberation by an assemblage including most of the coauthors listed on the title page and most of the CHEM Study Steering Committee. Among these thirty-five scientists and educators there were seven or eight individuals with international recognition in chemical research. The consensus of this group was that a mature scientist believes in the usefulness of the atomic hypothesis because he himself has felt innumerable successes in a wide variety of applications based on this hypothesis. From a scientist's point of view, it would be incorrect to single out one of these applications as *the* reason or even as the most important reason why he has such confidence in this theory. In a modern discussion of the experimental basis for belief in atoms, mass spectrometry, infrared spectroscopy, and a dozen other types of data are fully as important as are combining weights. To enumerate all or even several of these at the beginning of the course, without corroborating experiments, would hardly promote the experimental theme of this course.

For these reasons our task in Chapter 2 is not to present *the* evidence for atoms; *the* evidence is too diverse, too manifold, too esoteric. Rather, we must begin with a small part of the evidence and, in an atmosphere of tentativity, let the particulate model grow as new facts are learned. Only after the student has a substantial background can we present anything resembling a full picture.

"MODERN" EVIDENCE FOR ATOMS

Some attempts to circumvent the historical introduction and present an experimental basis for the atomic theory are based upon the "modern" methods of demonstrating the particulate nature of matter. Electron microscope, X-ray diffraction, and mass spectrometer photographs can be presented. These complicated methods present an experimental basis for the atomic theory, but they leave the student with neither understanding nor opportunity to challenge. In considering mass spectrometry, the eleventh grade student must accept, on faith, that there are such things called electrons that boil out of a hot filament, that they are accelerated by an electrical voltage, and that, when passed through a gas, these unseeable electrons produce electrically charged particles (Is the argument now circular?), which, in turn, can be accelerated by another voltage. Then he must accept the statement that such a moving charged particle (if it exists) would follow a known curved path in a magnetic field. Hence lines on a photographic plate (How are the lines produced?) show the existence of atoms. What an illusion it is, however, to pretend that the experimental approach is satisfactorily shown by such an esoteric experiment!

With these considerations in mind, we have concluded that the optimum introduction consists in proposing the atomic theory tentatively to explain a limited range of data accessible through simple and easily understood experiments. The theory is considered, then, to be a working hypothesis to be used, tested, modified as needed, and ultimately to be judged by its continued success over an ever-widening area. This is a legitimate scientific approach, and it is desirable to exhibit it early in the course.

CHEMICAL EVIDENCE FOR THE EXISTENCE OF ATOMS

The logic by which chemical evidence leads to the atomic hypothesis is direct.

1. *There are compounds and elements.* Operationally, an element is a substance that *cannot* be decomposed into two or more distinct substances, and a compound is a substance that *can* be decomposed into two or more distinct substances.
2. *Compounds* are found to have *definite composition* (in terms of the relative weights of the elements contained).
3. When two elements are found together in two different compounds, the relative weights are related by a simple whole number ratio (*the law of simple multiple proportions*).
4. Gases react in simple proportions by volume, and the volume of any gaseous product bears a whole number ratio to that of any gaseous reactant (*the law of combining volumes*).

The first evidence, that there are elements and compounds, is consistent with, but does not imply the atomic hypothesis. This is shown by the fact that the differentiation between elements and compounds had been made for centuries before Dalton proposed the atomic hypothesis.

The second evidence raises a real question about the structure of matter. Why are compounds so particular about their composition? This question causes one to consider models of the structure of matter—models that would "explain" the definite composition of compounds. Once again, however, the evidence is consistent (in an intuitively satisfying way) with the atomic theory, but does not suggest it by itself.

The third evidence *does* suggest the atomic hypothesis. Simple integer relationships suggest "units" or "portions." A given amount of oxygen can react with one portion of hydrogen, or with two portions, but not with 1.8732 portions. These simple integer relationships interweave all of chemistry. Thus the composition of NH_3 is simply related to the compositions of NO and H_2O_2. For example,

0.0625 g hydrogen reacts with 1.000 g oxygen (in H_2O_2)
0.8750 g nitrogen reacts with 1.000 g oxygen (in NO)
3(0.0625) g hydrogen reacts with 0.8750 g nitrogen (in NH_3)

Such evidence naturally leads to a model involving "portions," "particles," or, finally, atoms.

The fourth evidence again involves, but in quite another way, simple integer relationships in that the volumes are related simply. Two volumes of hydrogen react with one volume of oxygen and produce two volumes of water vapor (all at the same temperature and pressure). Once again these integer relationships lead to models made up, somehow, of "units" or "portions" and point the way to the atomic hypothesis.

This last evidence is, by far, the simplest. It involves the integer relationships that lead to a particulate model without the need for a prior development of the concepts of elements and compounds. Furthermore, the arithmetic manipulations inherent in the combining weight argument are totally absent. These manipulations furnish a substantial obstacle to the student who does not feel confident in mathematics. Hence we have concluded that gas behavior offers the most readily assimilated basis for the atomic theory. Having thus proposed the theory, we are afforded an intuitively simple introduction to the ideas of balancing chemical equations, to weight relations, to a differentiation between elements and compounds, etc. Then in Chapter 14, after the student has accumulated a significant background of experience, we return to a review of the evidence for the atomic theory, beginning with already familiar chemical evidence. Even then, halfway through the course, the operation of a mass spectrometer is somewhat mysterious, but at least this complicated machine is mentioned only after an entire semester of laboratory work. Furthermore, this timely review of evidence for atoms can be presented in such a way that the student will see how a scientific theory gains general acceptance. Consistency among many kinds of data establishes confidence in a theory. Any single behavior must be interpreted within a web of premises. The credibility of the interpretation is attested by its reasonableness when viewed in the pattern of agreement with the other types of evidence.

THE ORIGIN OF THE ATOMIC HYPOTHESIS

Even though they may recognize the relative simplicity and logical adequacy of the combining volume data, some teachers are offended because the treatment is not an accurate account of the historical origin of the atomic hypothesis. It surely is not—no pretense is made to historical accuracy.

We see two possible motivations in a discussion that does adhere to the actual origin of the atomic hypothesis: to relate the chronology of the process, and to convey the logic by which chemical evidence supports the atomic theory. To a certain extent, a simple chronological discussion must reveal the logic, hence the first motivation can be said to include the second. But the reverse is not true. If it is intended only to clarify the logic by which chemical evidence supports the atomic theory, there is no obligation to display the tortuous process by which this logic was recognized. There is no need to lead the student up Dalton's path of incorrect atomic weights. There is no need to drag the student through the half-century of confusion that beclouded the acceptance and effective use of this theory. Indeed, if one's intent is to ensure that the student *understands* the logic, it is *undesirable* to relate the logic to the chronology because it accents difficulty. The argument by which one proceeds from combining weights to a hypothesis of atoms is straightforward, but it is not simple. It is not made simple by telling the student that it took the world's best scientists fifty years to follow this logic and that he has three periods in which to do the same.

Why, then, do some educators (e.g., Conant) argue for the "case history," or the historical presentation? It is because there is a deeper motivation in relating chronology than in merely "setting the record straight" on who discovered what and when. The chronological development reveals that the path to understanding our environment is fraught with wrong turns. It shows that the views accepted in the light of today's knowledge are likely to need modification tomorrow. It proves by example the remark made on Textbook p. 3: "It is inherent in the exploration of the unknown that not every step is an advance. Yet there is no other way to advance than by taking steps." The historically accurate account inevitably reveals the aptness of the fable of the lost child given in Chapter 1. These are useful gains, and there is no doubt that they need to be made in this course if it is to be a satisfactory introductory science course. In fact the importance we place upon conveying these aspects of scientific progress is shown by their prominence in Chapter 1 (via the lost child fable) and throughout the book (via emphasis on uncertainty and tentativity). A historical approach is deliberately used in Chapter 15 to show the development of our understanding of the energy states of atoms. This example serves the foregoing purposes admirably and was deliberately selected in preference to a historical development of the origin of the atomic hypothesis. Freeing the development of the atomic hypothesis from chronology makes it possible to use the simplest and most easily grasped presentation of the logic by which chemical evidence supports the atomic theory.

INTERPRETATION OF COMBINING VOLUME DATA

One of the most important goals of an introductory chemistry course is to encourage the student to think critically. To do so, we have maintained a tight and self-contained logic through the discussion of the combining volumes of gases.

For example, Problem 6 considers the volume ratios in the reaction between hydrogen and chlorine to form hydrogen chloride. The conclusion of the problem is that if chlorine molecules contain an even number of atoms, then hydrogen molecules must also contain an even number of atoms. However, they could both contain an odd number of atoms, as far as the logic is concerned.

A familiar but logically inaccurate argument states that since *one* molecule of chlorine leads to *two* molecules of hydrogen chloride, there *must* be an even number of atoms in a chlorine molecule. This conclusion cannot be drawn without an additional premise, seldom stated. The premise is that the chlorine molecules contain no atoms found in hydrogen molecules. (Of course, the assertion that hydrogen and chlorine are different elements is a special case of this premise.) Yet the data analyzed give no basis whatsoever for this premise. For example, the molecule of hydrogen might have molecular formula H_3. If this were true, the combining volume data for formation of hydrogen chloride would be consistent with such equations as

$$H_3 + HCl_2 = 2H_2Cl$$
$$H_3 + H_3Cl_2 = 2H_3Cl$$
$$H_3 + HCl_4 = 2H_2Cl_2$$

All of these equations state that one volume of hydrogen plus one volume of chlorine gives two volumes of hydrogen chloride.

Naturally we are repelled by the suggestion that chlorine might have such formulas as HCl_2, H_3Cl_2, or HCl_4. The student, however, has no basis for such prejudice. He is merely looking at the data available to him. Although we do not necessarily wish to present erroneous formulas for chlorine, neither do we wish to train the student to jump to a desired result on the basis of arbitrary premises. In fact, it is a very difficult matter to "prove" convincingly that hydrogen is an element and that chlorine contains no hydrogen atoms.

Initially, the treatment in Chapter 2 focuses on the types of conclusions that come directly from combining volume data. The integer ratios suggest the existence of molecules made up of atoms, and they help decide whether a given molecule contains an even or odd number of atoms. Later, when we distinguish between elements and compounds, we must face the question: How do we decide whether hydrogen is an element or a compound?" The answer is that all attempts to show that the gas hydrogen is a compound must fail (that is, all attempts to decompose the compound into two distinct compounds must fail). Thus it takes a large accumulation of experimental evidence to establish that hydrogen is an element (of which combining volume evidence is part). It takes only *one* experiment (and Avogadro's Hypothesis) to establish that each hydrogen molecule (no matter what atoms it contains) contains an even number of atoms *if* each chlorine molecule contains an even number (no matter what atoms the chlorine molecule contains).

WHAT IS A MOLECULE?

A molecule is a collection of atoms held together with sufficient attractive force such that they can be treated as a unit under the conditions of study. This means the unit found in gaseous sodium chloride is a NaCl molecule, just as gaseous hydrogen chloride consists of HCl molecules. In principle, free radicals, gaseous ions such as H_2^+, and ionic complexes in water, such as $CrCl_6^{-3}$, deserve to be called molecules as much as does benzene. We see that we have made an extremely broad definition of a molecule. This has been done deliberately for these two reasons:

1. There is only one cause for atoms to remain close together—the special attractive forces resulting from electrons being simultaneously attracted to two nuclei. (Chapter 16 develops this point.)

2. The species that are traditionally "stable" as molecules, ions, free radicals, and complexes are stable only because of the particular physical conditions available on our planet.

By using the broader definition we plan to keep the student's attention focused on the single cause of bonding and remind him that at conditions different from those in our world, different molecules will be prevalent.

We *do not* propose to discard the terms ion, free radical, etc. used to specify certain kinds of molecules, but you should make a point of the similarities. Monatomic molecules should cause no trouble. They serve as the limiting case of a group of atoms.

MOLECULAR WEIGHT DETERMINATION

This subject may come up through questions—it is not intended that it be presented to the class at this early time. The molecular weight of a gas is usually determined by some application of Avogadro's Hypothesis. The student will make such a determination in Expt. 6. You might indicate briefly the logical procedure in this fashion: We will assume that equal volumes of gases (at the same conditions) contain equal numbers of molecules. By weighing fixed volumes of two gases, we find their relative weights, and from these we can compute the molecular weight of one gas *if* the other is known.

The molecular weight of liquids and of soluble solids is usually found from colligative properties. The freezing point and boiling point of a solution differ from those found for the pure solvent. The lowering of the freezing point (or rise in boiling point) is proportional to the concentration of dissolved particles.

Very-high-molecular-weight compounds (polymers and a number of biological materials such as proteins) require other methods. The most common are osmotic pressure, light scattering, viscosity, and sedimentation rates in ultracentrifuges.

THE MOLE

The mole is a concept of paramount importance. This importance comes from the great simplification that this concept gives to our understanding of the chemical equation and its meaning. As a result, all the operations based on an equation become quite easy. Balancing the equation is related directly to molecules (and the models used to illustrate them). Stoichiometric problems all have a *single* method of solution. Molar heat of reaction and other molar properties are easily understood.

In spite of the importance of the mole, or Avogadro's number of particles, it is strange that, for the chemistry met during the first semester, there is no need to know Avogadro's number. The chemist does not need to know N to solve conventional problems (such as weight or concentration relations). He needs to know only that there *is* such a number. This is why there are no chemical methods for finding N.

There are many problems in modern chemistry for which the chemist does need to know N. Some examples are the determination of atomic dimensions, molecular structures, packing in crystals, and atomic energy levels. The methods outlined below for measuring N were first designed and performed by physicists.

AVOGADRO'S NUMBER

The French physicist, Perrin, undertook, in the early years of the twentieth century, a series of measurements on the Brownian motion of small particles of a natural gum, gamboge. His experimental observations related to the distribution of gas molecules in a gravitational gradient. The fundamental equation for distribution can be readily derived from an equation suggested by L. Boltzmann. According to Boltzmann, the fraction of particles which have an energy equal to or larger than some given value E is given by the relationship

$$\frac{n_E}{n_\Sigma} = e^{-E/kT} \qquad (1)$$

in which n_Σ is the total number of particles and k is Boltzmann's constant (1.3803×10^{-16} erg degree^{-1}). The potential energy of a particle of mass m in a gravitational field with acceleration constant g is given by $E = mgh$; h is the height of the particle above some reference height measured in the direction of the field gradient. Substituting this value of E and $R = kN$ (R is the molar gas constant, and N is Avogadro's number) into equation (*1*) and integrating gives

$$\frac{\Delta n}{n} = \frac{-mgN\,\Delta h}{RT} \tag{2}$$

in which Δn is the change in the number of particles per unit volume at two different heights separated by Δh. The other symbols have their earlier significance.

Perrin prepared uniform gum particles of mass m and observed their distribution in a suspending liquid as a function of height. Thus the only factor in equation (*2*) not susceptible to direct evaluation is N, and Perrin found this number to be 6.8×10^{23} molecules per mole. This number, which is 13% above the best currently accepted value, represented the first reliable value determined for N. It should be remarked parenthetically that Perrin was the first to use the term Avogadro's number (or constant).

An independent evaluation of N, suggested by E. Rutherford, was based on the amount of helium produced by the alpha decay of certain radioactive nuclides. A known quantity of radon gas (produced from radium) was enclosed in a thin-walled container, and the helium (produced when radon undergoes radioactive disintegration) would diffuse through the walls of the container into a second volume previously pumped out to a high vacuum. By measuring the volume of helium gas produced during a known time interval, the fraction of a molar gas volume which this represented could be calculated. From the known decay constant of radon, it was possible to calculate the number of helium atoms that had been formed. From these data, Avogadro's number can be calculated from the relationship

$$N = \frac{2.24 \times 10^4}{V_{\mathrm{He}}} n(1 - e^{-(0.693t/t_{1/2})}) \tag{3}$$

in which V_{He} is the volume of helium collected (corrected to standard conditions) from the decay of n atoms of radon after a time t. The symbol $t_{1/2}$ in this relationship is the half life of $^{222}_{86}\mathrm{Rn}$ expressed in the same time units as t. The value of N calculated by Rutherford and his co-workers, particularly B. Boltwood and H. Geiger, was 6.16×10^{23} atoms per mole.

The first high-precision value for N was obtained on the basis of Millikan's determination of the magnitude of the electron charge, e. Millikan's experiments followed the reasoning laid down by Stokes and Perrin (and developed by Einstein) and were related to the measurements of settling rates of particles in a gravitational field. The earlier experiments, however, required an accurate knowledge of the viscosity of air and of the flow dynamics of gases, as well as a careful selection of particles of uniform size. Millikan avoided these problems by balancing the gravitational force downward with an electrostatic force upward. His observations could thus be confined to essentially stationary particles in an electric field.

The result of Millikan's experiments was a precise value of the electron charge, e, which could then be used to evaluate Avogadro's number from a relationship based on Faraday's law of electrolysis. Faraday had suggested that it was possible to define one mole of electrons as a definite quantity of electricity. This quantity is called one faraday, F, and represented in the chemical literature by

$$F = Ne \tag{4}$$

The value of F can be readily determined from electrochemical experiments, and since such experiments involve only a sequence of weighings which can be carried out to a high precision, the numerical value of the faraday is well known. The value is 9.6519×10^3 coulombs. With Millikan's value for e, it then became possible to calculate a reliable value for N from equation (*4*); that is

$$N = \frac{F}{e} = \frac{9.6519 \times 10^3 \text{ emu/mole}}{1.60203 \times 10^{-20} \text{ emu/electron}}$$

$$F = 6.023 \times 10^{23} \text{ electrons/mole} \tag{5}$$

This quantity F defines the number of electrons per mole, and it also defines the number of any other kind of particle (such as atoms or molecules) per mole of such particles. This number is Avogadro's number.

We may complete the list of some representative methods which have been used to evaluate

N by mentioning a calculation based on the X-ray determination of crystal parameters. Using the X-ray reflection technique it is possible to calculate the spacing, d, between adjacent layers of a regular crystalline solid. Let us illustrate this method by reference to sodium chloride, which crystallizes in a cubic lattice. A cube, or unit cell, of NaCl constructed with four chlorine atoms and four sodium atoms occupying the eight vertices will actually contain one-half of a sodium atom and one-half of a chlorine atom, since one-eighth of each atom is in the cell we are discussing. The cell has a side of 2.814×10^{-8} cm.

One mole of NaCl weighs 58.45 g and occupies $58.45/2.165 = 27.00$ cm^3. The volume containing one Na and one Cl is $2(d)^3 = 4.457 \times 10^{-23}$ cm^3. Thus the number of NaCl units in one mole, N, is

$$\frac{27.00 \text{ cm}^3/\text{mole}}{4.457 \times 10^{-23} \text{ cm}^3/\text{NaCl unit}} = 6.058 \times 10^{23} \text{ NaCl units/mole}$$

The difference between this value and the "best value" probably lies in the experimental difficulty of getting crystals that have no void spaces or cracks.

THE ATOMIC WEIGHT SCALES

The choice of the first atomic weight was an arbitrary one, and there is not unanimous agreement on the best choice. For a long time the chemist used an atomic weight scale based on "naturally occurring" oxygen as 16.0000. A problem arose when it was later found that there are three isotopes (of weight 16, 17, and 18) *and* that the isotopic composition of O_2 is not necessarily constant. The physicists then defined an atomic weight scale based on $^{16}O = 16.0000$. For most chemical purposes the scales are equivalent, but they are not exactly equal (physical scale weight/chemical scale weight = 1.00027). Late in 1961 at least one international group agreed to use ^{12}C = exactly 12.0000 as the standard. Such a standard has advantages because C ions are easy to measure in the mass spectrometer and carbon forms many high-mass molecule ions and hydrides which can act as standards up to high-mass numbers. Oxygen does not have these high-mass ions. Use of the ^{12}C scale implies a change of atomic weights based on O = 16.0000 by a factor 0.9999550. Notice that discussion of these alternate scales will be more appropriate in Chapter 6, where isotopes are introduced. The atomic weight chart inside the back cover is based on $^{12}C = 12.0000$.

THE NAMING OF CHEMICAL ELEMENTS

The nomenclature of elements is not a topic to which you should devote time. There are no rules for the names, and the classifications are of little help in studying chemical properties. An occasional, casual mention of the basis for a name can provide interest and a mental hook for remembering.

A number of substances which are today recognized as elements have been known to man for many centuries, some of them since before recorded history. Among these are the elements copper, silver, gold, iron, sulfur, lead, tin, mercury, and carbon. The names applied to these materials have been so firmly fixed in the language that applying a particular "scientific" name has not been possible.

For the more recently isolated elements, the origin of their names falls roughly into three classes: *neoclassical*, *geographical*, and *honorary*. The neoclassical names, usually taken from Latin or Greek roots, are those applied in such a way that a chemical or physical property of the element is revealed thereby. The roots of helium and hydrogen are well known. Silicon is named for the Latin word silex, for flint.

The geographical group of names includes elements such as europium, holmium (after the Latinized form of Stockholm), lutetium (after a variant of the name of the patron saint of Paris), berkelium, californium, americium, francium, scandium (after Scandinavia), yttrium (after the town of Ytterby in Sweden), rhenium (after the Rhine River in Germany), and strontium (after the town of Strontian in Scotland).

The honorary names—largely applied to the most recent synthetic elements—include einsteinium, fermium, mendelevium, and lawrentium, as well as gadolinium and samarium.

A list of the origin of names can be found in *The Restless Atom*, by A. Romer, Doubleday, New York (1960). In *Discovery of the Elements*, a book published by *J. Chemical Education*, 1956, M. E. Weeks describes each element and the chemists associated with its isolation. The book contains some useful background information and may be of interest to some students.

Modern convention invests the discoverer or group of discoverers with the prerogative for suggesting a name for the new element. If the claim of discovery is recognized by the International Union of Pure and Applied Chemistry, the suggested name is usually adopted internationally. Official adoption does not, however, necessarily place the name of the element into general or undisputed usage. For example, the recently adopted official name for element 74 is wolfram. English and American chemists, among others, appear almost universally to prefer the name tungsten, and it is this appellation which appears most frequently in the technical literature of the English-speaking world.

CONSTRUCTION OF MOLECULAR MODELS

Section 2-3.2 deals with models. Several kinds are presented to make the point that a given kind shows only certain features and fails to show others. Chemists use different kinds for different purposes. An important point to make is that any model is just what the name implies. It gives only a partial representation, and this is usually flawed. For example, molecules do not have definite boundaries, as do our models.

The following directions will permit you to make models of a dozen or so substances frequently referred to in the text. The plan is essentially this: styrofoam balls of the proper diameter (van der Waals radius) are cut so as to give proper separation (covalent radius) when glued together.

Before giving the details, let us describe the source of data. For the distance between bonded atoms we use covalent radii. These are deduced from interatomic distances in molecules, as determined by the methods of X-ray diffraction, electron diffraction, and molecular spectroscopy. Pauling* (and others) have attempted to divide these bond lengths into additive contributions from each atom. The additivity of such assigned radii is not perfect, but it is sufficiently good such that the radii have wide acceptance among chemists. Note that we *never* measure a radius; we always measure an internuclear distance. Furthermore, X-ray measurements of solids are not as good as those made on gaseous molecules, hence they are used *only* when reliable gas phase work is not available—which is often, of course. For the sphere diameter we use the van der Waals radii determined from interatomic distances between nonbonded atoms in crystals. The result is a "distance of nearest approach" for nonbonded atoms. These are also given by Pauling. Table 2-I gives some values. For actual construction, some scale must be chosen. A scale of 2 cm = 1 Å gives a size that is convenient for

Table 2-I

Some Covalent and van der Waals Radii

Element	Covalent Radii (r_c in Å)	van der Waals Radii (r_v in Å)	Angle Between Bonds (degrees)
hydrogen	0.30	1.2	—
hydrogen (in H_2)	0.37	1.2	—
carbon (single-bonded)	0.77	1.7	109.5
nitrogen (single-bonded)	0.70	1.50	109
nitrogen (in N_2)	0.55	1.50	—
oxygen (in O_2)	0.60	1.40	—
oxygen (two single bonds)	0.66	1.40	105
sulfur (two single bonds)	1.04	1.85	92
fluorine	0.64	1.35	—
chlorine	0.99	1.80	—

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* L. Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press (1960), Chapter 7. Useful tables are on pp. 224, 256, and 260.

classroom use. This makes the model 200 million times as large as the actual molecule.

The construction of atom models is divided according to the number of "bonds"—that is, according to how many segments are cut off. The procedure is the same for all "one-bond" atomic models (H, Cl, F), although different dimensions must be used. Likewise for "two-bond" (O, S), three-bond (N) and four-bond (C) models.

Procedure: General

Select the styrofoam sphere. If the proper diameter is not available, an oversized one can be rolled down. The reduction in diameter is limited to a few millimeters, depending on the sphere diameter and the density of the styrofoam. Use books or piles of paper to get the proper height, then roll with a piece of plywood resting on the books. This produces a compact and more durable surface. In addition, it is easy to paint and looks better.

An easy way to establish the position of the cut is to construct plane figures as follows.

Model of Atom with One Bond

(a) Draw a circle with radius equal to the van der Waals radius. Use whatever scale you choose; all values in Table 2-I will be doubled if you use 2 cm = 1 Å. Mark the center.

(b) Draw a diameter of the circle.

(c) Measure out one r_c from the center, and draw a perpendicular.

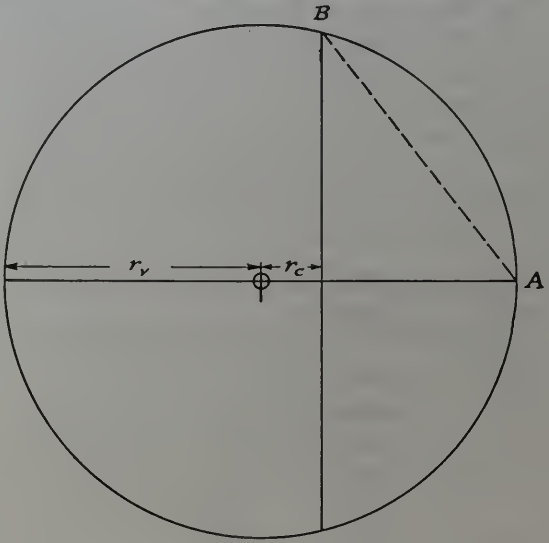
The results should be as shown in the diagram at the top of the next column.

(d) Now set a compass for the distance *AB*, and draw a circle on the sphere using this radius.

(e) Use a hack saw blade to saw the segment off, leaving a few millimeters extra on the sphere. Sand this off with fairly coarse garnet paper. You can use sandpaper, but it is less satisfactory. Proceed gently; the styrofoam cuts very easily. *Note:* Painting can be done before or after assembly.

(f) Paint the curved surfaces with white latex-base paint. This acts as filler and undercoat to protect the plastic, which dissolves in some enamels.

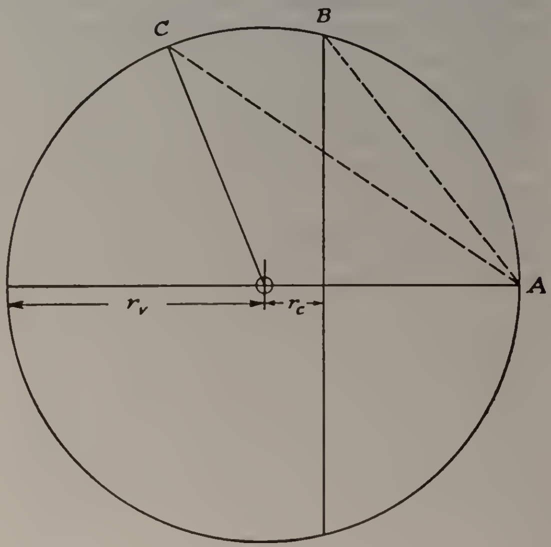
(g) Enamel is best for the second coat of paint.



Model of Atom with Two Bonds

Repeat steps a–c as for the single-bonded atomic model.

(d) Construct a radius from the center at the angle given in Table 2-I. The results are as shown in the diagram below.



(e) Mark a dot on the sphere.
(f) Set *AC* on the compass, and lay it off from the dot. Make a second dot on the sphere.
(g) Now set *AB* on the compass, and draw a circle around each dot.
(h) Saw, sand, and paint as before. Be careful that sanding maintains the angle.

Models of Atoms with Three or Four Bonds

Repeat steps a–f as for double-bonded atomic models.

(g) Using the two dots as centers and *AC* as the compass setting, locate one (or two) more dots, equidistant from the two marked. Draw short arcs from each marked spot to get the new point at the intersection(s).
(h) Now set *AB* on the compass, and draw a circle around each point on the sphere.
(i) Saw, sand, and paint as before.

Procedure: Assembly

After the models are prepared, there are two ways to assemble them. For "permanent" models, glue the flat faces together with a few drops of white plastic glue (Elmer's or Wilhold are good). A few models, particularly two of H_2 and one of O_2, should come apart easily, for illustrating the formation of water and the balancing of chemical equations (Chapter 3). For this, two modifications are needed. Some kind of peg is required for holding the atomic models together, and half the hydrogens must be hollowed out to fit on a spherical part of an oxygen. For the peg, use a piece of pipe cleaner glued in at one end. To hollow out an atom model, first cut the flat face, gouge some out with a knife or your fingernails. Then, finish it off by holding a $\frac{1}{2}$ inch strip of garnet paper over the oxygen-size sphere and gently rotating the hydrogen. Some extra pipe cleaner "bonds" are required. With a compass point, punch a hole in the oxygen for the "bond" to a hydrogen.

REFERENCE INFORMATION

Suppliers

Of the many suppliers of styrofoam, those below are given as sources of three typical types of spheres. Others may be found listed in the yellow pages of a phone book under Plastics, Foam. Send for price lists.

Star Band Co., Broad and Commerce Sts., Portsmouth, Va. (abraded spheres which can be compressed to obtain great range of diameters).

Foam Plastics Inc., Forest Lake, Minn. (molded spheres, compressible, smooth surface).

Plasteel Corp., 26970 Princeton, Inkster, Mich. (molded pellets, noncompressible).

Data for other models

L. Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press (1960).

A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press (Oxford Univ. Press) (1962).

Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publ. #11, The Chemical Society, Burlington House, London, 1958.

Uses

Numerous articles in *J. Chem. Ed.* have described uses and ways to make models.

Answers to Exercises and Problems

Ex. 2-1. If 32.00 grams of hydrogen chloride gas (at 0°C and one atmosphere) occupy 19.65 liters, then a larger weight of hydrogen chloride is needed to occupy the larger volume, 22.4 liters. Show that the weight needed is 36.5 grams.

Answer

Since 32.00 grams occupy 19.65 liters,

$$\frac{32.00\text{ g}}{19.65\text{ liters}} \times 22.4\text{ liters} = 36.5\text{ g}$$

Ex. 2-2. In Section 2-2.2 (p. 25) it was noted that two volumes of hydrogen gas combine with one volume of oxygen gas and that two volumes of gaseous water are produced. According to Avogadro's Hypothesis, this means that *two* molecules of hydrogen combine with *one* molecule of oxygen to form *two* molecules of water. If we define

X = number of atoms in a molecule of hydrogen
Y = number of atoms in a molecule of oxygen
Z = number of atoms in a molecule of water

then we have the algebraic relationship,

$$2X + Y = 2Z$$

(a) Convince yourself that from these data alone we can conclude that Y must be *even* (that is, oxygen molecules must contain an even number of atoms).
(b) By solving for X in terms of Y and Z, convince yourself that from the above data alone, X could be odd or even.

Answer

(a) If $2X + Y = 2Z$, then

$$Y = 2(Z - X)$$

Since both X and Z are integers, $Z - X$ will be an integer. Double any integer is an even number, hence Y must be even.

(b) If $2X + Y = 2Z$, then

$$X = \frac{2Z - Y}{2} = Z - \frac{Y}{2}$$

As shown in part (a), the data given establish that *Y must be an even integer*. Hence $Y/2$ is necessarily an integer, though $Y/2$ can be either odd or even. (Thus if $Y = 2$, $Y/2 = 1$, whereas if $Y = 4$, $Y/2 = 2$.) The data give no clue at all concerning whether Z is odd or even. Hence X is an integer (it is the difference between two integers), but the data do not indicate whether it is odd or even.

Ex. 2-3. What differences between water, oxygen, and hydrogen can you point out from your own experience? For example, you might consider
(a) boiling and melting points,
(b) role in combustion,
(c) role in supporting life.

Answer

(a) Water boils at 100°C and freezes at 0°C The student will probably not know these properties for oxygen and hydrogen, but he should know that these gases boil at much lower temperatures than 0°C.
(b) Oxygen is needed for combustion—water hinders it, although it is usually a product of combustion.
(c) Oxygen and water are needed for life. Hydrogen gas is not.

Ex. 2-4. Carbon dioxide has the formula CO_2. Remembering that the prefix "di" means two, and "tri" means three, write the molecular formula for each of the following substances: carbon disulfide, sulfur dioxide, sulfur trioxide. (If you don't know the symbol for an element, use the table inside the back cover of the book.)

Answer

carbon disulfide:	CS_2
sulfur dioxide:	SO_2
sulfur trioxide:	SO_3

Ex. 2-5. Show that the weight of a mole (the molecular weight) of CO_2 is 44.0 grams and that the weight of a mole of SO_2 is 64.1 grams.

Answer

A mole of CO_2 molecules contains one mole of carbon atoms and 2 moles of oxygen atoms and weighs $12 + 2(16.0) = 44$ g/mole.

A mole of SO_2 molecules contains one mole of sulfur atoms and 2 moles of oxygen atoms and weighs $32.1 + 2(16.0) = 64.1$ g/mole.

Ex. 2-6. In Experiment 6 you calculated the ratio of the weight of carbon dioxide to the weight of the same volume of oxygen. Oxygen has been assigned a molecular weight of 32.0. From the molecular weight of oxygen and your measured ratio, calculate the molecular weight of carbon dioxide. Estimate the uncertainty in your result. Compare to the value obtained in Exercise 2-5.

Answer

Let us assume that a particular weight ratio obtained in Expt. 6 for equal volumes of carbon dioxide and oxygen was

$$\frac{\text{g carbon dioxide gas}}{\text{g oxygen gas}} = 1.37$$

A molecular weight contains 6.02×10^{23} molecules, which by Avogadro's Hypothesis occupies a fixed volume (for a given T and P). Consequently a molecular weight ratio will be a ratio of weights of equal volumes of gas:

$$\frac{\text{molecular weight carbon dioxide}}{\text{molecular weight oxygen}} = 1.37$$

molecular weight carbon dioxide gas

$$= 1.37 \times (32.0)$$
$$= 43.8 \text{ g/mole}$$

The weighing uncertainty in the data of Expt. 6 was estimated by the student in question 5 of that experiment. The uncertainty should be near 5 or 6%. Since this number is used in a product with 32.0, a defined number, the relative uncertainty should be the same in the student's answer. Acceptable values would be 44 ± 3 g, or 43.8 g ± 6%.

Ex. 2-7. What is the molecular weight of each of the substances sulfur (formula, S_8), ammonia (formula, NH_3), and nitrogen (a diatomic molecule)?

Answer

One mole of S_8 weighs

$$8 \times (32.1) = 256.8 = 257 \text{ g}$$

One mole of NH_3 weighs

$$14.01 + 3(1.008) = 14.01 + 3.024 = 17.03 \text{ g}$$

One mole of N_2 weighs

$$2(14.01) = 28.02 \text{ g}$$

Ex. 2-8. Calculate the weight of 6.02×10^{23} molecules of carbon monoxide, CO.

Answer

There are 6.02×10^{23} molecules in one mole of CO. One mole of CO weighs

$$12.01 + 16.00 = 28.01 \text{ g}$$

Ex. 2-9. How many moles of iron atoms are present in 1.73 grams of iron?

Answer

One mole of iron atoms weighs 55.8 g. Hence 1.73 g contain

$$\frac{1.73 \text{ g}}{55.8 \text{ g/mole}} = \frac{1.73}{55.8} \text{ mole} = 0.0310 \text{ mole}$$

Pr. 1. Hydrogen, helium, and carbon dioxide are all gases at normal temperatures. What differences among the properties of these gases account for the following?

(a) Hydrogen and helium are used in balloons, whereas carbon dioxide is not.

(b) Helium is less dangerous to use in balloons than is hydrogen.

Answer

The answers are supposed to be accessible to the student through his previous knowledge, without additional class discussion.

(a) Hydrogen and helium are less dense than air, whereas carbon dioxide is more dense than air.

(b) Hydrogen is flammable, whereas helium is not.

Pr. 2. Four differences between helium gas and nitrogen gas are listed below.

(a) Dry air contains 80% nitrogen but only 0.0005% helium (by volume).

(b) Helium is much less dense than nitrogen.

(c) Helium has much lower solubility in water than nitrogen has.

(d) Helium is much more expensive than nitrogen.

Which difference could account for the fact that a diver is much less likely to suffer from the bends if he breathes a mixture of 80% helium and 20% oxygen than if he breathes air? (The bends is a painful, sometimes fatal, disease caused by the formation of gas bubbles in the veins and consequent interruption of blood flow. The bubbles form from gas dissolved in the blood at high pressure.)

Answer

(c) Helium-oxygen mixtures are used for diving at extreme depths because of the low solubility of helium in the blood (which is mostly water) reduces the likelihood of the "bends."

Pr. 3. The most important step in the process for the conversion of atmospheric nitrogen into important commercial compounds such as fertilizers and explosives involves the combination of one volume of nitrogen gas with three volumes of hydrogen gas to form two volumes of ammonia gas.

From these data and Avogadro's Hypothesis, how many *molecules* of hydrogen combine with one *molecule* of nitrogen? How many *molecules* of ammonia are produced from one *molecule* of nitrogen?

Answer

one volume of nitrogen	combines with	three volumes of hydrogen	to give	two volumes of ammonia.

Therefore, by Avogadro's Hypothesis,

one molecule of nitrogen	combines with	three molecules of hydrogen	to give	two molecules of ammonia.

Pr. 4. Gaseous uranium hexafluoride is important in the preparation of uranium as a source of "atomic energy."

A flask filled with this gas is weighed under certain laboratory conditions (temperature and pressure), and the weight of the gas is found to be 3.52 grams. The same flask is filled with oxygen gas and is weighed under the same laboratory conditions. The weight of the oxygen in the flask is found to be 0.32 gram.

What is the ratio of the weight of one uranium hexafluoride molecule to the weight of an oxygen molecule? State any guiding principles needed in answering this question.

Answer

The equal volumes contain equal numbers of molecules if Avogadro's Hypothesis is assumed. Therefore,

$$\frac{\text{wt uranium hexafluoride molecule}}{\text{wt oxygen molecule}} = \frac{\text{wt uranium hexafluoride gas}}{\text{wt oxygen gas sample}} = \frac{3.52}{0.32} = 11$$

Pr. 5. Two volumes of hydrogen fluoride gas combine with one volume of the gas dinitrogen difluoride to form two volumes of a gas G.

(a) According to Avogadro's Hypothesis, how many molecules of G are produced from one molecule of dinitrogen difluoride?

(b) If X = number of atoms in a molecule of hydrogen fluoride,
Y = number of atoms in a molecule of dinitrogen difluoride, and
Z = number of atoms in a molecule of G,
write the relation among X, Y, and Z appropriate to the combining volumes given.

(c) For each of the following possible values of X and Y, calculate the required value of Z.

If X is	and	Y is	then	Z must be
1		2		
1		4		
2		2		
2		4		

(d) No odd value of Y is suggested in question (c). Prove that Y *must* be an even integer.

Answer

(a) Two *volumes* of G are produced from one *volume* of dinitrogen difluoride; therefore two *molecules* of G are produced from one *molecule* of dinitrogen difluoride

(b) $2X + Y = 2Z$

(c)

X	Y	Z
1	2	2
1	4	3
2	2	3
2	4	4

(d) If $2X + Y = 2Z$, then

$$Y = 2(Z - X)$$

Since both X and Z are integers, $Z - X$ will be an integer. Double any integer is an even number, thus Y must be even.

Note to teacher: This example is very similar to Exercise 2-2. It carries the student through this argument for a system not involving elements to show him that the volume data alone do not give a basis for deciding whether a gas is or is not an element. The gas G is NHF_2 (nitrogen monohydrogen difluoride).

Pr. 6. There are a number of gas mixtures that combine in the general pattern

one volume of gas *A*	combines with	one volume of gas *B*	to form	two volumes of gas *C*

For example,

one volume of carbon dioxide	combines with	one volume of carbon disulfide	to form	two volumes of carbon oxysulfide
one volume of hydrogen	combines with	one volume of chlorine	to form	two volumes of hydrogen chloride

If X = number of atoms in a molecule of A,
Y = number of atoms in a molecule of B, and
Z = number of atoms in a molecule of C,

(a) Show that if X is even, Y must be even.
(b) Show that if X is odd, Y must be odd.

Answer

The volume data, by Avogadro's Hypothesis, imply that $X + Y = 2Z$. Hence $Y = 2Z - X$.

(a) No matter what value Z has, $2Z$ is an *even* integer. Therefore if X is also an even integer, the difference between two even numbers *must* be an even number. Thus, if X is even, Y must be even.

(b) On the other hand, if X is odd, the difference between an even number ($2Z$) and an odd number (X) *must* be odd. Thus, if X is odd, Y must be odd.

Pr. 7. A pure white substance, on heating, forms a colorless gas and a purple solid. Is the substance an element or a compound?

Answer

Since at least two substances were formed, as shown by the two different products, the original substance must have been a compound.

Pr. 8. What do the following symbols represent? K, Ca, Co, CO, Pb.

Answer

K represents one atom or one mole of atoms of the element potassium.

Ca represents one atom or one mole of atoms of the element calcium.

Co represents one atom or one mole of atoms of the element cobalt.

CO represents one molecule or one mole of molecules of a compound containing one atom of carbon and one atom of oxygen in each molecule.

Pb represents one atom or one mole of atoms of the element lead.

Pr. 9. Write formulas for
silicon dioxide (common sand, or silica)
sulfur dichloride
nitrogen trifluoride
aluminum trifluoride
dinitrogen difluoride

Answer

SiO_2, SCl_2, NF_3, AlF_3, N_2F_2.

Pr. 10

(a) Write formulas for
hydrogen chloride
hydrogen bromide
hydrogen iodide
boron trichloride
carbon tetrachloride
nitrogen trichloride
oxygen dichloride

(b) Locate in the table inside the front cover the symbol for each element involved in these compounds.

Answer

(a) HCl, HBr, HI, BCl_3, CCl_4, NCl_3, OCl_2.

(b) No written answer is expected, and class discussion of the locations is not intended. Let students who notice the regularities wonder about them.

Pr. 11. For each of the following substances give the name of each kind of atom present and the total number of atoms represented in the formula shown.

Name	Formula
(a) graphite (pencil lead)	C
(b) diamond	C
(c) sodium chloride (table salt)	$NaCl$
(d) sodium hydroxide	$NaOH$
(e) calcium hydroxide	$Ca(OH)_2$
(f) potassium nitrate	KNO_3
(g) magnesium nitrate	$Mg(NO_3)_2$
(h) sodium sulfate	Na_2SO_4
(i) calcium sulfate	$CaSO_4$

Answer

Note that the point of the problem is to establish familiarity with the symbols. Refer to the "formulas" to avoid the word "molecules," but otherwise postpone discussing the distinction between molecular and empirical formulas.

Elements	Total number of atoms shown
(a) carbon	1
(b) carbon	1
(c) sodium, chlorine	2
(d) sodium, oxygen, hydrogen	3
(e) calcium, oxygen, hydrogen	5
(f) potassium, nitrogen, oxygen	5
(g) magnesium, nitrogen, oxygen	9
(h) sodium, sulfur, oxygen	7
(i) calcium, sulfur, oxygen	6

Pr. 12. All of the following substances are called "acids." What element do they have in common?

(a) nitric acid	HNO_3
(b) hydrochloric acid (or hydrogen chloride)	HCl
(c) hydrofluoric acid (or hydrogen fluoride)	HF
(d) sulfuric acid	H_2SO_4
(e) phosphoric acid	H_3PO_4

Answer

All of the substances contain hydrogen.

Pr. 13. Here are the names of some common chemicals and their formulas. What elements does each contain?

(a) hydrogen peroxide	H_2O_2
(b) jeweler's rouge	Fe_2O_3
(c) light bulb filament	W
(d) tetraethyl lead	$Pb(C_2H_5)_4$
(e) baking soda	$NaHCO_3$
(f) octane	C_8H_{18}
(g) household gas	CH_4

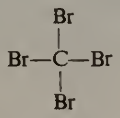
Answer

- (a) hydrogen, oxygen;
- (b) iron, oxygen;
- (c) tungsten;
- (d) lead, carbon, hydrogen;
- (e) sodium, carbon, oxygen, hydrogen;
- (f) carbon, hydrogen;
- (g) carbon, hydrogen.

Pr. 14

(a) What does the molecular formula CBr_4 mean?

(b) What information is added by the following structural formula?



$$\begin{array}{c} Br \\ | \\ Br\text{—}C\text{—}Br \\ | \\ Br \end{array}$$

Answer

(a) Four atoms of bromine are combined with one atom of carbon to form one molecule of carbon tetrabromide.

(b) Each of the bromine atoms is individually attached to the carbon atom. Note that this type of structural formula does not suggest exact spatial arrangements.

Pr. 15. How many particles are there in a mole?

Answer

6.02×10^{23} particles.

Pr. 16. A stone about the size of a softball weighs roughly a kilogram. How many moles of such stones would be needed to account for the entire mass of the Earth, about 6×10^{27} grams?

Answer

$$6 \times 10^{27}\text{ g} = 6 \times 10^{24}\text{ kg}$$

$$\begin{array}{c}\text{Moles of kilograms}\\ \text{(stones)}\end{array} = \frac{6 \times 10^{24}\text{ kg of stones}}{6 \times 10^{23}\text{ kg/mole}}$$

$$= 10\text{ moles of stones}$$

Pr. 17. If we had one mole of dollars to divide among all the people in the world, how much would each of the three billion inhabitants receive?

Answer

Population = 3 billion persons = 3×10^9 persons

$$\frac{6.02 \times 10^{23}\text{ dollars}}{3 \times 10^9\text{ persons}} = 2.01 \times 10^{14}\text{ dollars/person}$$

or about 200,000 billion dollars for each person.

Pr. 18. How many moles of atoms are in

(a) 9.0 grams of aluminum *Ans.* (a) $\frac{1}{3}$ mole.

(b) 0.83 grams of iron

Answer

(a) 27 g of aluminum contain one mole of aluminum atoms

$$9\text{ g} = \frac{9\text{ g}}{27\text{ g/mole}} = \frac{1}{3}\text{ mole}$$

(b) 56 g of iron contain one mole of iron atoms

$$0.83\text{ g} = \frac{0.83\text{ g}}{56\text{ g/mole}} = 1.5 \times 10^{-2}\text{ mole}$$

Pr. 19. The most delicate balance can detect a change of about 10^{-8} grams. How many atoms of gold would be in a sample of that weight?

Answer

1 mole gold = 6.02×10^{23} gold atoms = 197 g

$$\text{g} \times \frac{\text{mole}}{\text{g}} \times \frac{\text{atoms}}{\text{mole}} = \text{atoms}$$

$$10^{-8} \times \frac{1}{197} \times 6.02 \times 10^{23}$$

$$= 3 \times 10^{13}\text{ gold atoms in }10^{-8}\text{ g}$$

Pr. 20. How many moles of oxygen atoms are in one mole of nitric acid molecules? Of sulfuric acid molecules?

Answer

The molecular formula of nitric acid is HNO_3. Hence one mole of nitric acid contains three moles of oxygen atoms. A mole of sulfuric acid, with molecular formula H_2SO_4, contains four moles of oxygen atoms.

Pr. 21. Determine the weight, in grams, of one silver atom. *Ans.* 1.79×10^{-22} gram.

Answer

Since 6.02×10^{23} silver atoms weigh 108 grams, one atom will weigh

$$\frac{108 \text{ g/mole}}{6.02 \times 10^{23} \text{ atoms/mole}} = 1.79 \times 10^{-22} \text{ g/atom}$$

Pr. 22. Write the formulas for the following compounds, and give the weight of one mole of each: carbon disulfide, sulfur hexafluoride, nitrogen trichloride, osmium tetroxide.

Answer

CS_2,	76.2 g;
SF_6,	146.1 g;
NCl_3,	120.5 g;
OsO_4,	254.2 g.

Pr. 23. Consider the following data

Element	Atomic Weight
A	12.01
B	35.5

Elements *A* and *B* combine to form a new substance, *X*. If four moles of *B* atoms combine with one mole of *A* to give one mole of *X*, then the weight of one mole of *X* is

(a) 47.5 g;
(b) 74.0 g;
(c) 83.0 g;
(d) 154.0 g;
(e) 166.0 g.

Answer

(d) $12.01 + 4(35.5) = 154.0$ g.

Pr. 24. Calculate the molecular weight for each of the following: SiF_4, HF, Cl_2, Xe, NO_2.

Answer

SiF_4	$28.1 + 4(19.0)$	= 104.1 g/mole
HF	$1.0 + 19.0$	= 20.0 g/mole
Cl_2	$2(35.5)$	= 71.0 g/mole
Xe	131.3	= 131.3 g/mole
NO_2	$14.0 + 2(16.0)$	= 46.0 g/mole

Pr. 25. If $1\frac{1}{2}$ moles of hydrogen gas (H_2) react in a given experiment, how many grams of H_2 does this represent?

Answer

$$\text{moles} \times \frac{\text{g}}{\text{mole}} = \text{g}$$

$$1.5 \times 2.0 = 3.0 \text{ g } H_2$$

Pr. 26. How many moles are contained in 49 grams of pure H_2SO_4? *Ans.* 0.50 mole.

Answer

The molecular weight of H_2SO_4 is

$$32.1 + 4(16.00) + 2(1.008) = 98.1 \text{ g/mole}$$

$$\frac{\text{wt}}{\text{mol wt}} = \frac{\text{g}}{\text{g/mole}} = \text{moles}$$

$$\frac{49}{98.1} = 0.50 \text{ mole}$$

Pr. 27. A chemist weighs out 10.0 grams of water, 10.0 grams of ammonia, and 10.0 grams of hydrogen chloride (hydrochloric acid). How many moles of each substance does he have?

Answer

The molecular formulas are H_2O, NH_3, and HCl.

Substance	Molecular Weight
H_2O	$16.00 + 2(1.008) = 18.02$ g/mole
NH_3	$14.01 + 3(1.008) = 17.03$ g/mole
HCl	$35.5 + 1.008 = 36.5$ g/mole

$$\frac{\text{wt}}{\text{mol wt}} = \text{moles}$$

H_2O	$\frac{10.0}{18.02} = 0.555$ mole
NH_3	$\frac{10.0}{17.03} = 0.587$ mole
HCl	$\frac{10.0}{36.5} = 0.274$ mole

Pr. 28

(a) The ratio of the weight of a liter of chlorine gas to the weight of a liter of oxygen gas, both measured at room temperature and pressure, is 2.22. Calculate the molecular weight of chlorine.

(b) How does this value compare with the atomic weight of chlorine found in the chart of atomic weights? What is the formula of a molecule of chlorine?

Answer

(a) By Avogadro's Hypothesis, equal volumes (at the same *T* and *P*) contain equal numbers of molecules. Hence the ratio of the weights of equal volumes is the same as the ratio of the molecular weights.

$$\frac{\text{mol wt chlorine}}{\text{mol wt oxygen}} = \frac{\text{wt 1 liter chlorine}}{\text{wt 1 liter oxygen}} = 2.22$$

$$\text{mol wt chlorine} = (2.22)(32.00) = 71.1 \text{ g/mole}$$

(b) The atomic weight of chlorine is 35.5 g/mole of atoms.

$$\frac{71.1}{35.5} = 2.00 \frac{\text{moles of atoms}}{\text{moles of molecules}}$$

or 2.00 atoms/molecule. The formula of a chlorine molecule is Cl_2.

Pr. 29. A flask of gaseous CCl_4 was weighed at a measured temperature and pressure. The flask was flushed and then filled with oxygen at the same temperature and pressure. The weight of the CCl_4 vapor will be about

(a) the same as that of oxygen
(b) one-fifth as heavy as the oxygen
(c) five times as heavy as the oxygen
(d) twice as heavy as the oxygen
(e) one-half as heavy as the oxygen

Answer

The molecular weight of CCl_4 is 154.0 g/mole. The CCl_4 vapor will weigh $154.0/32.00 = 4.814$, or about five times the weight of oxygen. Choice (c) is the correct answer.

Pr. 30. Suppose chemists had chosen a billion billion (10^{18}) as the number of particles in one mole. What would the molecular weight of oxygen gas be?

Answer

The weight of one oxygen molecule is

$$\frac{32.0}{6.02 \times 10^{23}} \text{ g}$$

Thus the weight of 10^{18} molecules would be

$$\frac{32.0}{6.02 \times 10^{23}} \times 10^{18} = 5.32 \times 10^{-5} \text{ g}$$

Pr. 31. One volume of hydrogen gas combines with one volume of chlorine gas to produce two volumes of hydrogen chloride gas (all measured at the same temperature and pressure). A variety of other types of evidence suggests that hydrogen is an element and that its molecules are diatomic.

(a) Which one of the following possible molecular formulas for the substance chlorine is *not* consistent with the volumes that combine? (Use only the data given here; do not presume the molecular formula of hydrogen chloride.)

(i) Cl_2
(ii) Cl_4
(iii) H_2Cl_2
(iv) H_3Cl_2
(v) H_4Cl_2

(b) For each formula in part (a) that *is* consistent with the combining volumes data (and the formula H_2 for hydrogen), calculate the molecular weight indicated by that formula.

(c) For each acceptable formula in part (a) predict the molecular formula for the substance hydrogen chloride.

Answer

(a) The only restriction placed on the molecular formula of the substance chlorine by the combining volume information is that if hydrogen contains an even number of atoms, then chlorine must *also* contain an even number of atoms (see Problem 6). Proving that the substance hydrogen is an element provides no basis for concluding that the substance chlorine is an element. Hence the only molecular formula that can be eliminated on the basis of these data alone is (iv), because it contains an odd number of atoms.

(b) Using the atomic weights now accepted, the molecular weights would be

(i) Cl_2	71.0
(ii) Cl_4	142.0
(iii) H_2Cl_2	73.0
(iv) impossible	
(v) H_4Cl_2	75.0

(c) Notice that this question amounts to balancing an equation. Do not pursue this topic in class; it is the subject of the next chapter. The student should work out the answer assuming that atoms are conserved.

(i) HCl;
(ii) HCl_2;
(iii) H_2Cl;
(iv) impossible;
(v) H_3Cl.

Suggested Quiz Probelms

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

The following statements apply to problems 1–3. Why does a gas enclosed in a balloon exert pressure on the walls of the balloon? One possible answer is the following model: The gas is a spongy material—like foam rubber. When it is compressed, the force exerted increases; but when it is released, it expands again.

1. Which of the following experimental evidence is NOT consistent with this proposed model?
   (1) A gas fills the container.
   (2) Increasing the pressure causes the volume to decrease.
   (3) Increasing the amount of gas increases the pressure.
   (4) A gas has mass.
   (5) When the gas is compressed and cooled it changes into a liquid.

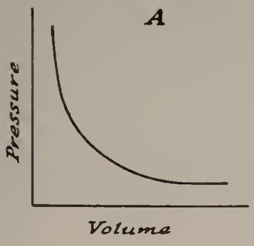
   Answer: (5).

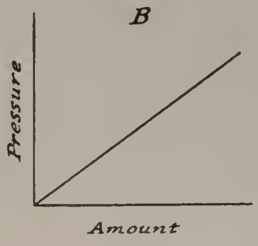
2. Describe the changes that occur when a gas is treated in the following ways.
   (1) A sample of gas is compressed at a constant temperature.
   (2) Gas is added to a steel container at a constant temperature.

   Answer: (1) The volume decreases.
   (2) The pressure increases.

3. Draw a curve representing the following relationships for a gas.
   (1) Pressure vs. volume (temperature and amount constant).
   (2) Pressure vs. amount (volume and temperature constant).

   Answer





4. How many moles of each kind of atom are in a mole of each of the following molecules?
   (1) H_2SO_4.
   (2) NO_2.
   (3) CO_2.
   (4) CH_3COOH.

   Answer
   (1) 2 moles H atoms; 1 mole S atoms; 4 moles O atoms.
   (2) 1 mole N atoms; 2 moles O atoms.
   (3) 1 mole C atoms; 2 moles O atoms.
   (4) 2 moles C atoms; 4 moles H atoms; 2 moles O atoms.

5. Assume that we have equal volumes of two different gases, *A* and *B*, at the same temperature and pressure. The sample of gas *A* weighs 1.60 g, and the sample of gas *B* weighs 3.55 g.
   (1) What is the weight of one molecule of *B* as compared to one molecule of *A*?
   (2) Assume that gas *A* is oxygen. What is the molecular weight of gas *B*?

   Answer
   (1) $\frac{3.55 \text{ g of } B}{1.60 \text{ g of } A} = 2.22$
   One molecule of *B* is 2.22 times as heavy as one molecule of *A*.
   (2) $(32 \text{ g/mole}) \times 2.22 = 71.0 \text{ g/mole}$

6. How many grams are contained in one mole of each of the following?
   (1) Sodium chloride, NaCl (table salt).
   (2) Water, H_2O.
   (3) Silver, Ag.
   (4) Potassium nitrate, KNO_3.
   (5) Magnesium sulfate, $MgSO_4$.

   Answer
   (1) 58.5 g/mole.
   (2) 18.0.
   (3) 107.9.
   (4) 101.1.
   (5) 120.4.

7. How many atoms are contained in a *mole* of each of the following?
   (1) Sulfuric acid, H_2SO_4.
   (2) Calcium hydroxide, $Ca(OH)_2$.
   (3) Nitrogen dioxide, NO_2.
   (4) Acetic acid, CH_3COOH.
   (5) Sucrose, $C_{12}H_{22}O_{11}$.

   Answer

   (1) $7 \times 6.02 \times 10^{23}$ atoms/mole.
   (2) $5 \times 6.02 \times 10^{23}$ atoms/mole.
   (3) $3 \times 6.02 \times 10^{23}$ atoms/mole.
   (4) $8 \times 6.02 \times 10^{23}$ atoms/mole.
   (5) $45 \times 6.02 \times 10^{23}$ atoms/mole.

8. How many molecules are there in 16.0 grams of methane (CH_4)?

   Answer: 6.02×10^{23}.

9. The following tests were made.
   (1) A white solid was heated gently, producing a gas which was partially condensed to a colorless liquid and a second white solid.
   (2) A dark gray solid was heated gently, producing a purple vapor. The solid disappeared, leaving no residue.
   (3) The white solid formed from two colorless gases, ammonia and hydrogen chloride, is the only product. On heating the solid the two gases are reformed.

   In which tests are compounds formed?

   Answer

   In (1) and (3). In (2) there is no evidence for more than one substance taking part or forming. In fact the vaporization of iodine is described.

10. How many moles of water molecules are there in 180 grams of water?

    Answer

    $$1 \text{ mole } H_2O = 18 \text{ g};$$

    therefore

    $$180 \text{ g } H_2O = 10 \text{ moles.}$$

11. What is the weight of a single molecule of water?

    Answer

    $$\frac{18}{6.023 \times 10^{23}} = 3.0 \times 10^{-23} \text{ g}$$

12. In an experiment similar to Expt. 7, a strip of zinc metal, Zn, was placed in an aqueous solution of lead nitrate, $Pb(NO_3)_2$. A spontaneous change took place in which 10.4 grams of lead were formed, and the zinc strip lost a weight of 3.3 grams.

    If a mole of Pb weighs 207.2 grams and a mole of Zn weighs 65.4 grams, how many moles of each metal were involved in the change? What is the relationship between moles involved?

    Answer

    $$10.4 \text{ g} \times \frac{1 \text{ mole Pb}}{207.2 \text{ g}} = 0.050 \text{ mole Pb}$$

    $$3.3 \text{ g} \times \frac{1 \text{ mole Zn}}{65.4 \text{ g}} = 0.050 \text{ mole Zn}$$

    For each mole of lead that changes, one of zinc also changes.

13. A chemist found experimentally that one volume of chlorine combines with two volumes of nitric oxide to give two volumes of nitrosyl chloride. A molecule of nitrosyl chloride has an odd number of atoms, but a molecule of chlorine has an even number.
    (1) Use X, Y and Z to represent the number of atoms in one molecule each of chlorine, nitric oxide, and nitrosyl chloride in that order. Derive the relation between X, Y, and Z.
    (2) Using only the data given plus the relation in (1), can you decide whether nitric oxide has an odd or an even number of atoms per molecule? Explain.
    (3) Nitrosyl chloride has three atoms per molecule, and chlorine is diatomic. How many does nitric oxide have?

    Answer

    (1) $X + 2Y = 2Z$
    (2) $2Y = 2Z - X$
    Since Z is odd, $2Z$ is even; X is given as even, thus $2Z - X$ is even, and hence $2Y$ is even.

Since two times either an odd or even number is even, we cannot decide about the "oddness" or "evenness" of nitric oxide.

(3) $2Y = 2(3) - 2$
$= 6 - 2 = 4$
$Y = 2$

Nitric oxide has two atoms per molecule.

Note to teacher: Nitrosyl chloride is NOCl, a reddish yellow gas that condenses at −5.8°C and freezes to blood red crystals at −61°C. It decomposes fairly readily to NO and Cl_2 and is quite reactive.

14. Three volumes of hydrogen are required to combine completely with one volume of nitrogen to form two volumes of ammonia. Suppose we combine one mole of hydrogen with one mole of nitrogen.
(1) Are both gases used up in the process?
(2) If not, which gas remains? How much?
(3) How many moles of ammonia are formed?

Answer

(1) Using Avogadro's Hypothesis, we can see from the volume data that three molecules of hydrogen combine with one molecule of nitrogen to form two molecules of ammonia. Since we start with a mole of each gas, both gases are not used up in this process.

(2) $\frac{2}{3}$ mole of nitrogen remains since one mole of hydrogen requires only $\frac{1}{3}$ mole of nitrogen.

(3) $\frac{2}{3}$ mole of ammonia is formed, since the volume of ammonia formed is twice the volume of nitrogen ($2 \times \frac{1}{3}$).

15. Why is a correct formula more valuable to a chemist than the name of the substance?

Answer

The formula shows the elements that are present and the relative amounts of each element. Some formulas show the arrangement of the particles in the substance. This information is very useful in studying the the reactions that substances may undergo. Some names tell nothing of the composition, whereas others reveal some or all of it.

CHAPTER

3

CHEMICAL REACTIONS

Intent and Approach

In this chapter you should develop the student's understanding of elements, compounds, molecules, equations, and moles such that he can proceed with Chapters 4–6. This is the point at which to introduce the mole method of working problems, but not the place for extensive drill. The mole method should just grow from the balanced equation. Balancing equations is also not to be heavily emphasized as a technique. Rather, it should follow as a natural thing from the conservation of atoms—as readily visualized with the molecular models you use to illustrate reactions. The balancing should seem an important but simple step in writing a correct set of symbols to express experimental knowledge. Use models to show how balancing is a simple but important step. Emphasizing the meaning of an equation is a good way to summarize these ideas.

Outline

1. Chemical reactions are introduced via the decomposition and formation of water (3-1.1).
2. Conservation of mass (3-1.3) leads to equations (3-2, 3-2.1, 3-2.2).
3. Section 3-2.3 deals with calculations based on equations.

New Concepts

1. Conservation of mass.
2. The mole and its use in solving problems.
3. How changes in matter are shown by equations and the meaning of the equation.

Development

PRINCIPLES OF CHEMICAL REACTIONS (3-1)

Formation of Water from Hydrogen and Oxygen (3-1.1)

Decomposition of Water (3-1.2)

These sections are the student's first real look at some chemical reactions. Therefore, make an effort to show them fully. Demonstrate the reactions, and write equations, illustrating as many as you can by using models which can be reassembled to show conservation of atoms. Some student may want to know why he cannot have a lone oxygen atom left over. The best answer to this question comes from experiment: lone

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Problems*				*Topic*
			Ex.	EASY	MEDIUM	HARD	
Finish reading Expt. 8	1	Cont. Expt. 8 (50 min)					Conservation of Mass
Read S 3-1/3-1.2 (pp. 38–40)	2	Finish Expt. 8 (15–20 min) Discuss Quiz (10 min) and text	1–3	1	2, 3		Formation and Decomposition of Water
Write up Expt. 8	3	Discuss Expt. 8					
Read S 3-1.3/3-2 pp. 40–42)	4	Discussion	4	6	4, 5		Equations
Read S 3-2.1/3-2.2 (pp. 42–44)	5	Discussion	5, 6	7	8, 9	10, 11	More on Equations
Read S 3-2.3 (p. 44)	6	Discussion and Review. Quiz.	7–10	12–14	15, 16	17–19	Calculations from Equations

Optional Experiments: (See Laboratory Manual Appendix 6)

8a Mass Relationships Accompanying Chemical Changes II

8b The Formula of a Hydrate

oxygen atoms haven't been found (in any substantial amount); therefore oxygen must be very reactive.

Do not fail to bring the heat of reaction into your discussion. Chapter 7 will develop the subject, but this is the place to make the student aware that he must account for it. He will already know, in a rough way, several kinds of reactions which give out heat—burning things; dissolving some things; adding water to some solids (lime, plaster of Paris); metabolic use of food—and some that require energy—boiling water (or other liquids); dissolving some solids (hypo); melting solids.

Expt. 8, MASS RELATIONSHIPS ACCOMPANYING CHEMICAL CHANGES, fits here. See p. 101 for guide.

Conservation of Mass (3-1.3)

EQUATIONS FOR CHEMICAL REACTIONS (3-2)

Here is the place to make extensive use of the molecular models. The entire idea of balancing an equation should be expressed in terms of physical objects. This makes the concept quite easy for the student. Go through several simple equations using the models.

Equation writing should flow as a natural result of conservation laws and the models you have used. The point to stress here is the meaning of the equation. This can be developed on at least two levels. In a general way the equation represents what happened. (*Note:* We can write an equation only after the products are known—by experiment or by coordinating rules based on actual tests.) Thus the first step toward an equation is an expression of chemical fact: hydrogen reacts with oxygen to give water and energy, or, in symbols, $H_2 + O_2$ gives H_2O + energy. We "balance" the expression to agree with experience, which says that we cannot destroy or create matter, and the equals sign, or arrow, is put in to express the conservation of atoms:

$$2H_2 + O_2 = 2H_2O + \text{energy}$$

At this stage the statement becomes an equation *and* takes on a molecular meaning. From the models used we know this equation expresses the reaction of 2 *molecules* of hydrogen with one *molecule* of oxygen to give two *molecules* of water (plus some energy). Now we fall back on our knowledge of arithmetic. We can double an equation, and it will still be true. Triple it, multiply it by 10, by 1000, or by 6.02×10^{23}, and it will still be true. Thus we can write

$$(2)(6.02 \times 10^{23})\ H_2 + (6.02 \times 10^{23})\ O_2 = (2)(6.02 \times 10^{23})\ H_2O + (6.02 \times 10^{23})\ \text{energy}$$

But this is a long way of writing

$$2\ \text{moles}\ H_2 + 1\ \text{mole}\ O_2 = 2\ \text{moles}\ H_2O + \text{molar heat of reaction}$$

Hence the equation also shows the relative number of moles of chemicals involved. *Make sure the student sees and understands this dual meaning of an equation.* Avoid laying too much stress on the energy term, but use it to set up the idea for later.

Writing Equations for Reactions (3-2.1)

Other Examples of Chemical Equations (3-2.2)

These two sections provide practice with the ideas of the previous two. Concentrate on the meaning rather than any mechanics of balancing.

Calculations Based on Chemical Equations (3-2.3)

The mole relation expressed by an equation is the key to working any problem based on that equation. The mole method involves these steps:

1. Write and balance the equation.
2. Use the equation to find how many moles of desired substance are related to one mole of the given one.
3. Use step 2 and the moles of given substance to find the moles of desired substance formed.

At the beginning and end of many problems another step is sometimes needed.

$$\text{convert from} \begin{cases} \text{given units to moles, or} \\ \text{moles to desired units.} \end{cases}$$

This conversion is not part of the mole method but is a unit conversion problem added on. It is, however, of practical importance, because we measure chemicals in grams or cubic centimeters or other units, but almost never in moles.

At this stage emphasize the mole method and its advantage—*a single way to approach all problems based on equations.* It is best to keep conversions simple—use only grams ⟶ moles and moles ⟶ grams—until later. The student should be assigned problems based on equations in *every* chapter and test. This will provide the constant drill needed for mastery. Initially, place emphasis on problems of two types:

1. How many moles of A will react with y grams of B by the reaction ··· ?
2. How many grams of A will be produced from y moles of B by the reaction ··· ?

The mole method is the fundamental way to work problems—fundamental in that it is tied directly to the experimental meaning of a chemical equation. This method, with its three steps, is easy for the student, because it is uniform for all problems *and* because the logical connections to the equation and its balancing, and to the molecular models, are made clear. The teachers who tested the material in 1960–1963 found that the mole method went over easily and effectively.

The so-called proportion method is actually the mole method with the supporting framework unstressed. As a result, it is not nearly so clear to a beginner. Do not use it.

OPTIONAL EXPERIMENTS

Expt. 8a, MASS RELATIONSHIPS ACCOMPANYING CHEMICAL CHANGES II,

Expt. 8b, THE FORMULA OF A HYDRATE, can fit here. See pp. 105 and 107 for guides.

EXPERIMENT 8 MASS RELATIONSHIPS ACCOMPANYING CHEMICAL CHANGES

PURPOSE. To allow the student to "discover" the law of conservation of mass; to further the establishment of molar relations in order that this may later serve as a basis for balancing equations; and to develop some common laboratory techniques.

PRELAB DISCUSSION. Students will move directly into this from Expt. 7, which requires little discussion. As yet, they do not know the terms "reaction" and "equation," but these occur early in Chapter 3. Emphasize the need to learn the laboratory techniques presented, and avoid discussion of what is "expected" as experimental results. Discuss the dark color of silver from Expt. 7, and tell students that this will not affect their results.

TIMING. Start this experiment as soon as Expt. 7 is finished. Immediately add 6 M HNO_3 to the silver obtained in Expt. 7 in order that the slow reaction can occur overnight. Heating to speed the reaction is not recommended. Both the hot HNO_3 and the fumes from it are dangerous. While the experiment is in progress, the first assignment in Chapter 3 may be made, but as much as possible of the experiment should precede the reading. Do not assign Sec. 3-1.3 before this experiment.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

250 ml beaker (from Expt. 7)
100 ml beaker (or another 250 ml beaker may be used)
stirring rod
wash bottle
filter paper
funnel and support
burner, ring stand, ring, wire gauze
graduate (10 or 25 ml)
arrangement for drying (see lab hint 1)
10 ml 6 M nitric acid (384 ml conc. reagent HNO_3/liter)
2–2.5 g sodium chloride (solid) (see lab hint 6)

TIME REQUIRED. This should take $1\frac{1}{2}$ periods.

First day (at end of Expt. 7): 10–15 minutes, Part I. (Add 6 M HNO_3, and set aside to react and evaporate.)
Second day: full period; Part II(a–l).
Third day: final weighing; 15–20 minutes.

PRECAUTIONS. See the precaution about silver nitrate, indicated in Expt. 7. Use care with 6 M acid; flood spills or spatters with water. Avoid inhaling fumes in I(b). Use hood, fan, and open windows to disperse fumes, and take special precautions if sand baths are used (see p. 68).

LABORATORY HINTS

1. The product in Part I *must not* be dried in an oven, since the fumes will cause severe corrosion. Two or three infrared lamps in the fume hood make the most satisfactory arrangement. In some climates, overnight evaporation near an open window is sufficient. If necessary, sand baths may be used (see p. 68), but the room must have forced ventilation. The product in Part II may be dried in an oven. A sand bath is not recommended for this drying step, because AgCl will spatter violently if dried too rapidly. If no other means is available, tell the students to minimize spattering by putting a watch glass over the beaker and by removing the beaker frequently to break up the AgCl clumps with a stirring rod. Sometimes excessive heating gives a dark product which does not interfere with the quantitative results.

2. In I(b) there may be a slight blue color, indicating that some copper remained mixed with the silver from Expt. 7. It will not precipitate in II(f), thus it will introduce a slight error in the final calculations, but the error will probably be less than other errors, and not enough to be noticeable.
3. In II(g) heating the mixture is very important in coagulation of the precipitate. On the other hand, students must be cautioned to heat the mixture gently to avoid bumping.

   Make a remark about the darkening of the AgCl on exposure to light. Point out that although the change is quite visible, no weight change will be measurable with the balances used.
4. If the AgCl melts (m.p. 455°C)—it will do so only if the sand bath is used—the resulting "cake" will tend to stick to the beakers. It may be remelted and poured into a "collection" beaker provided. (See next lab hint.) That which remains may be dissolved by leaving a concentrated solution of photographer's hypo (sodium thiosulfate) in the beaker for two or three days.
5. Collection of AgCl: The AgCl resulting from this preparation is often pure enough to dissolve in sodium thiosulfate for use in Expt. 25. It may also be saved for Expt. 2 (melting) for next year. If there is doubt about its purity, washing with warm water will remove traces of Na^+ and NO_3^-. It is questionable whether many teachers will want to bother with reclaiming silver nitrate, but for the sake of those who do, the following procedure is included. It is a modification of a system used by the University of California stockroom, and is presented as a "recipe" with no attempt at explanation. If silver wastes from other sources are included, the AgCl should be allowed to stand overnight in 6 *M* NaOH or KOH and then be filtered and washed.

   Suspend (or resuspend) the AgCl in 6 *M* NaOH (for 100 grams of Ag, use about 500 ml of NaOH), and boil it for $\frac{1}{2}$ hour, during which time add sucrose (about 250 grams or 1 cup for 100 grams of Ag) in small amounts at frequent intervals. Stirring is not necessary, only occasional swirling. At first there is considerable frothing, and then the solution becomes dark brown. Finally a heavy, gray precipitate forms.

   Filter and wash this precipitate, and dissolve it in as little nitric acid as possible. For about 100 grams of Ag, use 60–70 ml of concentrated (15–16 *M*) HNO_3. Filter and pour the filtrate into 2 *M* NaOH to precipitate brown Ag_2O. (For 100 grams of Ag, use about 500 ml of 2 *M* NaOH.)

   Filter, wash, dry, and store the Ag_2O. It can be dissolved in HNO_3 when $AgNO_3$ solution is needed.
6. It is hoped that by this time the student will have gained sufficient facility to weigh a specified amount of solid easily. Some discussion of this may be necessary, especially on why one pours out an approximate quantity from the stock bottle. It is wise to have a container with the correct approximation fastened to or near the stock bottle. Smooth paper should be available and the reason given for using a smooth surface paper rather than a piece of paper towel or filter paper.

POSTLAB DISCUSSION. Collect data from all students in order that the sum of the weights of the $AgNO_3$ and NaCl may be compared to the sum of the weights of the AgCl and $NaNO_3$ with excess NaCl (called "residue" in beaker #2). This comparison (answer to question 2) is the basis for Sec. 3-1.3, which should be assigned after the experiment. Prepare a class graph to show the comparison in order that all may see the central tendency. Since some students' results will not be good, this will insure that everyone understands the experiment.

For review, discuss the molar relationship of the silver compounds measured in Expts. 7 and 8. Make sure the student knows why the moles of $AgNO_3$, Ag, $AgNO_3$ (made in Expt. 8), and AgCl are the same. Later in the chapter, have the student work Exercises 9 and 10 to bring out the equation for this reaction and to calculate the moles of NaCl actually used.

SAMPLE DATA

Weight of:	
silver from Expt. 7	2.56 ± 0.02 g
$AgNO_3$ used in Expt. 7	4.05 ± 0.02 g
beaker #1	72.60 ± 0.01 g
beaker #1 and solid $AgNO_3$	76.67 ± 0.01 g
beaker #1, filter paper, and solid AgCl	76.55 ± 0.01 g
beaker #2	51.48 ± 0.01 g
beaker #2 and NaCl	53.74 ± 0.01 g
piece of filter paper	0.56 ± 0.01 g
beaker #2 and solid residue	54.38 ± 0.01 g

CALCULATIONS

	Weight (g)	Number of moles
Ag (from Expt. 7)	2.56 ± 0.02	2.37×10^{-2}
$AgNO_3$ (used in Expt. 7)	4.05 ± 0.02	—
$AgNO_3$ (produced in Expt. 8)	4.07 ± 0.02	2.39×10^{-2}
NaCl (added)	2.26 ± 0.02	3.86×10^{-2}
AgCl (in beaker #1)	3.39 ± 0.03	2.36×10^{-2}
Residue (in beaker #2)	2.90 ± 0.02	—

ANSWERS TO QUESTIONS

1. How does the weight of $AgNO_3$ produced in this experiment compare to the weight used in Expt. 7? How do you account for any similarity or difference?

   Answer: These should agree quite well unless Ag was lost in Expt. 7, and in such a case, the ratio of Ag to Cu would give a clue. Since this is early in the course, errors in weighing technique are often discovered at this time.

2. Compare the sum of the weights of the $AgNO_3$ and NaCl used with the sum of the weights of the AgCl and the residue in beaker #2. Your conclusions will be more meaningful if they are based on class data compiled by your teacher. What is the significance of these results?

   Answer: See the postlab discussion. This is the most important part of this experiment. Make sure all students understand that these weights are equal for this and all other reactions.

3. Compare your results for the number of moles of silver used, of silver nitrate produced in Part I, and of silver chloride produced in Part II by computing the ratio between the moles of silver and each of the other substances, $AgNO_3$ and AgCl. Use the nearest whole number to express your result. What can you conclude about the number of moles involved in this series of chemical changes?

   Answer: Expressed to the nearest whole number, the ratios will certainly be 1/1. This should bring up a discussion as to why the Ag/NaCl mole ratio is not also 1/1, but discussion of this should be delayed until after Sec. 3-2.3 has been assigned in order that the student may calculate the weight of NaCl that would actually react.

4. Pure silver nitrate is a white solid. How do you account for any color which may be present in your sample or in the samples prepared by other students?

Answer: Some students will observe a blue color. Recalling that the color of the "discarded" solution in Expt. 7 was blue, they will probably suggest the presence of some copper compound as an impurity.

ADDITIONAL INVESTIGATION—*to be undertaken as an extracurricular experiment. Consult your teacher before proceeding.*

Devise an experiment to determine the composition of the residue in beaker #2. Study Exercises 3-9 and 3-10 as a preliminary step to this investigation.

The student may see two kinds of crystals and guess that two substances are present. He may think to add $AgNO_3$ solution to see if there is more chloride. The most valuable extension is to collect qualitative data to show that the NaCl which reacts (in the main experiment) is related to the $AgNO_3$ in the simple 1/1 mole ratio.

EXPERIMENT 8a MASS RELATIONSHIPS ACCOMPANYING CHEMICAL CHANGES II (In Appendix 6, Optional)

PURPOSE. To give the student additional practice in the techniques developed in Expt. 8 plus additional experimental basis for the law of conservation of mass and for balancing equations.

PRELAB DISCUSSION. Do not use class time to discuss this experiment except to refer the student to techniques in Expt. 8.

TIMING. If done, this experiment should follow Expt. 8. Experiment 8a implies more knowledge of Chapter 3, hence it is not good as an introduction or for the "discovery" of the law of conservation of mass.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

100 or 250 ml beaker
100 or 250 ml Erlenmeyer flask
balance (±0.01 g)
stirring rod
wash bottle
filter paper
funnel and support
ring stand, ring, wire gauze
burner
arrangement for drying (see lab hint 1)
1.66 g $Pb(NO_3)_2$
0.97 g K_2CrO_4

TIME REQUIRED. Since this experiment loses most of its value unless performed carefully, allow about $1\frac{1}{2}$ periods. Drying must be done overnight if this schedule is followed, so use the break at procedures (*j*) and (*k*).

Another natural stopping point is after (*d*). Depending upon the number of balances available, the first steps may take 20–30 minutes. Since filtration requires 15–20 minutes, this step should not be started unless there is enough time to finish. Filtration is the only step that is not easy to interrupt, thus the experiment is well adapted to the use of a number of short times in the laboratory, and may be extended over several days.

PRECAUTIONS. By now, students should be familiar with handling hot containers and burners. Avoid allowing chromates to contact the skin, since they sometimes cause skin rashes. Some students may know that KNO_3 is an ingredient of gunpowder; therefore, be sure to control its disposal.

LABORATORY HINT

1. For drying, see p. 101. Drying may also be done on hot plates. These are especially valuable during the first stages of evaporation of water from the filtrate with KNO_3. If either a hot plate or a sand bath is used to dry the opened filter cones with $PbCrO_4$, the 250 ml beaker should be placed inside a 400 ml beaker to prevent charring of the filter paper.

POSTLAB DISCUSSION. Since this is an optional experiment, little class time need be used in discussing it. If a number of students collect data, an opportunity should be given for them to compare their results with each other.

Students are interested in the fact that $PbCrO_4$ makes a good paint pigment. It may be ground and used in water (as "poster paint") or in a drying oil.

SAMPLE DATA. Previous years' results for $PbCrO_4$ show slightly better agreement with calculated values than do those for KNO_3. For the former, 71% were within ±10% of the theoretical 0.005 mole; for the latter, 65% were within ±10% of the theoretical 0.010 mole. The results for the $PbCrO_4$ were more often high than low, which may have been the result of incomplete washing or incomplete drying. The values for KNO_3 were generally a little low, with the result that the total weight of products very nearly equaled the weight of the reactants.

CALCULATIONS

1. Determine the weight of each product.

   Answer: Since 0.005 mole of each reactant was used, one would expect 0.005 mole of $PbCrO_4$ (or 1.62 grams) and 0.010 mole of KNO_3 (or 1.01 grams).

2. Compare the sum of the weights of reactants with the sum of the weights of products. Are your results what you expected them to be? Justify your answer.

   Answer: The weights of the reactants are very nearly equal to the weights of the products. It is important to be sure that the student does not expect them to be exactly equal, but that he recognizes the precision possible in this experiment and remarks on his results in light of this.

3. How many moles of each of the reactants were used and how many moles of each product were produced?

   Answer: 0.005 mole of K_2CrO_4, 0.005 mole of $Pb(NO_3)_2$, about 0.005 mole of $PbCrO_4$, and about 0.01 mole of KNO_3 (see discussion under *Sample Data*).

4. Write the formulas for the two reactants on the left of an arrow sign and the formulas for the two products on the right of the same arrow. Put the word *(solid)* after each formula to indicate the solid state condition of the original and of the final substances. There are other changes that have occurred during the reaction about which you will learn later.

   Below each substance write the number of moles you used or formed. Utilizing the number of moles involved, balance the equation.

   Answer: The student should write 0.005 below each of the formulas except KNO_3, and below this, 0.01. He should then fill in the coefficients to balance the equation.

   $$Pb(NO_3)_2\textit{(solid)} + K_2CrO_4\textit{(solid)} = PbCrO_4\textit{(solid)} + 2KNO_3\textit{(solid)}$$

   It is not wrong to include coefficients of 1 for the first three substances, but since the student will have read Sec. 3-2.1 at this time, he will probably omit them.

5. Are your data consistent with the idea that atoms are conserved in a chemical reaction?

   Answer: Since the sum of the weights of the reactants equals the weight of all the products, the data are consistent with the idea that atoms are conserved. This follows the reasoning presented in Sec. 3-1.3.

EXPERIMENT 8b THE FORMULA OF A HYDRATE
(In Appendix 6, Optional)

PURPOSE. To give the student experience in quantitative analysis and additional reinforcement of the mole concept.

PRELAB DISCUSSION. See lab hints 1, 3, and 5.

TIMING. Experiment 8b can be used as an optional experiment. It is not necessary to the flow and development of the course. If done, it should follow Expt. 8, sometime toward the end of Chapter 3.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

burner
crucible and cover
crucible tongs (see lab hint 5)
triangle
ring stand and ring
balance (±0.01 g)
desiccator (see lab hint 4)
about 5 g of a hydrate

Suitable hydrates are:

$BaCl_2 \cdot 2H_2O$	barium chloride
$MgSO_4 \cdot 7H_2O$	magnesium sulfate
$Na_2CO_3 \cdot H_2O$	sodium carbonate
$CuSO_4 \cdot 5H_2O$	copper sulfate
$MnSO_4 \cdot H_2O$	manganese sulfate

Additional hydrates may be used. Consult a handbook. Many of the common hydrates are not suitable for use in this experiment. When in doubt, try the material beforehand.

TIME REQUIRED. This experiment requires two 45–50 minute periods.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. The student should be cautioned not to overheat the hydrates, since this may decompose the dehydrated salt.
2. It is suggested that the experiment be done as an "unknown" to encourage independent student work and interest.
3. It is also suggested that the weight of one mole of the anhydrous salt, and not its name, be given to the student at first. He should then calculate the ratio of moles of anhydrous salt to water and use these to find a simple numerical relation for the formula.
4. A simple desiccator can be made from a wide-mouth peanut butter jar having a good seal. A triangle with wires bent downward like a three-legged stool is placed inside with some anhydrous calcium chloride.
5. If a desiccator is not used, there is a tendency for the student to weigh the crucible while still too hot. Remind him of the errors of weighing hot objects.

CALCULATIONS

Calculate the number of moles of the anhydrous salt you prepared. How many moles of water were associated with 1 mole of anhydrous salt? Write the empirical formula for the hydrate.

$$\text{Moles of anhydrous salt prepared} = \frac{\text{wt of anhydrous salt (g)}}{\text{g/mole}}$$

$$\text{Moles of water} = \frac{\text{wt loss (g) during heating}}{\text{18 g/mole of water}}$$

ANSWERS TO QUESTIONS

1. Suggest reasons for weighing the crucible and anhydrous salt each time just as soon as it has cooled, not before or later.

   Answer: If the crucible is cooled without the use of a desiccator, the anhydrous salt will pick up moisture from the air as it cools. If allowed to stand too long, it will pick up an appreciable weight, depending on the unique properties of the salt being used. On the other hand, weighing the crucible before it cools may cause convection currents, which give a buoyancy error, as well as cause damage to the balance pan.

2. Do your results agree exactly with those for a definite hydrate? If not, what are some plausible explanations for the deviation?

   Answer: Student response.

3. Can you suggest reasons why the above method might not be suitable for all hydrates?

   Answer: Some hydrates may decompose, giving off other gases at temperatures used to drive off the water of hydration; others may require too much heat to drive off their water.

Supplementary Material

None.

Background Discussion

THE INTRODUCTION OF THE ATOMIC THEORY

The primary goal of this course is to convey an understanding of the nature of science. The next most important goal—and the minimum goal of any introductory chemistry course—is to convey to the student the meaning of balanced chemical equations, which embody the central idea of chemistry. A balanced equation describes a possible chemical reaction; a chemist must understand all of the implications, the properties, and the controlling conditions that are involved.

Consider the equation

$$2H_2 + O_2 = 2H_2O$$

It tells an experienced chemist that there is a possible reaction and that, if it occurs, then:

(a) Exactly two molecules of water are produced for every two molecules of hydrogen consumed and for every one molecule of oxygen consumed.

(b) Exactly two moles of water are produced for every two moles of hydrogen consumed and for every one mole of oxygen consumed.

(c) There are 36.04 grams of water produced for every 4.04 grams of hydrogen consumed and for every 32.00 grams of oxygen consumed.

(d) The system will change. Initially it is characterized by a set of properties that identify two substances, hydrogen and oxygen; finally it will be characterized by an entirely different set of properties, those that identify a third substance—water.

We have chosen to inform the student that the reaction given implies (a), (b), (c), and (d) by placing in his hands molecular models. A student might be given a single model of O_2 and the instructions "Fill out a check-out slip for the number of models of H_2 needed to rearrange the O_2 model into as many H_2O models as possible." Ninety-five percent of the students will immediately count how many hydrogen atoms are required and ask for two molecular models of H_2. The other 5% will ask for one model of H_2, get back to their desks, and quickly notice that they have an atom of oxygen left over. They will return for another H_2 model. There, without any discussion, each student has balanced his first chemical equation. Every time, thereafter, that he must balance an equation, his thoughts will be guided by this first experience. Conceptually, he will never experience difficulty in balancing a chemical equation.

Assume that there are 25 students in the class and that we passed out 25 models of O_2. If we ask how many total H_2O models were formed by the class, even the least perceptive student will have no difficulty answering "50," when he is looking at the two H_2O models he himself formed using one model of O_2. How many from a dozen models of O_2? How many from one million models? How many from 6.023×10^{23} models?

Thus, the application of an equation to a larger number of molecules (e.g., a mole) is as easy, conceptually, as balancing the equation. But these models represent atoms, each of which has a characteristic mass. What weight of water will be formed from the one molecule of O_2? The student will readily see that it is the mass of two atoms of oxygen and four atoms of hydrogen. What weight of water is formed from one *mole* of O_2? It will be the weight of two *moles* of oxygen atoms and four *moles* of hydrogen atoms. Where can these weights be found? They are in a table inside the back cover. They are called atomic weights. Very quickly the student can comprehend the weight relations implied by the chemical equation.

The conceptual ease with which the student can grasp all the implications of the chemical equation, given the molecular models, explains why we begin this course with an authoritarian presentation of the atomic theory. Its success in the classroom during years of use justifies the approach: the conclusion (a) is easy to grasp; it readily leads to the mole concept (b); and the weight relationships (c) are all implied.

Historically, of course, the logic was the opposite of that presented here. The changes in properties (d) led to the identification of substances. A multitude of weight relationships (c) were needed before enough evidence was available for the inductive step which Dalton performed in deciding there must be atoms, implying (b) and (a). This is a difficult line of reasoning, even in retrospect. It presents the student with an intellectual test that many will fail. In return for hewing to the line of logic, we sacrifice facility in using and understanding the chemical equation.

What about the experimental approach? Yes, we have here deserted our wish to avoid an authoritarian presentation of the principles of chemistry. It is a deliberate act—done for what seems to be a crucially important gain. Tell the student this; encourage him to keep asking what evidence there is for the assumed atomic theory. He will hear the atomic theory referred to many times, and will use it to interpret many experimental observations. By the time he finishes Chapter 14 and a detailed discussion of the experimental basis for the atomic theory, he will know the evidence.

Answers to Exercises and Problems

Ex. 3-1. Suppose ten hydrogen molecules and ten oxygen molecules are mixed. How many molecules of water could be formed? What would be left over?

Answer

Ten hydrogen molecules could combine with five oxygen molecules to make ten molecules of water. Five oxygen molecules would be left over.

Ex. 3-2. One million oxygen molecules react with sufficient hydrogen molecules to form water molecules. How many water molecules are formed? How many hydrogen molecules are consumed?

Answer

One million oxygen molecules could form two million water molecules, consuming two million hydrogen molecules in the process.

Ex. 3-3. How much heat is released when two moles of hydrogen burn? One-half mole?

Answer

The burning of two moles of H_2 will release

$$2(68{,}000)\text{ cal} = 136{,}000\text{ cal}$$

The burning of $\frac{1}{2}$ mole of H_2 will release

$$\tfrac{1}{2}(68{,}000)\text{ cal} = 34{,}000\text{ cal}$$

Ex. 3-4. Write an equation containing the information expressed in your answer to question 1 of Expt. 7.

Answer

$$\text{Cu}(\textit{solid}) + 2\text{AgNO}_3(\textit{in water}) \longrightarrow 2\text{Ag}(\textit{solid}) + \text{Cu(NO}_3)_2(\textit{in water})$$

Notice that the term "aqueous" and the abbreviation "*(aq)*" have not yet been used. The designation "*(in water)*" is a desirable prelude to the later use of "*(aq)*," to be defined in Chapter 5.

Ex. 3-5. Ammonia gas, NH_3, can be burned with oxygen gas, O_2, to give nitrogen gas, N_2, and water, H_2O. See if you can follow the logic of the following steps in balancing this reaction.

$$NH_3 + O_2 \longrightarrow N_2 + H_2O$$
$$NH_3 + O_2 \longrightarrow 1N_2 + H_2O$$
$$2NH_3 + O_2 \longrightarrow 1N_2 + H_2O$$
$$2NH_3 + O_2 \longrightarrow 1N_2 + 3H_2O$$
$$2NH_3 + \tfrac{3}{2}O_2 \longrightarrow 1N_2 + 3H_2O$$

State briefly what was done in each step.

Answer

The student should follow the logic of conserving atoms: first, nitrogen atoms; then, hydrogen atoms; and, finally, oxygen atoms to reach the balanced equation.

(1) $NH_3 + O_2 \longrightarrow N_2 + H_2O$
Write formula for products and reactants.

(2) $NH_3 + O_2 \longrightarrow 1N_2 + H_2O$
Choose one element to work on (N).

(3) $2NH_3 + O_2 \longrightarrow 1N_2 + H_2O$
Arrange to conserve atoms of this element.

(4) $2NH_3 + O_2 \longrightarrow 1N_2 + 3H_2O$
Do the same for another element (H), usually in a molecule containing the already balanced element.

(5) $2NH_3 + \tfrac{3}{2}O_2 \longrightarrow 1N_2 + 3H_2O$
Continue with the other elements (O).

Ex. 3-6. A paraffin candle burns in air to form water and carbon dioxide. Paraffin is made up of molecules of several sizes. We shall use the molecular formula $C_{25}H_{52}$ as representative of the molecules present. One mole of candle contains the Avogadro number of these molecules.

Formulas of Reactants		Formulas of Products
$C_{25}H_{52} + O_2$	$\longrightarrow$	$H_2O + CO_2$

Suppose one mole of paraffin (which weighs 353 grams) is burned. Using the method shown in the preceding example, we obtain

$$C_{25}H_{52} + yO_2 \longrightarrow 26H_2O + 25CO_2$$

We still have not determined the coefficient for O_2. Since 76 O's are required for the products $[26 + (2 \times 25) = 76]$, they must have been present in the reactants. Show that it follows that y must be 38:

$$C_{25}H_{52} + 38O_2 \longrightarrow 26H_2O + 25CO_2 \qquad (11)$$

Answer

To provide 76 oxygens, 38 molecules of O_2 are needed, each providing two atoms of oxygen.

Ex. 3-7. Show that 3.80 moles of oxygen are needed to burn 35.3 grams of paraffin by reaction (*11*).

Answer

The molecular weight of paraffin is

$$25(12.01) \times 52(1.008) = 352.7\text{ g/mole}$$

Hence 35.3 g of paraffin equals 35.3/353 = 0.100 mole. But, by reaction (*11*), one mole of $C_{25}H_{52}$ reacts with 38 moles of O_2; hence 0.100 mole of $C_{25}H_{52}$ reacts with 3.80 moles of O_2.

Ex. 3-8. How many moles of oxygen, O_2, are required to produce 242 grams of magnesium oxide by equation (*6*)?

$$2Mg + O_2 \longrightarrow 2MgO \qquad (6)$$

Answer

The molecular weight of MgO is 24.3 + 16.00 = 40.3 g/mole.

$$242 \text{ g MgO} \times \frac{1 \text{ mole}}{40.3 \text{ g}} = 6.00 \text{ moles MgO}$$

By equation (*6*), one mole of O_2 produces two moles of MgO.

$$6.00 \text{ moles MgO} \times \frac{1 \text{ mole } O_2}{2 \text{ moles MgO}} = 3.00 \text{ moles } O_2$$

Ex. 3-9. Write the equation for the reaction which took place in Expt. 8, Part II. What was the residue you obtained on evaporation of the solution in beaker #2?

Answer

$$AgNO_3(\textit{in water}) + NaCl(\textit{in water}) = AgCl(\textit{solid}) + NaNO_3(\textit{in water})$$

$NaNO_3$(*solid*) and the excess NaCl(*solid*) are in the residue. Notice that the term "aqueous" and the abbreviation "*(aq)*" have not yet been used. The designation "*(in water)*" is a desirable prelude to the later use "*(aq)*," to be defined in Chapter 5.

Ex. 3-10. In Expt. 8 you determined the number of moles of silver chloride formed in the reaction of some sodium chloride with a known amount of silver nitrate. How many moles of sodium chloride reacted with the silver nitrate? Compare this with the number of moles of sodium chloride you added.

Answer

The following data are an example of what you might expect from the students:

moles $AgNO_3$ used = 0.030;
moles AgCl produced = 0.031;
moles NaCl reacted = 0.031;
moles of NaCl reacted = moles of AgCl produced;
moles NaCl added = 0.049;
0.018 mole of NaCl in excess.

Pr. 1. One volume of hydrogen gas combines with one volume of chlorine gas to give two volumes of hydrogen chloride gas. On the basis of many reactions, we have learned that the molecular formulas are, for hydrogen, H_2, for chlorine, Cl_2, and for hydrogen chloride, HCl. The reaction, in symbols, is

$$H_2 + Cl_2 = 2HCl$$

(a) According to this reaction, how many *molecules* of hydrogen chloride, HCl, can be formed from one *molecule* of hydrogen, H_2?
(b) How many *moles* of hydrogen chloride, HCl, can be formed from one *mole* of hydrogen, H_2?
(c) Four *molecules* of chlorine, Cl_2, will produce how many *molecules* of HCl?
(d) Eight *moles* of hydrogen chloride are formed from how many *moles* of Cl_2?

Answer

(a) Two molecules of HCl.
(b) Two moles of HCl.
(c) Eight molecules of HCl.
(d) Four moles of Cl_2.

Pr. 2. The reaction between nitric oxide, NO, and oxygen, O_2, is written

$$2NO + O_2 = 2NO_2$$

(a) Two *molecules* of nitric oxide give how many *molecules* of nitrogen dioxide, NO_2?
(b) Two *moles* of NO give how many *moles* of NO_2?
(c) How many moles of oxygen atoms are there in two moles of NO?
(d) How many moles of oxygen atoms are there in one mole of O_2?
(e) How many moles of oxygen atoms are there in two moles of NO_2?
(f) Use the answers to parts (c), (d), and (e) to verify that the reaction is written so as to conserve oxygen atoms.

Answer

(a) Two molecules of NO_2.
(b) Two moles of NO_2.
(c) Two moles of oxygen atoms.
(d) Two moles of oxygen atoms.
(e) Four moles of oxygen atoms.
(f) $2 + 2 = 4$.

Pr. 3

(a) Write the equation for the reaction between nitrogen and hydrogen to give ammonia on the basis of your answer to Problem 3 of Chapter 2, and assuming the following molecular formulas: nitrogen, N_2; hydrogen, H_2; ammonia, NH_3.
(b) Verify that your equation conserves nitrogen atoms.

(c) Verify that your equation conserves hydrogen atoms.

Answer

(a) The answer to Problem 3 of Chapter 2 was supposed to be

one molecule of nitrogen	combines with	three molecules of hydrogen	to give	two molecules of ammonia.

Hence

$$N_2 + 3H_2 = 2NH_3$$

(b) On the left, one molecule of N_2 contains two nitrogen atoms; on the right, two molecules of NH_3 also contain two nitrogen atoms.

(c) On the left, three molecules of H_2 contain six hydrogen atoms; on the right, two molecules of NH_3 also contain six hydrogen atoms.

Pr. 4. When ammonia is decomposed into nitrogen and hydrogen, the reaction absorbs heat. Written in terms of moles, the equation is

$$2NH_3 + 22\text{ kcal} = N_2 + 3H_2$$

(a) Two moles of ammonia produce how many moles of nitrogen?

(b) The production of one mole of nitrogen absorbs how much heat?

(c) The production of nine moles of hydrogen, H_2, absorbs how much heat?

(d) Calculate the weight of two moles of ammonia, and compare it to the sum of the weights of one mole of nitrogen, N_2, plus three moles of hydrogen, H_2.

Answer

(a) One mole of nitrogen.

(b) 22 kcal.

(c) 66 kcal.

(d) Two moles of NH_3 weigh

$$2[14.01 + 3(1.008)] = 2(17.034) = 34.068 = 34.07$$

One mole N_2 weighs $2(14.01) = 28.02$ g

Three moles H_2 weigh $3[2(1.008)]$

$$= 3 \times 2.016 = \frac{6.048\text{ g}}{34.068\text{ g}}$$

or 34.07 g.

Pr. 5. In the manufacture of nitric acid, HNO_3, nitrogen dioxide, reacts with water to form HNO_3 and nitric oxide, NO:

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

(a) Verify that the equation conserves oxygen atoms.

(b) How many molecules of nitrogen dioxide are required to form 25 molecules of nitric oxide?

(c) How many moles of nitric oxide are formed from 0.60 mole of nitrogen dioxide?

Answer

(a) 3 NO_2 molecules contain	6 oxygen atoms
1 H_2O molecule contains	1 oxygen atom
Reactant molecules contain	7 oxygen atoms
2 HNO_3 molecules contain	6 oxygen atoms
1 NO molecule contains	1 oxygen atom
Product molecules contain	7 oxygen atoms (same as in reactants)

(b) Three molecules of NO_2 form one molecule of NO, hence 3×25 molecules of NO_2 form 25 molecules of NO; that is, 75 molecules of NO_2 are required.

(c) Three moles of NO_2 form one mole of NO, hence 0.60 mole of NO_2 forms $0.60/3 = 0.20$ mole of NO.

Pr. 6. If 3 grams of substance *A* combine with 4 grams of substance *B* to make 5 grams of substance *C* and some *D*, how many grams of *D* would you expect?

Answer

Assuming conservation of mass, we have

$$3\text{ g} + 4\text{ g} = 5\text{ g} + D$$
$$7\text{ g} - 5\text{ g} = D$$
$$D = 2\text{ g}$$

Pr. 7. One step in the manufacture of sulfuric acid is to burn sulfur (formula, S_8) in air to form a colorless gas with a choking odor. The name of the gas is sulfur dioxide and it has the molecular formula SO_2. On the basis of this information:

(a) Write the balanced equation for this reaction.

(b) Interpret the equation in terms of molecules.

(c) Interpret the equation in terms of moles.

(d) Two moles of sulfur, S_8, would produce how many moles of sulfur dioxide, SO_2?

Answer

(a) $S_8 + 8O_2 = 8SO_2$.

(b) One molecule of S_8 reacts with eight molecules of O_2 to form eight molecules of SO_2.
(c) One mole of S_8 reacts with eight moles of O_2 to form eight moles of SO_2.
(d) Sixteen moles of SO_2.

Pr. 8. When iron rusts, it combines with oxygen of the air to form iron oxide, Fe_2O_3. Which of the following is FALSE?

(a) The equation is

$$3O_2 + 4Fe \longrightarrow 2Fe_2O_3.$$

(b) There are five atoms represented by the formula Fe_2O_3.
(c) Oxygen gas is triatomic.
(d) The mass of the reactants equals the mass of the products.
(e) Atoms are conserved.

Answer

Part (c) is false. Oxygen gas is diatomic.

Pr. 9. Balance the equation for each of the following reactions. Begin on the basis of one mole of the substance underscored.

(a) $Li + \underline{Cl_2} \longrightarrow LiCl$
(b) $Na + \underline{Cl_2} \longrightarrow NaCl$
(c) $Na + \underline{F_2} \longrightarrow NaF$
(d) $Na + \underline{Br_2} \longrightarrow NaBr$
(e) $\underline{O_2} + Cl_2 \longrightarrow Cl_2O$
(f) $O_2 + \underline{Cl_2} \longrightarrow Cl_2O$

Show that your answers to parts (e) and (f) contain the same information.

Answer

(a) $2Li + Cl_2 \longrightarrow 2LiCl$
(b) $2Na + Cl_2 \longrightarrow 2NaCl$
(c) $2Na + F_2 \longrightarrow 2NaF$
(d) $2Na + Br_2 \longrightarrow 2NaBr$
(e) $O_2 + 2Cl_2 \longrightarrow 2Cl_2O$
(f) $\frac{1}{2}O_2 + Cl_2 \longrightarrow Cl_2O$

Equation (e) indicates that one mole of oxygen reacts with two moles of chlorine to form two moles of Cl_2O. This implies that one-half mole of oxygen reacts with one mole of chlorine to form one mole of Cl_2O which is exactly the information given by equation (f).

Pr. 10. Balance the equations for each of the following reactions involving oxygen. Begin on the basis of one mole of the substance underscored.

(a) With metallic nickel:

$$Ni + \underline{O_2} \longrightarrow NiO$$

(b) With metallic nickel:

$$\underline{Ni} + O_2 \longrightarrow NiO$$

(c) With metallic lithium:

$$Li + \underline{O_2} \longrightarrow Li_2O$$

(d) With the rocket fuel hydrazine, N_2H_4:

$$\underline{N_2H_4} + O_2 \longrightarrow N_2 + H_2O$$

(e) With acetylene, C_2H_2, in an acetylene torch flame:

$$\underline{C_2H_2} + O_2 \longrightarrow CO_2 + H_2O$$

Answer. $C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O.$

(f) With the important copper ore, chalcocite, Cu_2S (the process called "roasting" the ore):

$$\underline{Cu_2S} + O_2 \longrightarrow Cu_2O + SO_2$$

(g) With the important iron ore, iron pyrite, FeS_2 (again, "roasting" the ore):

$$FeS_2 + O_2 \longrightarrow \underline{Fe_2O_3} + SO_2$$

Answer

(a) $2Ni + O_2 \longrightarrow 2NiO$
(b) $Ni + \frac{1}{2}O_2 \longrightarrow NiO$
(c) $4Li + O_2 \longrightarrow 2Li_2O$
(d) $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$
(e) $C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$
(f) $Cu_2S + \frac{3}{2}O_2 \longrightarrow Cu_2O + SO_2$
(g) $2FeS_2 + \frac{11}{2}O_2 \longrightarrow Fe_2O_3 + 4SO_2$

Pr. 11

(a) Balance the equations for the decomposition (to elements) of ammonia, NH_3, nitrogen trifluoride, NF_3, and nitrogen trichloride, NCl_3. Base each equation upon the production of one mole of N_2.

$$NH_3 \longrightarrow 1N_2 + H_2$$
$$NF_3 \longrightarrow 1N_2 + F_2$$
$$NCl_3 \longrightarrow 1N_2 + Cl_2$$

(b) Rewrite the equations to include the information that the decomposition of ammonia is endothermic, absorbing 22.08 kcal/mole N_2, the decomposition of NF_3 is endothermic, absorbing 54.4 kcal/mole N_2, and the decomposition of NCl_3 is exothermic, releasing 109.4 kcal/mole N_2.
(c) One of the three compounds NH_3, NF_3, and NCl_3 is dangerously explosive. Which would you expect to be the explosive substance? Why?

Answer

(a) $2NH_3 \longrightarrow N_2 + 3H_2$
$2NF_3 \longrightarrow N_2 + 3F_2$
$2NCl_3 \longrightarrow N_2 + 3Cl_2$

(b) $2NH_3 + 22.1\ \text{kcal} \longrightarrow N_2 + 3H_2$
$2NF_3 + 54.4\ \text{kcal} \longrightarrow N_2 + 3F_2$
$2NCl_3 \longrightarrow N_2 + 3Cl_2 + 109.4\ \text{kcal}$

(c) Nitrogen trichloride, NCl_3, is the compound most likely to be explosive because of the large energy release on decomposition. (It *is* explosive and it is *extremely dangerous*.)

Pr. 12. Graphite, a form of carbon, C, burns in air to produce the colorless gas, carbon dioxide. On the basis of this information:

(a) Write the equation for the reaction.
(b) If one mole of graphite is burned, how many moles of carbon dioxide are produced? What is the weight in grams of this amount of carbon dioxide?
(c) If two moles of graphite were burned, how many moles of carbon dioxide would be produced? What is the weight in grams?
(d) If five moles of graphite were burned in a vessel containing 10 moles of oxygen gas, what is the maximum number of moles of carbon dioxide that could be produced?

Answer

(a) $C + O_2 = CO_2$
(b) One mole of C gives one mole of CO_2, which weighs 44.01 g.
(c) Two moles of C give two moles of CO_2, which weigh 88.02 g.
(d) Five moles of C give five moles of CO_2. This would be mixed with five moles of unused O_2.

Pr. 13. If a piece of sodium metal is lowered into a bottle of chlorine gas, a reaction takes place. Table salt, NaCl, is formed.

(a) Write the equation for the reaction.
(b) How many moles of NaCl could be formed from one mole of Na?
(c) How many moles of NaCl could be formed from 2.30 grams of Na?

Answer

(a) $2Na + Cl_2 = 2NaCl$
(b) One mole of Na produces one mole of NaCl.
(c) 2.30 g of Na are 2.30/23.0 = 0.100 mole; this amount will produce 0.100 mole of NaCl.

Pr. 14. Methane, the main constituent of natural gas, has the formula CH_4. Its combustion products are carbon dioxide and water.

(a) Write the equation for the combustion of methane. Compare your answer with equation (5), Textbook, p. 41.
(b) One mole of methane produces how many moles of water vapor?
(c) One-eighth mole of methane would produce how many moles of carbon dioxide?
(d) How many moles of water vapor would be produced by 4.0 grams of methane?

Answer

(a) $CH_4 + 2O_2 = CO_2 + 2H_2O$
(b) One mole of CH_4 produces two moles of H_2O.
(c) One-eighth mole of CH_4 produces $\frac{1}{8}$ mole of CO_2.
(d) 4.0 g = 4.0/16.0 mole of CH_4 = 0.25 mole of CH_4, which yields 0.50 mole of H_2O.

Pr. 15. If potassium chlorate, $KClO_3$, is heated gently, the crystals will melt. Further heating will decompose it to give oxygen gas and potassium chloride, KCl.

(a) Write the equation for the decomposition.
(b) How many moles of $KClO_3$ are needed to give 1.5 moles of oxygen gas?
(c) How many moles of KCl would be given by $\frac{1}{3}$ mole of $KClO_3$?
(d) How many moles of oxygen gas would be produced by 122.6 grams of $KClO_3$?

Answer

(a) $2KClO_3 = 3O_2 + 2KCl$
(b) One mole of $KClO_3$ produces 1.5 moles of O_2.
(c) One-third mole of $KClO_3$ gives $\frac{1}{3}$ mole of KCl.
(d) 122.6 g of $KClO_3$ are one mole. One mole of $KClO_3$ produces 1.5 moles of O_2.

Pr. 16. One gallon of gasoline can be considered to be about 25 moles of octane, C_8H_{18}.

(a) How many moles of oxygen must be used to burn this gasoline, assuming the only products are carbon dioxide and water?
(b) How many moles of carbon dioxide are formed?
(c) How much does this carbon dioxide weigh? (Express your answer in kilograms.)
(d) What weight of carbon dioxide is released into the atmosphere when your automobile consumes 10 gallons of gasoline? Express this answer in pounds (1 kg = 2.2 pounds).

Answer

(a) $C_8H_{18} + \frac{25}{2}O_2(gas) \longrightarrow$
$8CO_2(gas) + 9H_2O(gas)$
One mole of C_8H_{18} requires $\frac{25}{2} = 12.5$ moles of O_2. Twenty-five moles of C_8H_{18} require $25(\frac{25}{2}) = 312$ moles of $O_2 = 3.1 \times 10^2$ moles of O_2.

(b) One mole of C_8H_{18} forms eight moles of CO_2. Twenty-five moles of C_8H_{18} form 200 moles of $CO_2 = 2.0 \times 10^2$ moles of CO_2.

(c) One mole of CO_2 weighs 44 g.
200 moles of CO_2 weigh 8800 g = 8.8 kg.

(d) 194 lb.

Pr. 17. Iron (Fe) burns in air to form a black, solid oxide (Fe_3O_4).

(a) Write the equation for the reaction.
(b) How many moles of oxygen gas are needed to burn one mole of iron?
(c) How many grams of oxygen gas is that?
(d) Can a piece of iron weighing 5.6 grams burn completely to Fe_3O_4 in a vessel containing 0.05 mole of O_2?

Answer

(a) $3Fe + 2O_2 = Fe_3O_4$

(b) Three moles of Fe need two moles O_2, therefore one mole of Fe requires $\frac{2}{3}$ mole of O_2.

(c) One mole of O_2 weighs 32.00 g, thus $\frac{2}{3}$ mole weighs $(\frac{2}{3})(32.00) = 21.33$ g.

(d) No, since 5.6 g Fe equals 0.10 mole. This requires $(\frac{2}{3})(0.1) = 0.066$ mole O_2. Only 0.05 mole is present, hence the iron cannot be completely converted to Fe_3O_4.

Pr. 18. Problem 5 relates to the manufacture of nitric acid.

(a) According to the equation given in that problem, how many grams of nitric acid are formed from one mole of nitrogen dioxide?
(b) How many *more* grams of nitric acid could be formed if the nitric oxide formed could be completely converted into nitric acid (assume one mole of nitric oxide gives one mole of nitric acid)?

Answer

(a) Three moles of nitrogen dioxide form two moles of nitric acid. Therefore one mole of nitrogen dioxide forms $\frac{2}{3}$ mole of nitric acid. The molecular weight of HNO_3 is 63.0 g. Hence $\frac{2}{3}$ mole of HNO_3 weighs 42.0 g.

(b) For every two moles of HNO_3 formed, one mole of NO is also formed. Hence the yield can be increased by 50% if the NO can be converted completely to HNO_3. Thus an additional 42.0/2 = 21.0 g can be formed.

Alternatively, one mole of NO_2 gives $\frac{1}{3}$ mole of NO. If this $\frac{1}{3}$ mole of NO is converted to $\frac{1}{3}$ mole of HNO_3, we obtain $(\frac{1}{3})(63.0) = 21.0$ g additional HNO_3.

Pr. 19. Hydrazine, N_2H_4, can be burned with oxygen to provide energy for rocket propulsion. The energy released is 150 kcal per mole of hydrazine burned.

(a) How much energy is released if 10.0 kg of hydrazine fuel are burned?
(b) Compare the energy that would be released if the same weight of hydrogen, 10.0 kg, were burned as a fuel instead (see Section 3-1.1).

Answer

(a) $N_2H_4 + O_2 = N_2 + 2H_2O$
One mole of N_2H_4 weighs 32.0 g. Hence,

$$10.0 \text{ kg} = 10.0 \times 10^3 \text{ g}$$

$$\frac{10.0 \times 10^3}{32.0} = 313 \text{ moles } N_2H_4$$

Heat released equals

$$(150 \text{ kcal/mole})(313 \text{ moles}) = 4.70 \times 10^4 \text{ kcal}$$

(b) One mole of H_2 weighs 2.016 g. Hence,

$$10.0 \text{ kg} = 10.0 \times 10^3 \text{ g}$$

$$\frac{10.0 \times 10^3}{2.02} = 4.95 \times 10^3 \text{ moles } H_2$$

Heat released equals

$$(68.0 \text{ kcal/mole})(4.95 \times 10^3 \text{ moles}) = 33.4 \times 10^4 \text{ kcal}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

1. Balance the following:
   (1) $Al + O_2 = Al_2O_3$
   (2) $Cu + S_8 = CuS$
   (3) $C_2H_5OH + O_2 = CO_2 + H_2O$
   (4) $FeS_2 + O_2 = Fe_2O_3 + SO_2$

   Answer
   (1) $4Al + 3O_2 = 2Al_2O_3$
   $2Al + 1\frac{1}{2}O_2 = Al_2O_3$
   (2) $8Cu + S_8 = 8CuS$
   (3) $C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$
   (4) $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$

2. One mole of nitrogen gas, N_2, reacts with three moles of hydrogen gas, H_2, to produce two moles of ammonia gas, NH_3.

   (1) Write the equation for the reaction.
   (2) If all the gases were measured at the same temperature and pressure, how would the volumes of the gases compare?
   (3) What weight of ammonia is produced by two moles of nitrogen?

   Answer
   (1) $N_2 + 3H_2 = 2NH_3$
   (2) One vol of N_2 to three of H_2, giving two of NH_3.
   (3) Two moles of N_2 give four moles ammonia;

   $$4(17\text{ g/mole}) = 68\text{ g }NH_3$$

3. Phosphorus, P_4, burns in air to form the oxide, P_4O_{10}.

   (1) Write the equation for this reaction.
   (2) How many moles of oxygen are required to burn 2.0 moles of phosphorus, P_4?
   (3) How many grams of P_4O_{10} would be produced when 0.20 moles of phosphorus, P_4, are burned?

   Answer
   (1) $P_4 + 5O_2 = P_4O_{10}$
   (2) Ten moles of O_2 are needed.
   (3) 0.20 mole P_4 would give 0.20 mole P_4O_{10}.

   $$0.20\text{ mole} \times \frac{284\text{ g}}{\text{mole}} = 56.8\text{ g }P_4O_{10}$$

   or

   $$57\text{ g }P_4O_{10}$$

4. The following equation represents the combustion of acetylene (C_2H_2).

   $$C_2H_2 + 2\tfrac{1}{2}O_2 = 2CO_2 + H_2O + 310\text{ kcals}$$

   (1) What specific information does this equation impart?
   (2) Assume that 0.5 mole of C_2H_2 is available for combustion. How many moles of each product would form? How much heat would be evolved?
   (3) How many moles of gaseous oxygen will react with 1 kg of C_2H_2?

   Answer
   (1) The equation reveals that one mole of acetylene reacts with $2\frac{1}{2}$ moles of oxygen to form two moles of carbon dioxide and one mole of water. The reaction liberates 310 kcals of heat per mole of acetylene. It also shows the ratio of molecules reacting and forming.
   (2) If 0.5 mole of acetylene were available, one mole of CO_2 and 0.5 mole of H_2O would be formed. The heat evolved would be 310 kcals/mole × 0.5 mole = 155 kcals.
   (3) 1 kg = 1000 g;

   $$\frac{1000\text{ g}}{26\text{ g/mole}} = 38.5\text{ moles }C_2H_2$$

   This would require

   $$38.5 \times 2\tfrac{1}{2} = 96.3\text{ moles }O_2$$

5. Consider these statements about a chemical equation. Which are FALSE?

   (1) Mass is conserved.
   (2) Molecules are conserved.
   (3) Atoms are conserved.
   (4) Moles are conserved.
   (5) There is only one set of numbers that

can represent the proper ratio of reacting molecules.

Answer: 2, 4, and 5 are false.

6. Balance the following:

(1) $CO + O_2 = CO_2$
(2) $Zn + O_2 = ZnO$
(3) $P_4 + S_8 = P_2S_5$
(4) $HgO = Hg + O_2$
(5) $C_2H_6 + O_2 = CO_2 + H_2O$

Answer

(1) $2CO + O_2 = 2CO_2$
(2) $2Zn + O_2 = 2ZnO$
(3) $4P_4 + 5S_8 = 8P_2S_5$
(4) $2HgO = 2Hg + O_2$
(5) $C_2H_6 + 3\frac{1}{2}O_2 = 2CO_2 + 3H_2O$

7. The equation for aluminum burning in air is

$$2Al + 1\tfrac{1}{2}O_2 = Al_2O_3$$

(1) How many moles of oxygen are required to react with 0.25 mole of aluminum?
(2) How many grams of Al_2O_3 are formed from 0.25 mole Al?
(3) Suppose one mole of Al and one mole of O_2 react completely. Which reactant remains? How many moles?

Answer

(1) Two moles of Al require 1.5 moles O_2. One mole of Al will require 1.5/2 = 0.75 mole.
0.25 mole of Al will require 0.75/4 = 0.187 mole.
(2) One mole of Al_2O_3 weighs 102 g.

$$102 \text{ g} \times 0.25/2 = 12.8 \text{ g } Al_2O_3$$

(3) Oxygen remains; $\frac{1}{4}$ mole.

8. Given the equation

$$nA + mB = xC + Q \text{ kcals}$$

in which A, B, and C are each a pure gaseous substance:

(1) Does this equation illustrate a "phase change" or a "chemical change"? Explain.
(2) Must $n + m = x$? Explain.
(3) Assume the molecular weight of A to be 24 and of C to be 72. In terms of n and x, express the number of moles of A required to form 100 grams of C.

Answer

(1) This represents a "chemical change." Note that each of the substances is in the gas phase. Since C represents a new species, a chemical change is represented.
(2) No. An equation always conserves atoms, but not necessarily moles. Since we do not know the composition of A, B, and C, then $n + m$ does not necessarily equal x.
(3) Moles of

$$A = (100 \text{ g})\left(\frac{\text{moles } C}{72 \text{ g}}\right)\left(\frac{n \text{ moles } A}{x \text{ moles } C}\right) = \frac{100\,n}{72\,x}.$$

9. Consider the equation $4D + 3E = D_4E_3$.

(1) Assume 0.1 mole of D_4E_3 is formed in a reaction. What is the *total* number of moles of D and E consumed?
(2) Assume that 1.2 moles of E react completely with D. What is the *total* number of moles in the reaction?

Answer

(1) 0.7 mole.
(2) $\frac{4}{3}D + E = \frac{1}{3}D_4E_3$. Therefore $1.2E$ requires $(\frac{4}{3})(1.2)$ moles D and gives $(\frac{1}{3})(1.2)$ mole D_4E_3. Total moles are $1.2 + 1.6 + 0.4 = 3.2$.

CHAPTER

4

THE GAS PHASE: KINETIC THEORY

Intent and Approach

This chapter uses a "straight-line" chain of reasoning to build toward connecting temperature with kinetic energy and describing a perfect gas. These ideas are important: in this chapter, for understanding gases; and later, for understanding liquids, rates of reaction, and equilibria. Here, as in earlier chapters, specific "gas law" formulas are not presented. The intent is that a student who understands the fairly simple basis of the absolute temperature scale will have no trouble making a temperature correction. The reverse is not necessarily true. This chapter also uses Avogadro's Law as a hypothesis to explain certain facts: combining volumes and the relative weights of equal volumes of gases. Of course, you should emphasize the student's own experimental work in weighing gases.

Outline

1. One mole of a gas occupies a very large volume (4-1.1)—a volume that is approximately constant for all gases: 22.4 liters at STP or 24.5 liters at 25°C and 1 atmosphere (4-1.2).
2. Avogadro's Hypothesis (4-1.3) provides a way to get relative molecular weights of gases.
3. Section 4-2.1 presents some necessary ideas: how to measure gas pressure, definition of STP, and the cause of gas pressure. Partial pressure follows (4-2.2).
4. Temperature can be related to average kinetic energy by using a sample of gas as a thermometer (4-2.3). From this follows the absolute (Kelvin) temperature scale (4-2.4).
5. The kinetic model leads to (or explains) Avogadro's Hypothesis (4-2.5).
6. The properties of gases studied in Chapter 1 and here are combined to define a perfect gas, and it is shown that the kinetic model is applicable to this ideal (4-2.6).

New Concepts

1. Avogadro's Hypothesis: equal volumes of gases at the same conditions of temperature and pressure contain equal numbers of molecules.
2. Relationship between temperature of gases and the kinetic energy of the molecules.
3. Partial pressure: each gas in a mixture contributes pressure independently of the others.
4. Absolute zero.
5. Perfect gas and its relation to the kinetic model.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems* EASY	 MEDIUM	 HARD	*Topic*
S 4-1.1/4-1.3 (pp. 49–52)	1	Discussion	1, 2	1–**3**[*]	4–**6**	7, **8**	Molar Volumes Avogadro's Hypothesis
S 4-2/4-2.2 (pp. 52–56)	2	Discussion	3, 4	9–11	12, 13, **15**	14. 16–**18**	Partial Pressure
Read Expt. 9	3	Expt. 9					Molar Volume of H_2
Write up Expt. 9	4	Discuss Expt. 9					
S 4-2.3/4-2.4 (pp. 56–58)	5	Film: GAS PRESSURE AND MOLECULAR COLLISIONS, Demonstration 1, Discussion	5, 6	19, **20**	21, 22	**23**, 24	Absolute Temperature
S 4.3 (p. 61)	6	Problems, Review					Review
	7	Test Chapters 1–4					

Sections 4-2.5/4-2.6 (pp. 58–61) are in reduced type, and not intended for general use. Problems 25(E), 26(M), and 27, and 28(H) apply.

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[*] Boldface indicates problems whose answers are given in the Textbook.

Development

THE VOLUME OCCUPIED BY ONE MOLE OF GAS (4-1)

The Volume Occupied by a Mole of Nitrogen, N_2 (4-1.1)

The relatively large volumes occupied by substances in the gas phase are made clear to the student by comparing the density of nitrogen in each of its three physical states. The relative volume occupied by one mole of nitrogen is calculated for each state. The ratio between the gaseous volume and the liquid volume of the same mass is about 1000/1. Point out that changes in volume and density accompanying changes in temperature and pressure are very small for solids and liquids in comparison to the changes for gases. In fact, the kinetic model is a "good" model partly because of the great distance between molecules that these volume changes reflect.

A model that treats gas molecules as round, hard, perfectly elastic spheres obeying the physical laws for such systems is an extremely useful one. Students should be reminded that its usefulness stems from its success in explaining the behavior of many gases over a wide range of temperatures and pressures. Most gases behave in accordance with this model when not near their boiling point and at fairly low pressures. Refer to the background material for a more advanced treatment of corrective factors that must be applied to systems which depart from "ideality"; i.e., systems that do not closely follow the predictions based on the model.

A Comparison of Molar Volumes of Gases (4-1.2)

This is a straight experimental section giving some values of molar volumes of gases. Note that sometimes the molar volume is given at 0°C and 1 atmosphere (22.4 liters); sometimes at 25°C and 1 atmosphere (24.5 liters). These two values are given on purpose—to get and keep both numbers before the student and to stress that 22.4 is not a "magic" number. It is just a gas volume of 1 mole at an arbitrary set of conditions. Do not use these two volumes as a temperature correction problem. This is a useful question but is ahead of the student.

Avogadro's Hypothesis (4-1.3)

Experiment 6 is typical of the type of data that comes from using Avogadro's postulate. The student "assumes" one molecular weight and then compares weights of identical volumes of other gases. Do not try to prove the law, but comment on its reasonableness, relate it to combining volume (as a review) and to balancing equations. Molecular models can help show how the volumes of reacting gases come to have simple ratios. But, we repeat, do not try to prove this law.

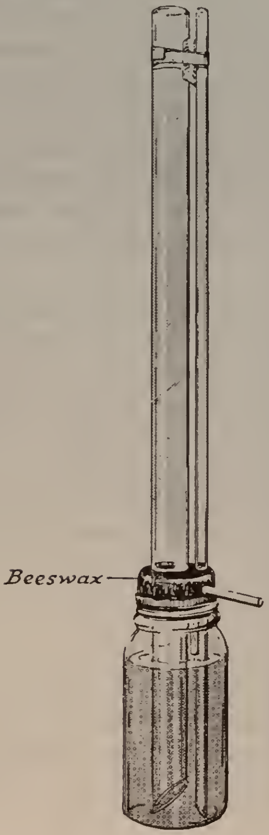
The determination of molecular weight may seem like a hollow exercise. Students may feel that molecular weight is "known"—that it can be found from the formula. Try reminding them that the formula is not really known until the weight of one mole is found. This is an important step that has been carried out for thousands of compounds—and will be carried out for many others.

THE KINETIC THEORY (4-2)

Gas Pressure (4-2.1)

The pressure of a gas is discussed first in terms of its measurement and second in terms of its cause. You can best develop this section by showing a mercury barometer and by using a curved glass tube, sealed at one end (see Figure 4-2b, Textbook, p. 54). This type is called a J-tube apparatus in the catalogs of some scientific instrument companies. The Torricellian barometer can be effectively demonstrated (see Figure 4-2a, Textbook, p. 54) as follows. Take a heavy-walled glass tube, which must be 31 inches or longer, and fill it with mercury. Carefully invert the tube into a beaker of mercury. Some of the mercury will run out of the glass tube until the height of the mercury column is just equal to the atmospheric pressure.

Questions frequently arise at this point in connection with the diameter of the tube, the use of a liquid other than mercury, the surface area of the exposed mercury in the beaker, and so on. Elementary physics texts review these principles. Briefly, the height of the liquid in the tube depends upon the liquid density and is independent of tube diameter or the surface area of exposed liquid in the beaker. Remember that the pressure is measured in terms of force per unit area. By demonstrating this with tubes of several diameters, it can easily be shown that the height *is* the same in each tube. The following illustration shows an apparatus that demonstrates this quite well.



To make this device, select a quart jar with an airtight lid. Cut holes in the lid to take 6, 10, and 25 mm glass tubes. Fashion the bottom ends of the larger tubes at an angle with a wire gauze. Clamp the tubes in place (off the jar bottom) and fasten a light cardboard dam around the jar top. Pour molten beeswax in the dammed space. To use the apparatus, fill the jar two-thirds full of an appropriate colored solution, for example, $KMnO_4$ or $Ni(NO_3)_2$.

In use, be sure to control the air flow in order that the liquid levels will change slowly. Rapid change reveals a different rate of rise or descent. This interesting aspect, caused by friction with the wall, should not be allowed to obscure the main issue. Stop blowing before the bottoms of the tubes are exposed. The subsequent rush of air sometimes carries liquid out of the tubes onto hapless demonstrators.

Film, GAS PRESSURE AND
MOLECULAR COLLISIONS,
fits here. See p. 133 for summary.

In demonstrations utilizing the curved tube, the relationships become more meaningful when students perform the actual measurements, record the data, and then graph the change in volume with respect to pressure. You can have some students take readings, others record data at the chalkboard, and still others plot data on a graph at the chalkboard.

STP. The remarks on p. 121 and in the Textbook establish that the conditions 0°C and 1 atmosphere have no special scientific basis but are picked for convenience, and that there is nothing special about the value 22.4 liters either.

Cause of Gas Pressure. Pressure is a result of the force (push) exerted by the gas molecules as they strike the surface of a container. This effect is described quantitatively in terms of force per unit area, and it follows that not only the concentration but also the mass and speed (velocity) of the particles must be considered.

Partial Pressure (4-2.2)

Experimental evidence shows that in mixtures of gases the total pressure is equal to the sum of the individual pressures due to each individual gaseous component. The pressure caused by any single component of the mixture is proportional to the number of particles of that component. Thus the ratio of the number of its molecules to the total number of molecules present gives the fraction of the pressure from that component. Remember that the individual gases in the mixture are subject to the same limitations imposed by "ideality" as discussed earlier.

Expt. 9, A QUANTITATIVE INVESTIGATION OF THE REACTION OF A METAL WITH HYDROCHLORIC ACID, fits here. See p. 127 for guide.

Temperature and Kinetic Energy (4-2.3)

From this section the student should get the idea that the temperature of a gas is a measure of the average kinetic energies of its molecules. It will then follow that the molecules of all gases at the same temperature must have the same average kinetic energies. For this to be possible, the lighter molecules of lower-molecular-weight gases must move faster, and the heavier molecules of the higher-molecular-weight gases must move slower in order for the net "push" or force per unit area (pressure) to be the same for each molecular collision.

Absolute Temperature (4-2.4)

Demo. 1, PRESSURE-TEMPERATURE RELATION, fits here. See p. 125 for guide.

The effect of temperature changes on gas volume and the subsequent development of an absolute temperature scale can best be demonstrated by using some technique such as the one shown in this section of the Textbook (Figure 4-4) or in Demonstration 1. Data can be obtained in a manner similar to that described in Table 4-III (Textbook) and a graph prepared. This curve can then be extrapolated to show absolute zero occurring in the vicinity of −273°C. A comparison of absolute (Kelvin), centigrade, and Fahrenheit temperature scales fits in at this point. (Do not spend time on centigrade-Fahrenheit conversions.) Compare some standard reference points on the three scales. The student should be able to convert °C to °K and the reverse.

Avogadro's Hypothesis and the Kinetic Theory (4-2.5) (reduced type)

This and the following section in reduced type can be omitted without serious loss. In no case should a great amount of time be spent on them.

A good model must give a description of the major features of that part of nature it describes. Hence we expect any theory of gases to describe Avogadro's Hypothesis. This section gives such a connection between the law and the kinetic theory. It is not intended for classroom discussion.

The Perfect Gas (4-2.6) (reduced type)

The perfect gas is an example of something that scientists find quite useful—a hypothetical substance or state that is known to be incorrect in the sense that actual materials do not fit it exactly. The imaginary case is so simple, however, that it is easy to deal with and, if it is based on a good model, fits well enough to describe a major part of the observed behavior. This section and Table 4-V (Textbook) show how most gases are nearly perfect under "normal" conditions. Problem 28 reinforces the idea that deviations increase as the temperature is lowered toward the boiling point.

The reasons for the deviations lie in the limitations of our model. All gases will deviate slightly from the behavior predicted by the model because:

(a) Attractive forces exist between molecules, particularly at lower temperatures and higher pressures, where gases tend to condense to the liquid phase.
(b) Molecules are not perfect spheres, nor are they perfectly elastic.
(c) The volume occupied by the gas molecules themselves is not truly zero.

DEMONSTRATION 1 PRESSURE-TEMPERATURE RELATION

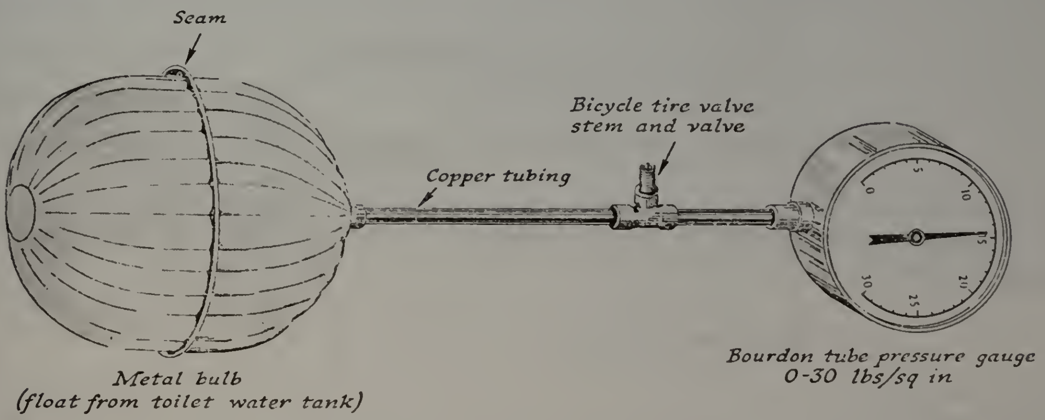
PURPOSE. To show the *P-T* relationship of a gas and to serve as an introduction to the absolute temperature scale.

TIMING. This demonstration should be done near the middle of Chapter 4, before discussing Sec. 4-2.4, *Absolute Temperature.*

EQUIPMENT NEEDED

1 apparatus as described below under *Laboratory Hint*
3 2-liter beakers or large battery jars
ice
dry ice
acetone or amyl alcohol
bicycle pump
burner
ring stand
ring and wire gauze

LABORATORY HINT. The apparatus can be constructed as shown in this drawing:



All connections must be made airtight. The bulb must be soldered around the seam to make it airtight. The gauge should be set to read atmospheric pressure with air in the bulb at atmospheric pressure. The apparatus is available from Welch Scientific Company, catalog no. 1602, price $17.50.

PROCEDURE

1. Prepare these three temperature baths:

   boiling water,
   ice-water mixture,
   dry ice-amyl alcohol or dry ice-acetone mixture.

   The bath containing dry ice will be at about −78°C. The liquid acts as a heat-conducting medium, but the temperature is determined by the $CO_2(s)$. The alcohol gives a bath that rarely froths or "bumps," is less of a fire hazard, and stays mushy better than one made with acetone. The alcohol has a stronger odor than the acetone.
2. Pump air into the apparatus to give a pressure of about 20 lb/inch^2 at room temperature. Record this pressure.
3. Obtain gauge pressure readings for each of the three other temperatures by immersing the

bulb completely in each of the baths. Read the pressure gauge with as much care as you can.

4. You may wish to repeat the experiment using a different starting pressure at room temperature by adding more air.

STUDENT ASSIGNMENT

1. Have the students plot the data with temperature along the abscissa and gauge pressure along the ordinate. The origin should be at $t = -300°C$ and $P = 0$.
2. Have the students extrapolate the line formed by the four measured points to the line $P = 0$.

EXPECTED RESULTS. Figure 4-1 gives an example of the expected results.

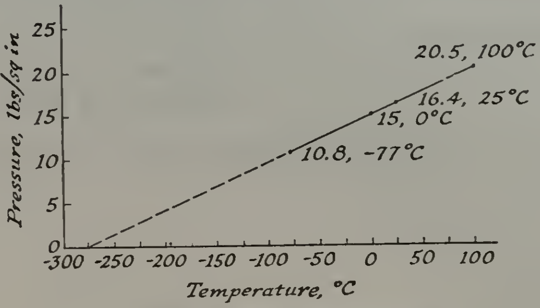


Fig. 4-1. **Pressure-temperature relationship** *for air.*

1. Determine what fraction the pressure change (ΔP) per degree centigrade is of the pressure at 0°C ($P_{0°C}$). Express the fraction with a numerator of one. As an example, for the temperature range 0–100°C,

$$\frac{\text{change in pressure per degree}}{\text{pressure at 0°C}} = \frac{\dfrac{\Delta P}{t_2 - t_1}}{P_{0°C}} = \frac{\dfrac{5.5}{100}}{15} = \frac{1}{272}$$

DISCUSSION. The next day's lesson develops the idea of absolute zero. The fractional change in pressure per degree centigrade change in temperature is generally very close to $\frac{1}{273}$. This can be used to "invent" the Kelvin temperature scale.

EXPERIMENT 9 A QUANTITATIVE INVESTIGATION OF THE REACTION OF A METAL WITH HYDROCHLORIC ACID

PURPOSE. To give an experimental basis for calculating the molar volume of hydrogen gas (room temperature, 1 atm) and later (after completing Chapter 4) at STP. This experiment is traditionally used as an "equivalent weight" determination, and it is important that you reflect on the reasons why we now include it. It is a very satisfying experiment, since both the precision and accuracy are high, and the manipulation is simple yet interesting.

PRELAB DISCUSSION. It is important that the student have an understanding of the various steps in this experiment. Since each of the measurements involved may be done with considerable precision, he should focus his attention on working carefully. Tell how the magnesium ribbon has been weighed, and point out the necessity for leaving square corners when a small piece is cut off. Discuss how the difference in density of the HCl solution and the water permits a water column to rest on top of the acid. Discuss the reason for adjusting the level of the water inside and outside the tube before reading the volume.

TIMING. This experiment should be done after assigning Sec. 4-2.2.

EQUIPMENT NEEDED

50 ml gas-measuring tube (see lab hint 2)
one- or two-hole stopper (size #0 or #00 to fit measuring tube)
thermometer
barometer (see lab hint 4)
ring stand and clamp
400 ml beaker
water reservoir (see lab hint 3)
graduate (10 or 25 ml)
metric ruler
5–6 cm of magnesium ribbon (see lab hint 1)
10 ml of 6 *M* hydrochloric acid (513 ml conc. reagent/liter)
10–15 cm fine Cu wire

TIME REQUIRED. The actual collection of gas takes place quite rapidly, hence the students who have seen the experiment demonstrated can probably do it in about 20 minutes, but class experience has shown that it usually requires about 40 minutes. Part of a second day will be needed for discussing the calculations.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. The magnesium ribbon, if free of corrosion, is very uniform. If the package has been opened previously, the outermost section should be discarded in order that an uncorroded sample is obtained. Weigh the ribbon in 1 meter lengths (about 1 g) in order that the precision on the ±0.01 gram balance will be 1 part in 100. If weighed on an analytical balance the precision is 1 part in 10,000, which, although unnecessary, may be useful if you wish to use the data from this experiment for further discussion of precision. The student is asked to measure the length of the ribbon to one part in 100, or ±0.5 mm, in his 5 cm strip, and this is certainly the least precise measurement. He should be reminded to observe the finite width of the ruler lines.

   It is wise for you to check the volume of H_2 from a given length of Mg either experimentally or by calculation, since it is desirable to collect as large a volume as can be measured in a single tube and because temperature and pressure differences make it impossible to predict the optimum length of Mg for every local set of conditions. At high altitudes a piece as short as 4 cm may be used.

2. If gas measuring tubes are not available, it is possible to calibrate the portion of a buret between the 50.0 ml mark and the valve, but there is some difficulty in reading the markings. An unmarked 10 mm (or more) diameter glass tube, closed or stoppered, may be used and the volume measured later in a graduate. The gas-measuring tube marked to 0.1 ml divisions gives an uncertainty of about ±0.05 or ±0.1% for 50 ml of hydrogen.
3. A battery jar or large beaker (2 or 3 liter size) is ideal, but 1 liter beakers or large jars or cans are quite satisfactory. Hydrometer cylinders are excellent also.
4. The degree of precision from other parts certainly does not warrant using the vernier scale in recording the barometer reading, but this may be done for instructional purposes and to give the students another "choice" when doing the final calculations. Nor does one need to use corrections for the temperature, latitude, etc. A correction of 2–3 mm in 700 mm is only 1 part in 200 or 300, and therefore more precise than some other measurements being used.

POSTLAB DISCUSSION. As previously suggested the precision of all the measurements in this experiment is high. If, when the results of the individuals in a class are compared, there is a trend—for example, if most of the individual results are low but in agreement with each other—the most likely source of error lies in the weighing of the Mg ribbon, and this should be rechecked.

Since the calculations are somewhat involved, you may wish to de-emphasize considerations of uncertainty until you collect data for a class discussion. Exercise 4-6 relates to this experiment. Details of a postlab demonstration are given after *Calculations* and *Answers to Questions*.

SAMPLE DATA

Weight of Mg ribbon	0.825 g/m	(±0.06%)
(weight of Mg ± 0.0001 g ~0.01%; length of meter of Mg ± 0.0005 m ~0.05%)		
Length of Mg ribbon used	5.50 ± 0.05 cm	(±1%)
Volume of hydrogen collected	47.5 ± 0.05 ml	(±0.1%)
Temperature of water	25 ± 0.2°C	(±1%)
Temperature of room	25 ± 0.2°C	(±1%)
Barometer reading (room pressure)	758 ± 2 to 3 mm	(~0.3%)
Vapor pressure of water	23.7 ± 0.25 mm	(~1%)

(The student has no basis for estimating the lack of precision in the vapor pressure value other than his knowledge of the uncertainty in the temperature. From the handbook one may estimate that a temperature range of ±0.2°C would give an uncertainty of about ±1%. For example, at 24.8°C, the vapor pressure is 23.5 mm; at 25.2°C, it is 24.0 mm.)

CALCULATIONS

1. Determine the weight of the magnesium you used from the grams per meter relationship and the length of the ribbon.

   Weight of Mg ribbon:

$$(0.825\ \text{g/m} \pm 0.06\%) \times (5.50\ \text{cm} \pm 1\%) \times 10^{-2}\ \text{m/cm} = 4.54 \times 10^{-2}\ \text{g} \pm 1.06\%$$

2. Determine the number of moles of magnesium used.

$$\frac{4.54 \times 10^{-2}\ \text{g Mg} \pm 1\%}{24.3\ \text{g/mole Mg}} = 1.87 \times 10^{-3}\ \text{mole Mg} \pm 1\%$$

3. Determine the partial pressure of the hydrogen gas.

$$P_{H_2} + P_{H_2O} = P_{\text{room}}$$
$$P_{H_2} = P_{\text{room}} - P_{H_2O}$$

With the sample data this gives

$$P_{H_2} = 758 - 24 = 734 \text{ mm} \pm 0.4\%$$

4. Determine the volume of the hydrogen gas at one atmosphere pressure (760 mm).

$$V_{\text{new}} = V_{\text{measured}} \left(\frac{P_{H_2}}{760}\right)$$

$$= 47.5 \times \frac{734}{760} = 45.9 \text{ ml} \pm 0.5\%$$

5. Calculate the volume of dry hydrogen which would be produced by one mole of magnesium at room temperature and one atmosphere pressure.

Since $1.87 \times 10^{-3} \pm 1\%$ mole Mg produced 45.9 ml ± 0.5% H_2,

$$\frac{45.9 \text{ ml} \pm 0.5\%}{1.87 \times 10^{-3} \text{ mole} \pm 1\%} = 24.5 \times 10^3 \text{ ml/mole} \pm 1.5\%$$

$$= (24.5 \text{ liters} \pm 0.4 \text{ liter})/\text{mole}$$

QUESTIONS AND ANSWERS

1. Given that one mole of Mg produces one mole of hydrogen, H_2, what is the volume of one mole of hydrogen at room temperature and 1 atmosphere pressure?

Answer: If one mole of Mg produces one mole of H_2 and, if 1 mole of Mg produces 24.5 liters H_2, then one mole of H_2 occupies 24.5 liters at room temperature and one atm.

2. If one mole of hydrogen weighs 2.0 g, what is the weight of a liter (the density) of hydrogen at room temperature and one atmosphere pressure?

Answer: At one atmosphere and 25°C, 24.5 liters of H_2 contain one mole of H_2. If one mole weighs 2.0 g, then

$$\frac{2.0 \text{ g}}{24.5 \text{ liter}} = 0.082 \text{ g/liter of } H_2 \text{ at 1 atm and } 25^\circ\text{C}$$

DEMONSTRATION. This experiment can be usefully extended to show the production of H_2 from equimolar weights of Na, Mg, and Al; which stresses that a ratio of one mole of metal to one mole of hydrogen produced is not true for all metals. Such an experiment serves as an introduction to Chapter 6 and is useful for drill on equation balancing. If the quantitative aspects are to be used by students in the suggested extracurricular investigation, keep this demonstration on a qualitative basis. Use large test tubes for the qualitative demonstration. Each should hold a minimum of 50 ml, but a larger volume is desirable.

Al: More precisely known weights are possible if a meter or more of the wire is weighed. Cut off a length estimated to produce enough H_2 at room conditions (over water) to fill the tube being used. (That is, if in Expt. 9 about 0.02 mole of Mg filled a 50 ml tube, measure 0.013 mole of Al.)

Since the oxide coating on Al gives a slow start, use more concentrated acid, and rest the tube on the bottom of the container such that the hole in the stopper is closed and the acid may thus remain in contact with the Al for some time. As soon as bubbles start, lift the tube slightly.

Mg: Same as Expt. 9, except use the same number of moles as of Al. This amount of Mg should produce only two-thirds as much H_2.

Na: See the technique below for getting Na metal into tubes and for calculating the weight. It may be convenient to estimate the Na for a trial run, measure the amount of H_2 gas produced, and use this to calculate how much the Na weighs per centimeter of tubing. Water may be substituted for dilute HCl, but if the sodium is encased in 6–8 mm tubing, be prepared for a slow reaction, since the H_2 gets trapped in the tube. A wire attached to the tube of Na enables one to jiggle it to dislodge bubbles.

ADDITIONAL INVESTIGATION—*to be undertaken as an extracurricular experiment. Consult your teacher before proceeding.*

Determine the volume of hydrogen gas produced when a mole of another metal reacts with an acid.

See the section below for suggestions about handling sodium. Aluminum wire is uniform, but slightly more HCl will be needed to get the reaction started (because of the aluminum oxide coating). Zinc and powdered iron may also be used, but the weighing must be done on an analytical balance if less than 50 ml of H_2 is to be collected and if the uncertainty of measurement is to be reasonably small.

PREPARING SODIUM METAL IN GLASS TUBES

The general method consists in letting the atmosphere push the molten sodium into a warm glass tube, where it solidifies. The tubes can then be cut and stored.

1. Have readily accessible:
    (a) About 6 pieces of 6 mm soft glass tubing, each about 30 cm long. (5 mm tubing might work, but experience with 4 mm tubing shows that the bore is so small as to retard the entrance of water. This is a disadvantage if you wish to demonstrate the reaction of sodium with water.)
    (b) About 20 cm^3 of sodium.
    (c) A crucible or test tube to hold the sodium.
    (d) A vacuum source with a control valve (a screw-type pinch clamp is okay). *Do not use an aspirator.*
2. Thoroughly dry the work place. Put on a pair of safety glasses—do not work alone. Hold a piece of sodium with tongs, and cut off the crust. Use paper towels to blot most of the oil off the sodium. If this is not done, an emulsion will form when the sodium is melted, making it virtually impossible to get a tube full of bright, solid metal.
3. Very gently warm the sodium in a crucible or test tube until melted (97.5°C). Remove the flame.
4. Attach the vacuum line (turned off) to a piece of 6 mm soft glass tubing, and warm the glass gently. If the tube is cold, the sodium will soon solidify, preventing complete filling of the tube.
5. Put the free end of the glass tube in the molten sodium, and slowly turn on the vacuum until sodium is pushed nearly to the top of the tube. Pinch off the vacuum, but keep the end of the tube under the sodium surface until that in the tube solidifies. If removed too soon, the molten sodium will run out of the tube, leaving a hollow pipe that will tarnish in a few months.
6. Repeat step (5) to fill as many tubes as desired.
7. These tubes can be cut and stored under kerosene or toluene. Toluene is better, since it absorbs less water. Nick the glass with a file, hold with toweling, and snap. The sodium may be cut with a knife, or merely twisted until separated.
8. Unused, melted sodium may be poured on a dry surface and, when solidified, returned to a

storage bottle. The crucible or test tube should be cleaned, and the scrap sodium disposed of by allowing it to react with small quantities of methanol. When the addition of more methanol causes no reaction, and when *all* solid material has reacted, pour the solution down the drain.

9. To obtain a specific weight of sodium metal, determine the volume of the tube. This can be done roughly by using linear measurements, or more precisely, by filling a known length of tube with mercury. The weight of mercury used, divided by its density (13.5 g/ml) will give its volume. The volume per centimeter multiplied by the density of sodium (0.97 g/ml) will give grams of Na per centimeter of tube.

Supplementary Material

Articles

M. Summerfield, High Temperatures: Propulsion, *Scientific American*, pp. 120–131, September 1954.

H. M. Davis, Low Temperature Physics, *Scientific American*, pp. 30–39, June 1949.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

GAS PRESSURE AND MOLECULAR COLLISIONS

A CHEM Study film

Running Time: 21 minutes

The film explores the relationship between gas pressure and molecular collision through study of the effects of varying the number of molecules per unit volume and of varying the temperature. The experimental study of the relative rates of effusion of H_2, O_2, CO_2, and SF_6 leads to the quantitative relationship between molecular weight, molecular velocity, and absolute temperature. Mechanical models illustrate the experimental observations.

This film was produced in collaboration with Dr. J. A. Campbell. One part of it shows the relation of gas pressure to absolute temperature; as does Demonstration 1.

Background Discussion

The general intent of this chapter is to increase the student's confidence in scientific models by showing how helpful a good one is. For this reason the student should be made to understand how the kinetic theory explains gaseous behavior. This approach has several advantages:

1. It follows the flow of the course, emphasizing models and the scientific thought process.
2. It gives a method of working gas behavior problems based on understanding rather than on the mechanical solution of algebraic equations.
3. It introduces a number of concepts that are used here and later—absolute temperature, distribution of particle energy (the average energy is related to temperature), and partial pressure.

The following material includes these topics

Scientific Models
The Kinetic Energy Equation
The Gas Constant, R
Kinetic Energy and Absolute Temperature
Real Gases
Critical Conditions
Value of Kinetic Energy and Heat Capacity

These sections discuss some of the more complex aspects of gas behavior. You will not want to take these up in detail during your lectures. For some inquiring student, you can abstract what is needed for his questions.

SCIENTIFIC MODELS

Our scientific probing represents a search for regularities. We seek to understand these regularities by constructing models of matter from which they might be predicted. Such a model, initially at least, is based on some familiar system whose behavior is clear. Frequently, however, the model must be so drastically modified that it bears little resemblance to familiar, well understood models. Often it reduces to a series of complex equations. But to remain useful the model must accurately predict experimental behavior; this is the test which all models must pass.

Of the three phases of matter, the gaseous state is the best understood. The kinetic molecular theory was used to explain gas pressure in Chapter 2. Its application to the explanation of several other properties of gases is developed in this chapter. An excellent opportunity exists for developing the student's confidence in the power of a scientific model.

THE KINETIC ENERGY EQUATION

In Chapter 4, the pressure exerted by a gas was explained in terms of the number of molecules n, their mass m, and their average velocity v. The proper "average velocity" is calculated by squaring each individual velocity, taking the average of these, and extracting the square root. This is called the root mean square velocity, and it is higher (8%) than a straight average. Just use the term "average velocity" without specifying. The number of collisions between a molecule and a given wall of a cubic container was shown to be $v/2d$. For a large number of molecules, on the average only one-third of them would bombard a given wall, thus the total number of collisions with the one wall can be set equal to $nv/6d$. Each time a molecule strikes a wall and rebounds, it must reverse direction; hence the total change of momentum is $2mv$. Multiplying $2mv$ by the number of collisions per unit time yields this equation for the force exerted by the gas:

$$F = (nv/6d) \times 2mv = \frac{nmv^2}{3d} \qquad (1)$$

Since pressure is force per unit area (d^2), equation (*1*) becomes

$$P = F/A = \frac{nmv^2}{3d^3} \qquad (2)$$

(This is equation 11 of the Textbook.) Since d^3 defines a volume, equation (*2*) is commonly written

$$PV = \tfrac{1}{3}nmv^2 \qquad (3)$$

which gives pressure times volume in terms of the mechanical properties of our model. The success of this equation is a rigorous test of the validity of our model.

If we consider one mole of gas, $n = N$. Then Nm (the number of molecules times the mass of one molecule) is M, the molecular weight of the gas. Equation (*3*) can then be written (by setting $\frac{1}{3} = \frac{2}{3} \times \frac{1}{2}$)

$$PV = \tfrac{2}{3} \times \tfrac{1}{2}Mv^2 \qquad (4)$$

The quantity $\frac{1}{2}Mv^2$ has been defined as kinetic energy (Sec. 4-2.5 of the Textbook), thus equation (*4*) can be written

$$\tfrac{2}{3} \times \tfrac{1}{2}Mv^2 = \tfrac{2}{3}\text{K.E.} \qquad (5)$$

But kinetic energy is related to absolute temperature.

$$\tfrac{1}{2}Mv^2 = cT$$

The constant c can be expressed as $\frac{3}{2}R$. The symbol R is called the gas constant. Substituting, we get, for one mole

$$PV = RT$$

or

$$\frac{PV}{T} = R \qquad (6)$$

THE GAS CONSTANT, *R*

Equation (*6*) is often called the perfect gas law, and the constancy of this quotient provides another test of the validity of our kinetic molecular model. From data given in Textbook Table 4-V (p. 60) some PV/T quotients for a mole of various gases have been computed by dividing PV by 273°K, and the results are recorded here in Table 4-I.

Although the values are not constant, they cluster close enough to an "ideal" value to suggest that our kinetic molecular model is a "good" model. Its predictions agree well with experimental values. The constant for an ideal gas (i.e., one defined by the kinetic molecular model) is 0.08206 liter-atm mole⁻¹ degree⁻¹. It can also be expressed in other units.

Observe that the experimental gas constant is smaller than the ideal gas constant for all gases given except H_2 and He and that the constants for H_2, He, N_2, and CO are quite close to the value for the ideal gas constant. The foregoing discussion has revealed some limitations of our model, but, as we shall see, those limitations do not destroy its utility. Rather, they have helped us to increase our understanding of real gases.

Table 4-I

Molar Gas Constant Values of Some Gases at 1 Atm and 0°C

Gas	R (liter-atm mole^{-1} degree^{-1})	Gas	R (liter-atm mole^{-1} degree^{-1})
H_2	0.08213	CH_4	0.08187
He	0.08211	CO_2	0.08152
"Perfect" gas	0.08206	HCl	0.08146
N_2	0.08203	NH_3	0.08090
CO	0.08203	Cl_2	0.08079
O_2	0.08200	SO_2	0.08015

KINETIC ENERGY AND ABSOLUTE TEMPERATURE

As early as 1703 the effect of temperature on the pressure of a gas confined at constant volume was studied. For what we now call a one degree centigrade rise in temperature above 0°C the pressure of a gas increases $\frac{1}{273}$ of its pressure at 0°C. These findings can be summarized by the equation

$$P = P_0 + \frac{1}{273}P_0t \qquad (7)$$

where P is any pressure of the gas, P_0 is its pressure at 0°C, and t is temperature on the centigrade scale. Solving equation (*7*) for t yields

$$t = 273\frac{P}{P_0} - 273 \qquad (8)$$

If equation (*8*) can be assumed valid at all temperatures, it predicts that the pressure of the gas will become 0 at 273° below 0°C. In terms of our kinetic molecular model, this must mean that the motion of the particles has ceased completely—that they are absolutely frozen. This state of complete rest is what the Textbook refers to as the absolute zero of temperature.

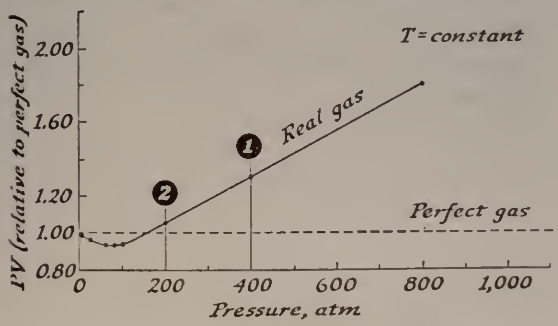
From this discussion, it appears that the temperature of a gas depends upon its molecular motion. The total kinetic energy of a gas has been defined as $\frac{1}{2}Mv^2$. Since mass cannot change with temperature, it must be v^2 which determines the temperature of a gas. For this reason we interpret the absolute temperature to be a measure of the square of the velocity of the molecules of a gas.

REAL GASES

Values of the gas constant for real gases listed in Table 4-I indicate that certain gases such as CO_2, HCl, NH_3, Cl_2, and SO_2 deviate considerably from ideal behavior. Data in Textbook Table 4-V show that the PV product also differs considerably from its ideal value of 22.414 liter-atm mole^{-1}, although equation (*6*) predicts that this product will be a constant at a given temperature. Not only is the product not a constant, but it is found to vary with pressure, as shown in Figure 4-2.

An examination of Figure 4-2 shows that when the gas expands from its volume at 400 atmospheres to its volume at 200 atmospheres, its PV product decreases (i.e., $P_1V_1 > P_2V_2$). We have shown by the previous discussion, and specifically by equation (*4*), that the PV product measures the kinetic energy or heat energy of a gas.

Fig. 4-2. **Variation of the PV product with pressure.**



When a gas expands, its temperature usually changes. This effect was noticed in 1852 by J. P. Joule and W. Thomson, and is still called the Joule-Thomson effect. The observed temperature change is the result of two factors: the separation of molecules against attracting forces; and the expansion of the gas, resulting from collisions and repulsive forces. Depending on the size of the two effects, this sum can be either a gain or loss of energy. Since the experiment is usually conducted under adiabatic conditions (no heat put in or taken out), the temperature can fall or rise.

Most gases, if not compressed too much or heated too much, will show a net cooling effect. Hydrogen and helium will warm at room temperature. Since curves such as that shown in Figure 4-2 vary with temperature, it is difficult to predict the conditions at which a gas will change from cooling to heating.

The decrease of energy that gases generally experience on expansion must be associated with some work done by gas. Apparently it is partly the work necessary to overcome the attractive forces postulated in Sec. 4-2.6 of the Textbook. It is these attractive forces that are partly responsible for the deviation of the gas constant from the ideal value. They are called van der Waals forces, after one of the first investigators to explore them in great detail. As a result of his extensive research, van der Waals proposed an equation which reproduces the properties of real gases at relatively high pressures much better than the ideal gas equation (*6*). The van der Waals equation for one mole of gas is

$$(P + a/V^2)(V - b) = RT \qquad (9)$$

Here a/V^2 is a correction factor for the attractive forces exerted by the molecules, and b is a correction factor for the volume actually occupied by the molecules. The corrective factors can be interpreted in the following manner. The actual force with which a molecule strikes the container wall (and thus the pressure we measure) is lower because the striking molecule is "held back" by the van der Waals attractive force. For this reason we add a correction to the observed pressure to approximate the ideal pressure. On the other hand, not all of the volume we measure for the gas sample (i.e., the volume of the container) is available to the molecules. Because they occupy some volume themselves, a corrective factor proportional to that occupied volume must be subtracted to get closer to the true, available volume.

CRITICAL CONDITIONS

It is found experimentally (first by Andrews in 1869 for CO_2) that there is a temperature above which a gas cannot be liquefied regardless of the applied pressure. This value is called the *critical temperature*, and the *critical pressure* is that which is just sufficient to produce liquid. Often these conditions are determined by watching the surface become fainter and disappear, since at the critical point liquid and gas are indistinguishable.

VALUE OF KINETIC ENERGY AND HEAT CAPACITY

Equation (*5*) can be used to calculate the kinetic energy of a gas. Since R is 1.98 cal/mole degree, we have

$$\text{K.E.} = \frac{3}{2}RT = \frac{3}{2}\left(1.98\,\frac{\text{cal}}{\text{mole degree}}\right)(273\text{ degrees})$$
$$= 811\text{ cal/mole}$$

Since the kinetic energy of a gas would be zero at 0°K (as was implied in Sec. 4-2.4 of the text), 811 cal must be the heat that has to be added to 1 mole of a monatomic gas to raise its temperature from 0° to 273°K (i.e., to 0°C). A monatomic gas is specified because kinetic energy is the only kind of mechanical energy such a gas can absorb. It cannot absorb rotational or vibrational energies. Dividing the total kinetic energy of the gas by its temperature gives a calculated heat needed to change the temperature of one mole by one degree.

$$\frac{811\text{ cal/mole}}{273\text{ degrees}} = 3\,\frac{\text{cal}}{\text{mole degree}}$$

We can compare this to the experimental value for the monatomic gas, argon. The measured value is 3.0 cal/mole degree, giving an excellent check between computed and experimental values. Such agreement gives us greater confidence in the validity of our kinetic molecular model.

Special notice should be taken of the fact that our theoretical calculation included no information about the specific nature of the gas. All monatomic gases should have specific heats of about 3.0 cal mole^{-1} degree^{-1}, and this has been found to be true. The ideal goal of chemical theory is to develop a theoretical model capable of explaining completely the different behavior of specific kinds of matter. We are not near this goal.

Answers to Exercises and Problems

Ex. 4-1. How many molecules of nitrogen are present in one liter of the gas at 0°C and one atmosphere pressure?

Answer

$$\frac{6.02 \times 10^{23} \text{ molecules/mole}}{22.4 \text{ liters/mole}} = 2.68 \times 10^{22} \text{ molecules/liter}$$

Ex. 4-2

(a) Calculate the volume (in milliliters) occupied by one nitrogen molecule in the solid phase.

(b) Recognizing that one milliliter is 1.00 cubic centimeter, estimate the size (in centimeters) of a cube that has the volume calculated in part (a). Use one significant figure. Now express your answer in Angstroms (1 Å = 10^{-8} cm).

Answer

(a) The molar volume of solid nitrogen is 27.2 ml/mole. Since a mole contains 6.02×10^{23} molecules, the volume per molecule is

$$\frac{27.2 \text{ ml/mole}}{6.02 \times 10^{23} \text{ molecules/mole}} = 4.52 \times 10^{-23} \text{ ml/molecule}$$

(b) The cube must have an edge length equal to the cube root of its volume.

$$\begin{aligned} \text{Edge length} &= (4.52 \times 10^{-23} \text{ cm}^3)^{1/3} \\ &= (45.2 \times 10^{-24} \text{ cm}^3)^{1/3} \\ &= 3.6 \times 10^{-8} \text{ cm} \\ \text{Edge length} &= 3 \text{ or } 4 \text{ Å}. \end{aligned}$$

Ex. 4-3. A container of fixed volume contains two moles of gas at room temperature. The pressure in the container is four atmospheres. Three more moles of gas are added to the container at the same temperature. Use the result just stated to show that the pressure is now 10 atmospheres.

Answer

Adding three moles of gas results in a total of five moles of gas, or 2.5 times as many moles as were originally present. Thus, there will be 2.5 times as many collisions between the gas molecules and the walls of the container, and the pressure will rise by a factor 2.5.

$$(2.5) \times (4 \text{ atm}) = 10 \text{ atm}$$

Ex. 4-4. Assume that 0.0050 mole of air contains 0.0040 mole of nitrogen, N_2, and 0.0010 mole of oxygen, O_2. What is the partial pressure of oxygen in the first bulb in Figure 4-3? What is the partial pressure of oxygen in the third bulb? Use three significant figures.

Answer

Fraction of O_2 moles in bulb 1

$$= \frac{0.00100}{0.00500} = 0.200$$

Fraction of O_2 moles in bulb 3

$$= \frac{0.00100}{0.00500 + 0.00110} = 0.164$$

Partial pressure of O_2 in bulb 1

$$= 0.200 \times 93.0 \text{ mm} = 18.6 \text{ mm}$$

Partial pressure of O_2 in bulb 3

$$= 0.164 \times 113 \text{ mm} = 18.6 \text{ mm}$$

Ex. 4-5

(a) Express the following temperatures in degrees Kelvin:

Boiling point of water: 100°C
Freezing point of mercury: −38.9°C
Boiling point of liquid nitrogen: −196°C

(b) Express the following temperatures in degrees Centigrade:

Melting point of lead: 600°K
A normal room temperature: 298°K
Boiling point of liquid helium: 4°K

Answer

(a)	b.p.	H_2O	373°K
	f.p.	Hg	234°K
	b.p.	N_2	77°K
(b)	m.p.	Pb	327°C
	room temp.		25°C
	b.p.	He	−269°C

Ex. 4-6. In Expt. 9, a student obtained the result that 2.00×10^{-3} mole of magnesium produced a volume of hydrogen that would occupy 49.0 ml at 25°C and one atmosphere pressure.

(a) If one mole of magnesium produces one mole of hydrogen, use these data to calculate the volume of one mole of hydrogen at 25°C (298°K) and one atmosphere.

(b) Calculate the volume one mole of hydrogen would occupy at 0°C (273°K) and one atmosphere.

Answer

(a) Since one mole of magnesium produces one mole of hydrogen, 2.00×10^{-3} mole of magnesium produces 2.00×10^{-3} mole of hydrogen. If 2.00×10^{-3} mole of hydrogen occupies 49.0 ml, then 1.00 mole occupies

$$\frac{49.0 \text{ ml}}{2.00 \times 10^{-3} \text{ mole}} = 24.5 \times 10^3 \text{ ml/mole}$$
$$= 24.5 \text{ liters at } 25°\text{C}$$

(b) At a lower temperature, the volume would be smaller:

$$\text{Volume at } 0°\text{C} = (\tfrac{273}{298}) \times 24.5$$
$$= 22.4 \text{ liters/mole.}$$

Pr. 1. How many molecules are there in a molar volume of a gas at 100°C? At 0°C?

Answer

There are 6.02×10^{23} molecules (Avogadro's number). A "molar volume" means "the volume occupied by one mole." Hence, a molar volume at any conditions contains 6.02×10^{23} molecules.

Pr. 2. What is the molar volume of water under each of the following conditions?

(a) Solid, 0°C;

density of ice = 0.915 g/ml

(b) Liquid, 0°C;

density of water (liquid, 0°C) = 1.000 g/ml

(c) Gas, 100°C;

density of water vapor (100°C, 1 atm) $= 5.88 \times 10^{-4}$ g/ml

Answer

(a) Molar volume of ice, 0°C;

$$\frac{18.0 \text{ g/mole}}{0.915 \text{ g/ml}} = 19.7 \text{ ml/mole}$$

(b) Molar volume of liquid water, 0°C;

$$\frac{18.0 \text{ g/mole}}{1.000 \text{ g/ml}} = 18.0 \text{ ml/mole}$$

(c) Molar volume of water vapor, 100°C;

$$\frac{18.0 \text{ g/mole}}{5.88 \times 10^{-4} \text{ g/ml}} = 3.06 \times 10^4 \text{ ml/mole}$$

Pr. 3. What is the molecular weight of a gas if at 0°C and one atmosphere pressure, 1.00 liter of the gas weighs 2.00 grams?

Answer: 44.8 g/mole.

Answer

At 0°C and one atm, one mole of gas occupies 22.4 liters.

Hence,

$$2.00 \frac{\text{g}}{\text{liters}} \times 22.4 \frac{\text{liters}}{\text{mole}} = 44.8 \frac{\text{g}}{\text{mole}}$$

Pr. 4. The gas sulfur dioxide combines with oxygen to form the gas sulfur trioxide.

$$2SO_2(gas) + O_2(gas) \longrightarrow 2SO_3(gas)$$

What ratio would you expect for the following?

(a) $\dfrac{\text{number of } SO_3 \text{ molecules produced}}{\text{number of } O_2 \text{ molecules consumed}}$

(b) $\dfrac{\text{volume of } SO_3 \text{ gas produced}}{\text{volume of } O_2 \text{ gas consumed}}$

Answer

(a) Two. The balanced equation shows that two molecules of SO_3 are produced per molecule of oxygen consumed.

(b) Two. Since equal volumes contain equal numbers of molecules, two volumes of SO_3 will be produced for every volume of oxygen consumed.

Pr. 5. A glass bulb weighs 108.11 grams after all of the gas has been removed from it. When filled with oxygen gas at atmospheric pressure and room temperature, the bulb weighs 109.56 grams. When filled at atmospheric pressure and room temperature with a gas sample obtained from the mouth of a volcano, the bulb weighs 111.01 g. Which of the following molecular formulas for the volcano gas could account for the data?

CO_2
OCS
Si_2H_6
SO_2

NF_3
SO_3
S_3
A gas mixture, half CO_2, half Kr

Answer

The two weighed gas samples contain the same number of molecules (by Avogadro's Hypothesis). Hence, the weights are in the ratio of the molecular weights.

Wt oxygen sample = 109.56 − 108.11 = 1.45 g

Wt volcano gas sample
= 111.01 − 108.11 = 2.90 g

$$\text{mol wt volcano gas} = \frac{2.90}{1.45} \times 32.00 = 64.0 \text{ g/mole}$$

(Notice that there is no need for an air buoyancy correction because the same buoyancy effect is obtained in each weighing, and they cancel out in the subtraction.) The molecular weights of the various possibilities are as follows.

CO_2	44.0	SO_3	80.1
OCS	60.1	S_8	256.0
Si_2H_6	62.2	$CO_2 + Kr$	$\frac{44.0 + 83.8}{2} = 63.9$
SO_2	64.1		
NF_3	71.0		

Thus either SO_2 or the CO_2-Kr mixture could account for the data.

Although it was not requested, notice that the experimental uncertainty in the weighings introduces about 2% uncertainty in the molecular weight determination. Thus the 62.2 g/mole molecular weight of Si_2H_6 is just outside the range defined by the uncertainty.

Pr. 6. Compressed oxygen gas is sold at a pressure of 130 atm in steel cylinders of 40 liters volume.

(a) How many moles of oxygen does such a filled cylinder contain?
(b) How many kilograms of oxygen are in the cylinder?

Answer: 6.7 kg.

Answer

A volume of 40 liters at 130 atmospheres would expand by a factor of 130/1 if the pressure were reduced to one atmosphere. Therefore the cylinder contains enough oxygen to occupy

$$\frac{130}{1} \times 40 = 5.2 \times 10^3 \text{ liters}$$

at one atmosphere.

(a) Since one mole occupies 24.5 liters at room temperatures and one atmosphere, the cylinder contains

$$\frac{5.2 \times 10^3 \text{ liters}}{24.5 \text{ liters/mole}} = 2.1 \times 10^2 \text{ moles}$$

(b) Wt of oxygen = $(2.1 \times 10^2 \text{ moles}) \times (32.0 \text{ g/mole}) = 6.7 \times 10^3$ g or 7 kg.

Pr. 7. A carbon dioxide fire extinguisher of 3 liters volume contains about 10 pounds (4.4 kg) of CO_2. What volume of gas could this extinguisher deliver at room conditions?

Answer

$$4.4 \text{ kg} = 4.4 \times 10^3 \text{ g} = \frac{4.4 \times 10^3 \text{ g}}{44 \text{ g/mole}}$$
$$= 1.0 \times 10^2 \text{ moles}$$

One mole occupies 24.5 liters at room conditions. Hence 1.0×10^2 moles occupy $(1.0 \times 10^2) \times (24.5)$ liters = about 2500 liters

(Notice that the 3 liter volume does not enter the calculation. It does, however, show that the extinguisher contains a condensed phase, liquid CO_2, giving the 1000-fold volume change on vaporization.)

Pr. 8. Hydrogen for weather balloons is often supplied by the reaction between solid calcium hydride, CaH_2, and water to form solid calcium hydroxide, $Ca(OH)_2$, and hydrogen gas, H_2.

(a) Balance the equation for the reaction and decide how many moles of CaH_2 would be required to fill a weather balloon with 250 liters of hydrogen gas at normal conditions.
(b) What weight of water would be consumed in forming the hydrogen?

Answer: 0.18 kg.

Answer

(a) $CaH_2(\textit{solid}) + 2H_2O(\textit{liquid}) \longrightarrow Ca(OH)_2(\textit{solid}) + 2H_2(\textit{gas})$

$$\frac{250 \text{ liters}}{24.5 \text{ liters/mole}} \text{ or about 10 moles } H_2 \text{ gas}$$

are needed.

By the balanced equation, it takes 5.0 moles of CaH_2 to produce 10 moles of H_2.

(b) By the equation, it takes ten moles of water to produce ten moles of H_2.

Ten moles of H_2O weigh

$$(10 \text{ moles}) \times \left(\frac{18 \text{ g}}{\text{mole}}\right) = 180 \text{ g, or } 0.18 \text{ kg}$$

Pr. 9. Gas is slowly added to the empty chamber of a closed-end manometer (see Figure 4-2B). Draw a picture of the manometer mercury levels, showing in millimeters the difference in heights of the two mercury levels:

(a) before any gas has been added to the empty gas chamber;
(b) when the gas pressure in the chamber is 300 mm;
(c) when the gas pressure in the chamber is 760 mm;
(d) when the gas pressure in the chamber is 865 mm.

Answer

The student should draw a picture like that in Figure 4-2B showing

(a) the two mercury levels at the same height;

(b), (c), (d) the mercury level on the left below the mercury level on the right by 300, 760, and 865 mm.

Pr. 10. Repeat Problem 9 but with an open-end manometer (see Figure 4-2C). Atmospheric pressure is 760 mm.

Answer

The student should draw a picture like that in Figure 4-2C showing

(a) the left mercury level 760 mm above the right (open-end) mercury level;
(b) the left mercury level 460 mm above the right mercury level;
(c) the two mercury levels at the same height;
(d) the left mercury level 105 mm below the right mercury level.

Pr. 11. The balloons that are used for weather study are quite large. When they are released at the surface of the earth they contain a relatively small volume of gas compared to the volume they acquire when aloft. Explain.

Answer

As the balloon rises, the pressure decreases. Since $PV =$ constant, then as pressure decreases, the volume must increase. In fact, if such a weather balloon were fully inflated at the surface of the earth, it would burst as the balloon rose, and the surrounding pressure would decrease. (Notice that the temperature drops as altitude increases. This tends to *reduce* the volume as the balloon rises. The percentage change in temperature is, however, relatively small when expressed in degrees Kelvin. In contrast, the pressure drops drastically at the highest altitudes reached by these balloons. The expansion due to the pressure change is by far the larger effect.)

Pr. 12. A 1.50 liter sample of dry air in a cylinder exerts a pressure of 3.00 atm at a temperature of 25°C. Without change in temperature, a piston is moved in the cylinder until the pressure in the cylinder is reduced to 1.00 atm. What is the volume of the gas in the cylinder now?

Answer

The amount of gas is constant, and the temperature is constant; hence the behavior is consistent with the regularity

$$PV = \text{constant}$$

Decreasing the pressure by a factor of three (3.00 atm/1.00 atm) increases the volume by the same factor.

$$\text{Final volume} = \left(\frac{3.00}{1.00}\right) \times 1.50 \text{ liters} = 4.50 \text{ liters}$$

Pr. 13. Suppose the total pressure in an automobile tire is 30 pounds/in.^{2} and we want to increase the pressure to 40 pounds/in.^{2} What change in the amount of air in the tire must take place? Assume that the temperature and volume of the tire remain constant.

Answer

The pressure is increased by the factor 40/30. Since volume and temperature are constant, the number of moles of gas in the tire must be increased by the same factor.

Pr. 14. The density of liquid carbon dioxide at room temperature is 0.80 gram/ml. How large a cartridge of liquid CO_2 must be provided to inflate a life jacket of 4.0 liters capacity at STP?

Answer

4.0 liters at STP contain

$$4.0 \text{ liters}/22.4 \text{ liters mole} = 0.18 \text{ mole}$$

$$0.18 \text{ mole } CO_2 = (0.18 \text{ mole}) \times (44 \text{ g/mole}) = 7.9 \text{ g}$$

$$\text{Volume } CO_2 = \frac{7.9 \text{ g}}{0.80 \text{ g/ml}} = 10 \text{ ml}$$

Pr. 15. A student collects a volume of hydrogen over water. He determines that there is 2.00×10^{-3} mole of hydrogen and 6.0×10^{-6} mole of water vapor present. If the total pressure inside the collecting tube is 760 mm, what is the partial pressure of each gas?

Answer: Partial pressure H_2 = 738 mm.
Partial pressure H_2O = 22 mm.

Answer

$$\begin{aligned} \text{Moles } H_2 &= 0.00200 \\ \text{Moles } H_2O &= \underline{0.000060} \\ \text{Total moles} &= 0.00206 \end{aligned}$$

Partial pressure

= fraction of total moles × total pressure

Partial pressure of H_2

$$= \frac{0.00200}{0.00206} \times 760 \text{ mm} = 738 \text{ mm}$$

Partial pressure of H_2O

$$= \frac{0.000060}{0.00206} \times 760 \text{ mm} = 22 \text{ mm}$$

Pr. 16. A sample of nitrogen is collected over water at 18.5°C. The vapor pressure of water at 18.5°C is 16 mm. When the pressure on the sample has been equalized against atmospheric pressure, 756 mm, what is the partial pressure of nitrogen? What will be the partial pressure of nitrogen if the volume is reduced by a factor 740/760?

Answer

The partial pressure of water is the vapor pressure, 16 mm. The remainder of the pressure (756 − 16 = 740 mm) is the partial pressure of nitrogen.

A reduction of the volume by the factor 740/760 will raise the partial pressure of nitrogen by the factor 760/740.

Final partial pressure of N_2

$$= (740 \text{ mm}) \times \left(\tfrac{760}{740}\right) = 760 \text{ mm}$$

Pr. 17. A candle is burned under a beaker until it extinguishes itself. A sample of the gaseous mixture in the beaker contains 6.08×10^{20} molecules of nitrogen, 0.76×10^{20} molecules of oxygen, and 0.50×10^{20} molecules of carbon dioxide. The total pressure is 764 mm. What is the partial pressure of each gas?

Answer

Each gas exerts a pressure in proportion to the number of its molecules.

$$\begin{array}{rl} & 6.08 \times 10^{20} \text{ molecules } N_2 \\ & 0.76 \times 10^{20} \text{ molecules } O_2 \\ & \underline{0.50 \times 10^{20} \text{ molecules } CO_2} \\ \text{Total:} & 7.34 \times 10^{20} \text{ molecules} \end{array}$$

$$\text{Fraction of } N_2 \text{ molecules} = \frac{6.08 \times 10^{20}}{7.34 \times 10^{20}} = 0.828$$

$$\text{Partial pressure of } N_2 = (0.828) \times (764) = 633 \text{ mm}$$

$$\text{Fraction of } O_2 \text{ molecules} = \frac{0.76 \times 10^{20}}{7.34 \times 10^{20}} = 0.104$$

$$\text{Partial pressure of } O_2 = (0.104) \times (764) = 79 \text{ mm}$$

$$\text{Fraction of } CO_2 \text{ molecules} = \frac{0.50 \times 10^{20}}{7.34 \times 10^{20}} = 0.068$$

$$\text{Partial pressure of } CO_2 = (0.068) \times (764) = 52 \text{ mm}$$

Pr. 18. A cylinder contains nitrogen gas and a small amount of liquid water at a temperature of 25°C (the vapor pressure of water at 25°C is 23.8 mm). The total pressure is 600.0 mm Hg. A piston is pushed into the cylinder until the volume is halved. What is the final pressure?

Answer: 1176 mm.

Answer

Initially the total pressure is 600.0 mm. The partial pressure of water is 23.8 mm. Hence the partial pressure of nitrogen is

$$600.0 - 23.8 = 576.2 \text{ mm}$$

When the volume is halved, the nitrogen partial pressure is doubled (PV = a constant) to give 1152.4 mm. The partial pressure of water, however, remains equal to the vapor pressure, 23.8 mm. Hence the observed pressure is

$$\begin{array}{rl} 1152.4 \text{ mm} = & \text{partial pressure } N_2 \\ \underline{23.8 \text{ mm} =} & \underline{\text{partial pressure } H_2O} \\ 1176.2 \text{ mm} = & \text{total pressure} \end{array}$$

Pr. 19. Consider two closed glass containers of the same volume. One is filled with hydrogen gas, the other with carbon dioxide gas, both at room temperature and pressure.

(a) How do the number of moles of the two gases compare?
(b) How do the number of molecules of the two gases compare?
(c) How do the number of grams of the two gases compare?
(d) If the temperature of the hydrogen container is now raised, how do the two gases now compare in:
  (i) pressure,
  (ii) volume,
  (iii) number of moles,
  (iv) average molecular kinetic energy.

Answer

(a) Equal (by Avogadro's Hypothesis).
(b) Equal (by Avogadro's Hypothesis).
(c) The weights are in the ratio of the molecular weights. CO_2 is heavier by the factor 44.0/2.02 = 21.8.
(d) (i) The bulb has higher pressure.
  (ii) The volumes remain the same.
  (iii) The number of moles remains equal because the bulbs are closed.
  (iv) The average kinetic energy of the hydrogen molecules will be higher because the temperature is higher.

Pr. 20. The boiling points and freezing points in degrees centigrade of certain liquids are listed below. Express these temperatures on the absolute temperature (degrees Kelvin) scale.

Liquid helium, boiling point = −269
Liquid hydrogen, freezing point = −259
Answer: 14°K
Liquid hydrogen, boiling point = −253
Answer: 20°K
Liquid nitrogen, freezing point = −210
Liquid nitrogen, boiling point = −196
Liquid oxygen, freezing point = −219
Liquid oxygen, boiling point = −183

Answer

Liquid helium b.p. = 4°K
Liquid hydrogen f.p. = 14°K
Liquid hydrogen b.p. = 20°K
Liquid nitrogen f.p. = 63°K
Liquid nitrogen b.p. = 77°K
Liquid oxygen f.p. = 54°K
Liquid oxygen b.p. = 90°K

Pr. 21. If exactly 100 ml of a gas at 10°C are heated to 20°C (pressure and number of molecules remaining constant), the resulting volume of the gas will be which of the following?

(a) 50 ml,
(b) 1000 ml,
(c) 100 ml,
(d) 375 ml,
(e) 103 ml.

Answer

(e) Approximately 103 ml. Change °C to °K by adding 273°; then since the temperature is increasing, the volume will increase to 293/283 of the original:

$$100 \text{ ml} \times \frac{293}{283} = 103 \text{ ml}$$

Pr. 22. Why is it desirable to express all temperatures in degrees Kelvin when working with problems dealing with gas relationships?

Answer

Either °C or °K can be used in determining volume (or pressure) changes caused by changing temperature. However, using the Kelvin scale is much simpler, for volume varies directly with it.

Pr. 23. A gaseous reaction between methane, CH_4, and oxygen, O_2, is carried out in a sealed container. Under the conditions used, the products are hydrogen, H_2, and carbon dioxide, CO_2. Energy is released, so the temperature rises during the reaction.

(a) Will the final pressure be greater or lower than the original pressure?
(b) By what factor does the pressure change if one mole of methane and one mole of oxygen are mixed and reacted (with the temperature changing from 25°C to 200°C).

Answer: 2.38.

Answer

The balanced equation is

$$CH_4(\mathit{gas}) + O_2(\mathit{gas}) \longrightarrow 2H_2(\mathit{gas}) + CO_2(\mathit{gas}) + \text{energy}$$

(a) Two moles of reactants give three moles of products, resulting in a pressure rise. The temperature rise also causes a pressure rise. Since the effects reinforce, the final pressure must be greater than the initial pressure.

(b) The pressure increases by a factor of 1.5 due to the change in the number of moles. There is an additional pressure change due to the increase in temperature, which rises by a factor 473/298 = 1.59.
The pressure rises by the factor (1.50) × (1.59) = 2.38.

Pr. 24. Automobiles are propelled by burning gasoline, typical formula C_8H_{18}, inside a container (the cylinder) that can change volume and drive the wheels. Oxygen reacts with the gasoline to form carbon dioxide and water, releasing enough energy to heat the gas from about 300°K to about 1500°K.

Balance the equation for the reaction and decide whether the work done by the gas in the cylinder is mainly due to pressure rise caused by change in number of moles of gas or due to pressure rise resulting from heating.

Answer

$$C_8H_{18}(\mathit{gas}) + 12\tfrac{1}{2}O_2(\mathit{gas}) \longrightarrow 8CO_2(\mathit{gas}) + 9H_2O(\mathit{gas})$$

Thus $13\frac{1}{2}$ moles of reactants give 17 moles of products, contributing a pressure rise of 17.0/13.5 = 1.26.

The temperature rise gives a pressure change of 1500/300 = 5.

Most of the pressure rise is caused by the increased temperature.

Pr. 25. Why does the pressure build up in a tire on a hot day? Answer in terms of the kinetic theory.

Answer

As the temperature of the air molecules rises, the kinetic energy increases. Since the volume of a tire remains almost constant, the increased velocity of the air molecules results in more collisions per unit time with the tire walls, and the force exerted per collision is greater. Thus the pressure rises.

Pr. 26. A vessel contains equal numbers of oxygen and of hydrogen molecules. The pressure is 760 mm Hg when the volume is 50 liters. Which of the following statements is FALSE?

(a) On the average, the hydrogen molecules are traveling faster than the oxygen molecules.
(b) On the average, more hydrogen molecules strike the walls per second than oxygen molecules.
(c) If the oxygen were removed from the system, the pressure would drop to 190 mm Hg.
(d) Equal numbers of moles of each gas are present.
(e) The average kinetic energies of oxygen and hydrogen are the same.

Answer

Part (c) is false. The pressure would drop to 380 mm Hg.

Pr. 27. The vapor pressure of a molten metal can be measured with a device called a Knudsen cell. This is a container closed across the top by a thin foil pierced by a small measured hole. The cell is heated in a vacuum, until the vapor above the melt streams from the small hole (it *effuses*). The weight of the material escaping per second tells the rate at which gaseous atoms leave.

Two identical Knudsen cells are heated at 1000°C, one containing lead and the other containing magnesium.

(a) Contrast the average kinetic energies of the lead and magnesium atoms within each cell.
(b) Contrast the average velocities of the lead and magnesium atoms leaving each cell.
(c) At this fixed temperature, the rate at which atoms leave is determined by two factors, the vapor pressure and the mass of the gaseous particles. Explain.

Answer

(a) Since the two gases are at the same temperature, they have the same average kinetic energy.
(b) Since the two gases have the same kinetic energy, the magnesium atoms, having much lower mass, must have much higher velocities.
(c) The number of atoms leaving per second is determined by the number of "collisions" per second of gaseous atoms with the hole. The vapor pressure indicates the number of molecules per unit volume, and the higher the vapor pressure, the more molecules that strike the surface per second. In addition, the higher the molecular mass, the slower the particles are moving at a given temperature. Hence both vapor pressure and molecular mass are important in fixing the number of atoms leaving the cell per second.

(*Note:* The vapor pressure of lead at 1000°C is about 1.2 mm, and that of magnesium at 1000°C is about 210 mm.)

Pr. 28. The following table indicates the boiling points and the molar volumes (0°C and 1 atm) of some common gases:

Gas	Formula	Boiling Point (°C)	Molar Volume (liters)
Helium	He	−269	22.426
Nitrogen	N_2	−196	22.402
Carbon Monoxide	CO	−190	22.402
Oxygen	O_2	−183	22.393
Methane	CH_4	−161	22.360
Hydrogen Chloride	HCl	−84.0	22.248
Ammonia	NH_3	−33.3	22.094
Chlorine	Cl_2	−34.6	22.063
Sulfur Dioxide	SO_2	−10.0	21.888

(a) What regularity is suggested in the relationship between the boiling points and molar volumes?
(b) Account for this regularity.

Answer

(a) The lower-boiling-point substances show less deviation from "ideality." Their molar volumes are more nearly equal to the 22.414 liter molar volume predicted for ideal gases at STP. The departure from ideality increases for gases having boiling points closer to the specified temperature, 0°C.

(b) In gases having higher boiling points, the forces of attraction between the molecules are greater, and hence they depart more from ideality. If these gases were heated (or if the pressure were reduced), the molecules could move farther apart, and the molar volume would approach 22.414 liters.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

In an experiment similar to Expt. 6, an empty (evacuated) container was weighed, then filled with oxygen, and weighed again. The container was again evacuated and weighed when filled with an unknown gas. Both gases were weighed at the same temperature and pressure. The following data were obtained:

Container empty	150.10 g
Container + oxygen gas	151.41 g
Container + unknown gas	151.82 g

1. Using Avogadro's Hypothesis calculate the molecular weight of the unknown gas. Show your calculations.

   Answer

   $$\text{Mol wt} = \frac{\text{wt unknown gas}}{\text{wt equal vol } O_2} \times 32.0 \text{ g/mole}$$

   $$\text{Mol wt} = \frac{1.72 \text{ g}}{1.31 \text{ g}} \times 32.0 \text{ g/mole}$$

   $$= 42.0 \text{ g/mole}$$

2. It is determined experimentally that the unknown gas contains carbon and hydrogen atoms in the ratio of 1/2. What is the simplest formula?

   Answer: CH_2.

3. Using the molecular weight obtained in question 1, and the simplest formula from question 2, determine the correct molecular formula for the unknown gas.

   Answer: C_3H_6.

4. A flask of nitrogen is collected over water at a total pressure of 740 mm of mercury. If the partial pressure of the water vapor is 15 mm of mercury, what is the pressure exerted by the nitrogen?

   Answer

   $$P_{N_2} + P_{H_2O} = P_{\text{total}}$$

   $$P_{N_2} = 740 \text{ mm} - 15 \text{ mm} = 725 \text{ mm Hg}$$

5. A particular gas sample is 1% oxygen molecules. How many oxygen molecules are there in one liter of the gas sample at STP?

   Answer

   $$(6.02 \times 10^{23}) \times \left(\frac{1}{22.4}\right)\left(\frac{1}{100}\right)$$

   $$= 2.68 \times 10^{20} \; O_2 \text{ molecules/liter}$$

Questions 6–9 refer to the following data.

A flask is filled with a mixture of two gases, oxygen (O_2) and sulfur dioxide (SO_2). Initially, the pressure in the container is 1500 mm, and the temperature is 20°C. One gram of each gas is present. No chemical reaction occurs between the two gases under these conditions.

6. What is the partial pressure exerted by each of the gases?

   Answer

   $$\frac{1 \text{ g}}{32 \text{ g/mole}} = \frac{1}{32} \text{ mole oxygen}$$

   $$\frac{1 \text{ g}}{64 \text{ g/mole}} = \frac{1}{64} \text{ mole sulfur dioxide}$$

   Since there are twice as many moles of oxygen as there are of sulfur dioxide, the partial pressure of oxygen, p_{O_2}, is twice the partial pressure of sulfur dioxide, p_{SO_2}.

   $$p_{SO_2} + p_{O_2} = 1500$$
   $$p_{O_2} = 2p_{SO_2}$$
   $$p_{SO_2} + 2p_{SO_2} = 1500$$
   $$p_{SO_2} = 500 \text{ mm}$$

   and

   $$p_{O_2} = 1000 \text{ mm}$$

7. If atmospheric pressure is 750 mm, and if the stopcock is opened to equalize the pressure inside and outside the container and then closed again, how many moles of each gas will remain in the container? (Assume that the temperature remains constant at 20°C.)

   Answer

   $$\frac{1}{32} \text{ mole} \times \frac{750 \text{ mm}}{1500 \text{ mm}} = \frac{1}{64} \text{ mole}$$

   $$\frac{1}{64} \text{ mole} \times \frac{750 \text{ mm}}{1500 \text{ mm}} = \frac{1}{128} \text{ mole}$$

8. To what temperature would the gases have to be changed to return the pressure to its original value of 1500 mm?

   Answer

   To double the pressure the absolute temperature must be doubled, the volume and amount remaining constant.

   $$20°C = 293°K$$
   $$2 \times 293°K = 586°K = 313°C$$

9. How does the average kinetic energy of the oxygen molecules compare to the avage kinetic energy of the sulfur dioxide molecules at 20°C?

   Answer: They are the same.

10. The molar volume of a gas is affected by pressure and is quite low at high pressure. The density of CO_2 gas at 210°C and 30 atm is 0.0834 g/ml.

    (a) What is the molar volume at these conditions?

    (b) How many molecules does this volume contain?

    Answer

    (a) $\frac{44}{0.0834} = 528$ ml/mole

    or 0.53 liters/mole

    (b) 6.02×10^{23}

Questions 11–13 refer to the following description.

Consider the following system as a scientific model describing a container filled with a gas. Some small spheres are added to an evacuated cylinder. Imagine the spheres to be in continuous random motion. They are also perfectly elastic—they rebound after colliding with each other or with the walls of the container without losing energy.

11. In order for our model to be analogous to a gaseous system, what must happen to the spheres in our model if the temperature is increased?

    Answer: They move faster.

12. What would happen to the piston if the temperature were increased?

    Answer: The piston would move up.

13. What would happen to the pressure if the piston were fixed in place and the temperature raised?

    Answer: The pressure would rise.

14. A welder has a cylinder of helium used in arc welding. The cylinder volume is 32 liters and the gas pressure is 110 atm at 25°C. The cylinder will burst if the pressure reaches 200 atmospheres. Which of the following is FALSE?

    (1) The cylinder contains 144 moles of He.

    (2) The He could fill a 3500 liter balloon at 25°C.

    (3) The welder can safely heat the cylinder to 325°C.

    (4) The pressure in mm Hg is 8.4×10^4.

    (5) Half again as much helium could be safely added to the cylinder.

    Answer

    325°C ≅ 600°K. At this temperature the pressure would be 220 atmospheres.

CHAPTER

5

LIQUIDS AND SOLIDS: CONDENSED PHASES OF MATTER

Intent and Approach

Structural information and molecular models are used to introduce four major topics: liquid-vapor equilibrium, properties of solutions, the electrical nature of matter, and kinds of solids. Chapter 5 is a logical extension of Chapter 4, but applies the kinetic theory to molecular motions and interactions in solids and liquids.

Keep in mind that Chapter 5 is part of the introduction and is intended only as a brief introduction to the structure of solids and liquids. For this reason, several topics first mentioned here are developed in more detail later. For example, Chapter 17 considers the properties of some solids and liquids in terms of the more detailed concepts of the chemical bond, and Chapter 10 discusses the chemical behavior of solutions. Don't anticipate the work of later chapters and go into too much detail in Chapter 5. You may get the student hopelessly involved with the above concepts at this point.

On the other hand, the topics of phase equilibrium and the properties of solutions are not considered elsewhere in the course. Explanations needed for these two topics arise from the kinetic theory, and can be developed fairly well now. The background section extends the Textbook discussion of liquids, solutions, and phase equilibria. You will not have time to present any appreciable amount of this detail to the student, but you may find review of this material helpful.

This chapter also contains the main discussion of the electrical nature of matter. At this point in the course your aim is to give a brief description of ionic solutions and of the different kinds of solids, particularly ionic. The electrical concepts will be used more extensively in Chapters 14–17 to support the theories of bonding and atomic structure.

We also find that it is convenient to introduce and use a number of new terms. Remember, however, that you should emphasize the *new concepts*, not the new terms. New words are used to simplify our presentation; don't lose the student in a maze of terminology.

Outline

1. A liquid may exist in dynamic equilibrium with its vapor (5-1.1, 5-1.2). The boiling point is studied.
2. Solid-liquid phase changes are discussed (5-1.3).
3. Properties of solutions may be applied in testing the purity of materials and in the purification of substances (5-2.1).
4. Gaseous, solid, and liquid solutions are considered (5-2.2–5-2.4).

5. Molar concentration is used for a quantitative description of solution concentration (5-2.5). Solubility is introduced (5-2.6).
6. The great differences in solutions are described (5-2.7) and used to introduce the electrical nature of matter.
7. Common electrical phenomena are recalled (5-3.1), then a more objective way of detecting charge is shown (5-3.2) and is used to measure the effect of distance (5-3.3).
8. These results allow the introduction of the electron-proton model of atomic structure (5-3.4).
9. The fundamental nature of electric force is discussed (5-3.5).
10. Ions can now be used to explain the conductivity of solutions (5-4.1), which can then be used to classify solids.
11. Precipitation reactions (5-4.2) are discussed.
12. The electrical conductivity of solids (5-4.3) is discussed, and ionic solids are then treated (5-4.4).

New Concepts

1. The liquid-vapor equilibrium in molecular terms; molar heat of vaporization.
2. The vapor pressure of liquids, the factors affecting it, and the relation between vapor pressure and boiling point.
3. Molar concentration.
4. The nature of solutions.
5. The electrical properties of matter.

Development

PURE SUBSTANCES (5-1)

Liquid-gas Phase Changes (5-1.1)

The change between the liquid phase and the gas phase brings up three points: (1) What determines the vapor pressure at a given temperature?; (2) Why is heat absorbed as a liquid evaporates *at constant temperature*?; and (3) What is the mechanism by which a particular particle goes from the liquid to the gas phase? These questions are related to some extent, but they are often incorrectly mingled in explaining vapor pressure and boiling. The *Background Discussion* contains a fuller discussion (p. 167) the gist of which is as follows:

(1) The value of vapor pressure is determined by a balance in the competition between energy and randomness. The energy change is easy to observe as heat is added; the randomness is shown by the sample becoming "more like a gas"—that is, less regular. This factor is not easy to observe and is usually omitted in beginning courses.

(2) Heat is absorbed to provide the increase in the potential energy of the gas particles over that of the particles in the liquid.

(3) Vaporization occurs when molecules having higher kinetic energy overcome the liquefying attractive forces. If evaporation takes place at constant temperature, there is no difference in the average kinetic energy of gas and of liquid—there is only a potential energy change as in (2). Don't use a *nonequilibrium* example, such as the evaporation of water from the hand. This particular example could be confusing, because the liquid will cool as it evaporates from the hand, especially if evaporation is rapid, and an incorrect implication may be drawn. A kinetic energy change (from

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
S 5-1/5-1.3 (pp. 65–69)	1	Review test; discussion Demonstration 2 Vapor pressure	1–5	1, 4, 7	2, 3, 5 8–11	6, 12	Pure Substances, Phase Changes
S 5-2/5-2.5 (pp. 70–72)	2	Discussion		13, 14, 16	15, **17**,* 18	19	Solutions, Concentration
Prepare for Expt. 10	3	Expt. 10, Part I					Precipitation Reactions
S 5-2.6/5-3.5 (pp. 72–78)	4	Expt. 10, Part II Film, ELECTRIC INTERACTIONS IN CHEMISTRY	6–8	20–22	23, 25	24	Electrical Nature of Matter
Write up Expt. 10	5	Discuss Expt. 10					
S 5-4/5-4.2 (pp. 78–80)	6	Discuss Demonstration 3 Electrical Conductivity	9	**26**	**27**, **29–31**	28, **32**	Ions and Their Reactions
Read Expt. 11	7	Expt. 11					Ionic Reactions
Write up Expt. 11	8	Discuss Expt. 11					
S 5-4.3/5-4.4 (pp. 80–82)	9	Discussion plus problems					Ionic Solids
	10	Review, Quiz					

*Boldface indicates problems whose answers are given in the Textbook.

> liquid to gas) does take place in the example cited, *but* this is not the proper point to be made, since it does not occur if an equilibrium system is used. The best course is to use the equilibrium example of a liquid boiling at a constant temperature.

The model also leads naturally to the conclusion that the amount of energy involved is proportional to the number of molecules separated in vaporization or fusion, hence we specify *molar heat of vaporization* and *molar heat of fusion.* (Recall that the student measured the heat of solidification of wax in Expt. 5.) You may use the model to help the student rationalize the fact that the heat of vaporization, which involves large molecular separations, is greater than the heat of fusion, which involves small molecular displacements.

Liquid-gas Equilibrium: Vapor Pressure (5-1.2)

The picture of an evaporating liquid developed in Sec. 5-1.1 is related to equilibrium where no measurable changes are visible. This important concept, equilibrium, will be developed in Chapter 9 and used frequently thereafter. At this point emphasize the apparent unchanging aspect of observed properties at equilibrium.

Demo. 2, VAPOR PRESSURE OF A LIQUID AT TWO TEMPERATURES, fits here. See p. 155 for guide.

The picture of vapor pressure leads to our definition of the boiling point in terms of vapor pressure and to the partial pressure of water vapor in a gas. (See also p. 170.)

Solid-liquid Phase Changes (5-1.3)

Use the approach outlined in 5-1.1.

SOLUTIONS (5-2)

Differentiating Between Pure Substances and Solutions (5-2.1)

Display samples of granite and of crystalline quartz or some other mineral. (Both can be found in nature or obtained from a mineral shop or scientific supply house.) Also display salt crystals, water, glycerine, salt water, and a mixture of salt and sand. Use these samples to point out the meaning of *heterogeneous* and *homogeneous*, *phase*, *system*, and *pure substance.* The experimental criteria for differentiating between a pure substance and a solution can be discussed best by illustration. Obtain data similar to that shown in Figure 5-4 (Textbook) for pure water and also for a solution of salt in water or glycerine in water. If samples of pure water and of a glycerine solution are placed in the freezing compartment of a refrigerator overnight, you can also demonstrate purification by crystallization, since the ice crystals coming out will be pure water coated with the glycerine solution. Distillation can be easily demonstrated.

You can raise an interesting philosophical question with your class relative to the question of purity. When is water pure? How do we tell? Is the same water pure if we use a more sensitive test for impurities? What is meant in advertisements listing a product as 99% pure? Pure what? By what test? Is it important to be so pure? Refer again to Sec. 1-2.1 of the text.

Gaseous, Solid, and Liquid Solutions (5-2.2, 5-2.3, 5-2.4)

The following examples may be helpful.

(a) *Gaseous solutions:* any mixture of gases, such as air (with or without water vapor), automobile exhaust, oxygen-acetylene used in welding torches, oxygen-helium for divers.

(b) *Solid solutions:* coin silver, sterling silver, commercial aluminum contains the element gallium in solid solution, silver and gold form a solid solution in all proportions from 100% silver to 100% gold.

(c) *Liquid solutions:* many examples, such as carbonated drinks (gas in liquid); gasoline, whiskey, antifreeze in water (liquid in liquid); sugar or salt in water (solid in liquid).

Expressing the Composition of Solutions (5-2.5)

There are several ways to express the concentration of a solution. For this course a single method is used. It is simple and is connected to the mole method of solving quantitative problems. For this reason, express all concentrations in molarity. Develop terminology as a matter of utility, not as an end in itself.

Expt. 10, AN INVESTIGATION OF THE REACTING VOLUMES OF TWO SOLUTIONS OF KNOWN CONCENTRATION,
fits here. See p. 159 for guide.

Solubility (5-2.6)

The purpose of this section is to develop a quantitative feeling about solubility. Make sure the idea of saturation is clear. The student will need this immediately for laboratory work dealing with precipitates, and will need it later for the study of equilibrium and solubility product. Chapter 10 will enlarge on this topic through the use of equilibrium concepts, but the groundwork starts here.

Notice that we have avoided using the word "insoluble." This word is too absolute and defeats one concept we wish emphasized in Chapter 9 and thereafter—that every reaction in a closed system establishes an equilibrium. Thus every substance "dissolves" to some extent. Many things, of course, do not dissolve to any appreciable extent, but the phrase "negligible solubility" indicates we have neglected something, however small.

Variations Among the Properties of Solutions (5-2.7)

This section begins the presentation of the electrical nature of matter by establishing conductivity as a property of solutions. The first point is that solubility varies in a given solvent and for different solids in the same liquid. Then conductivity is brought in as a classifying test. Some solutions conduct and some do not. This sets the stage for the several following sections on the electrical nature of matter. These sections may seem to be a diversion if the student is not definitely aware of the need for knowing about the close relation of electric charges to chemically interesting solutions.

ELECTRICAL NATURE OF MATTER (5-3)

Electrical Phenomena (5-3.1)

Most students have experienced or heard about electric shocks, so do not dwell on this point. They already believe there is electric charge. It is not important that the student list all the examples given, but he should now be more aware of the widespread occurrence of electrical phenomena within his own experience.

Detection of Electric Charge (5-3.2)

The electrometer, instead of an ammeter, is used as a charge detector because it responds to a static charge rather than to a current. The charge is distributed over the metal coating, and either remains there until "shorted off" with the wire or until it eventually "leaks" away as particles in the air gradually pick it up.

Film, ELECTRIC INTERACTIONS IN CHEMISTRY,
fits here. See p. 166 for summary.

The Effect of Distance (5-3.3)

The student needs only a qualitative feeling that the attractive force increases when the charged bodies are close together.

The Electron-proton Model (5-3.4)

Some students may feel the Textbook is quite cautious. They "know" atoms are made of electrons and protons and other wondrous particles; why all the fuss about it? Usually the question "How do you know atoms contain protons?" receives either no answer at all or a reply such as "So-and-so told me." You are then in a position to develop the concept. Employ any useful information the students give.

Electric Force: A Fundamental Property of Matter (5-3.5)

The idea that fundamental properties cannot be explained may seem awkward at first, but it need not. It merely expresses the known fact that not all things can be explained. Some fundamental properties of matter are implied when we say "it attracts other matter" (gravity) or "it has mass."

ELECTRICAL PROPERTIES OF CONDENSED PHASES (5-4)

The Electrical Conductivity of Water Solutions (5-4.1)

Demo. 3, ELECTRICAL CONDUCTIVITY,
fits here. See p. 157 for guide.

Here you should relate the observed differences in solutions (Sec. 5-2.7) to the presence or absence of charged species. Ion, as a word and as a concept, is new and needs emphasis. Since you will return to it in Chapter 10, you need not be exhaustive here, but the student should be aware that an important idea is contained in the term ion.

There may be questions about the location of the charge and why some substances give ions in solution whereas others do not. These questions are better postponed until the chapters on energy, structure, and bonding are reached. In particular, all discussion must be delayed until Chapter 6, because atomic structure has not been presented.

The term *(aq)* is introduced, and this is a good time to review the other symbols for state: *(g)*, *(l)*, and *(s)*. These will be used consistently throughout the course for several reasons.

1. They help make the equation a more adequate description of nature.
2. They focus attention on molecular surroundings and on the fact that some properties depend upon the surroundings. This is particularly true for ions and for the term *(aq)*, which is later used to suggest the ionic hydration sphere.
3. They are needed in Chapter 7, where the energy of a reaction depends on the state of the reactants and products.
4. They help put across the idea of "spectator ions" (those which are *not* reacting) and why they can be omitted from equations.

Emphasis on the importance of these symbols, combined with their regular use on your part, will pay off later.

Precipitation Reactions in Aqueous Solutions (5-4.2)

Two important points arise in this section: predominant reacting species and conservation of charges. The first is a systematizing principle. It permits the student to study, for example, $Cl^-(aq)$ chemistry rather than that of each chloride-producing compound separately. Among the benefits will be an easier understanding of the solubility rules and other periodic relations. Try to avoid an overpuritanical insistence on "predominant" in this phrase. Otherwise, equilibrium reactions involving appreciable amounts of several species will give trouble. The second point, charge conservation, is treated as an extension of the discussion on equation balancing in Sec. 3-2.1.

Expt. 11, REACTIONS BETWEEN IONS
IN AQUEOUS SOLUTION,
fits here. See p. 163 for guide.

The Electrical Conductivity of Solids (5-4.3)

This short section establishes experimental differences between metals and other (principally ionic) solids. It is, in part, a review of what the student already knows about metals.

Ionic Solids (5-4.4)

Emphasize that we are packing together spherical ions in a relatively simple geometrical arrangement. Display a model of an NaCl crystal. Make sure the student understands NaCl molecules do not exist in the solid state.

DEMONSTRATION 2 VAPOR PRESSURE OF A LIQUID AT TWO TEMPERATURES

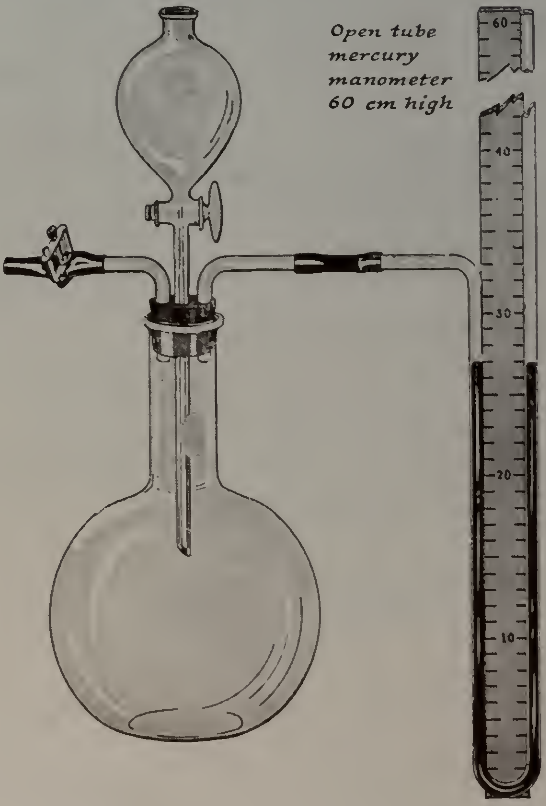
PURPOSE. To show that liquids have a vapor pressure; to show that this pressure rises as temperature increases; and to acquaint the student with the use of a mercury manometer in measuring pressure.

TIMING. This demonstration should be given after the student has read Sec. 5-1.2.

EQUIPMENT NEEDED

apparatus described in the lab hint
1 to 3 large Erlenmeyer or Florence flasks (250 or 500 ml)
3 hole rubber stopper to fit flask
dropping funnel
mercury manometer (55–60 cm)
pinch clamp
glass tubing (two 90° bends plus tubing for manometer)
rubber tubing

LABORATORY HINT. The apparatus may be constructed as shown.



PROCEDURE. Partially evacuate a flask. A pressure of about 600 mm (160 mm difference in manometer levels) is convenient. Evacuate the flask through the tube with the pinch clamp. Close the pinch clamp, and watch the manometer. If it shows no change in 2–3 minutes, there are no important leaks. Record the initial pressure by reading the level in each arm.

Place a few milliliters of acetone in the dropping funnel. Open the stopcock to allow a few drops to enter the flask. The movement of the mercury levels will be immediately visible. Record levels every 2–3 minutes until no more change is evident (about 15 minutes). Introduce another few drops of acetone to be sure all that will evaporate at this temperature has done so.

By this procedure you should observe a vapor pressure of about 150 mm. Some cooling will take place during evaporation, hence the value will be for a temperature probably less than 20°C. Repeat the procedure with the flask immersed in a warm water bath, or have two apparatus and run the two trials simultaneously.

Vapor pressures for acetone are:

Temp. (°C)	*Pressure (mm)*
15	147
18	169
21	193
24	220

Data from a trial run:

	Open Tube	*Tube to Flask*
Initial reading	165 mm	345 mm
Reading after entire procedure above (20 min)	242 mm	267 mm

Change in pressure:

$(345 - 165) - (267 - 242) = 180\text{ mm} - 25\text{ mm} = 155\text{ mm}$

Other calculations are done in the same way.

DISCUSSION. These are the points to make with this experiment.

1. Liquids vaporize, giving a definite vapor pressure.
2. Vapor pressure goes up as temperature increases. As secondary points, make it clear that vapor pressure is not changed by adding more liquid, and show how the manometer is used as a pressure gauge.

DEMONSTRATION 3 ELECTRICAL CONDUCTIVITY

PURPOSE. To provide experimental evidence of the nature of substances in solution.

TIMING. This demonstration should be performed in connection with Sec. 5-4.1.

EQUIPMENT NEEDED

electrical conductivity test apparatus
(see diagram)
150 ml ethanol or methanol
100 ml benzene
~10 g each NaCl, sugar, $AgNO_3$, and AgCl
50 ml 0.1 M NaCl
pipet or medicine dropper

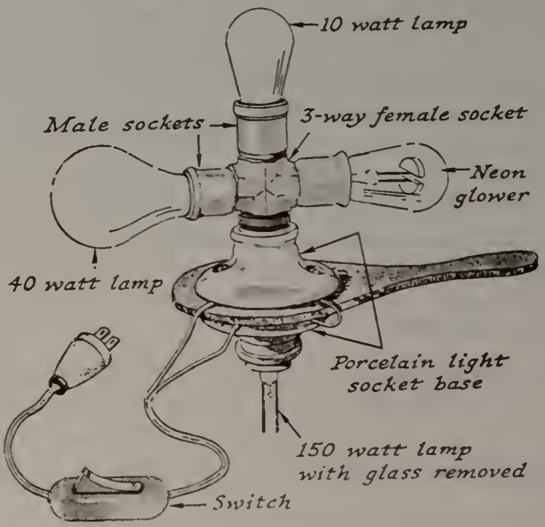
distilled water
ring stand, ring, triangle
burner
HCl generator with drying tube
2 or 3 small crucibles
15–20 2 ounce bottles or 50 ml beakers

The various reagents and materials can be placed in 2 ounce wide-mouth bottles with screw caps, and can be tested directly in the bottles. Most reagents can be stored in these same bottles for use again next year.

TIME REQUIRED. About 20–30 minutes.

SETUP

1. The demonstration apparatus shown permits testing a wide range of conductivities. Two porcelain receptacles are mounted back to back on a piece of plywood (shaped like a ping pong paddle) to permit the apparatus to be mounted on a ring stand or held by hand. The conducting wires are those which held the filament in a broken 150–250 W lamp. The wiring is done as shown in the diagram.



Caution: To avoid an electric shock, always turn off the switch or pull the plug while rinsing the electrodes or changing the solutions.

2. If only the neon glower is used (with other lamps not engaged), it will pick up very weak electrolytes, such as water, 95% alcohol, and glacial acetic acid. The 10 W lamp requires more

current, and, as a result, will show the effect of dilution on acetic acid or ammonia. Other, higher wattage lamps can be used to pick up stronger electrolytes. Electrometric titrations, such as 0.01 M H_2SO_4 + 0.01 M $Ba(OH)_2$, can be carried out, in which the lamps will be extinguished one after another as the end point is reached and then be relighted after it is passed.

STUDENT ACTIVITY. Have the students record the results in their lab notebooks and, after the experiment, write a summary report accounting for the differences in conductivity that they observe.

PART I (DEMONSTRATION OF CONDUCTIVITY)

Test the conductivities of the following:

water	
ethanol or methanol	
NaCl	(powdered, dissolved in water and in alcohol)
sugar	(powdered, dissolved in water and in alcohol)
$AgNO_3$	(powdered, molten and dissolved in water)
AgCl	(powdered, molten and "dissolved" in water)

The silver salts may be melted in a crucible. Both of these salts conduct. They also conduct when dissolved, but not enough AgCl dissolves to show with the 10 W bulb. Sugar may also be fused if heated very gradually, but it has a great tendency to char.

Note what the Textbook says about AgCl. Unfortunately the distilled water alone causes the neon glower to light up, and not enough AgCl dissolves to show on the 10 W bulb. You will need to point out to your students that it would require a device with a range between these two (or if you are using only the 10 W bulb, one below it).

PART II (EFFECT OF CONCENTRATION)

Substitute a 100 or 200 W bulb for the neon glower. If the probes are bent to about 1 inch apart and immersed to a depth of about 1 inch; a 0.001 M solution of NaCl will not cause the 10 W bulb to glow, but a 0.002 M solution will. A simple way of showing this is to add 0.1 M NaCl to a 50 ml beaker half full of distilled water. Five small drops (about $\frac{1}{4}$ ml) will produce a 0.001 M solution; and 10 drops, about 0.002 M. At a concentration of about 0.005 M, the 10 W bulb is about at its maximum brightness, and the 40–50 W bulb shows a slight glow. A 50 W bulb does not reach maximum brightness until the concentration is about 0.01 M, at which concentration there is no glow in a 200 W bulb. A faint glow appears in the 200 W bulb at about 0.02 M. Full brightness is achieved in 0.1 M NaCl. This demonstration gives clear evidence that the more ions there are, the greater is the conductivity.

PART III (EFFECT OF SOLVENT)

Test the conductivity of benzene. Using an HCl generator (conc. HCl + H_2SO_4), bubble a small amount of HCl into a test sample of benzene. Also prepare a water solution of HCl.

Compare the conductivity of the two solutions, then add water to the HCl dissolved in benzene, and compare the resulting conductivity to that observed for the two solutions.

DISCUSSION. The points to make in discussing the student's reports are:

1. Ion formation is dependent upon the solvent.
2. Dissolving does not always yield a solution containing ions.
3. The properties of ionic solutions vary with the concentration of ions.

EXPERIMENT 10 AN INVESTIGATION OF THE REACTING VOLUMES OF TWO SOLUTIONS OF KNOWN CONCENTRATION

PURPOSE. To provide the student with an opportunity to prepare a solution of given molar concentration, and to use this solution in a quantitative determination as a check on the molarity of the prepared solution.

PRELAB DISCUSSION. Consider presenting a sample calculation. Use a solid other than those called for in the experiment. For example, you might show how many grams of NaCl are needed to prepare 25 ml of a 0.50 *M* solution.

$$25 \text{ ml} \times \frac{1 \text{ liter}}{1000 \text{ ml}} \times 0.50 \frac{\text{mole NaCl}}{\text{liter}} = 0.0125 \text{ mole NaCl in 25 ml}$$

$$1 \text{ mole NaCl} = 58.5 \text{ g}$$

$$\frac{58.5 \text{ g NaCl}}{\text{mole}} \times 0.0125 \text{ mole needed} = 0.73 \text{ g NaCl in 25 ml of solution}$$

If you have a volumetric flask available, demonstrate the proper technique to use in making up a molar solution by first dissolving the solid in a small amount of water and then diluting the solution to the desired volume. Emphasize the importance of measuring the volumes precisely in this experiment. Show how this is done by using a medicine dropper to adjust the level in a graduated cylinder. If volumetric pipets are being used, demonstrate them and call attention to the common errors; sucking too hard and raising the pipet out of the liquid. Immediate mouth rinsing is the remedy. Tell the student to practice with water before trying $Pb(NO_3)_2$ solution.

Insist that the students do the concentration calculations as homework. In the laboratory have the students work in pairs and check each other's calculations before making the 0.50 *M* solutions.

$$0.50\,M = \frac{0.50 \text{ mole}}{\text{liter of soln.}} = \frac{0.0125 \text{ mole}}{25.0 \text{ ml of soln.}}$$

$$1 \text{ mole NaI} = 150 \text{ g}$$

$$\frac{150 \text{ g}}{\text{mole}} \times \frac{0.0125 \text{ mole}}{25.0 \text{ ml of soln.}} = \frac{1.87 \text{ g}}{25.0 \text{ ml of soln.}}$$

$$1 \text{ mole } Pb(NO_3)_2 = 331 \text{ g}$$

$$\frac{331 \text{ g}}{\text{mole}} \times \frac{0.0125 \text{ mole}}{25.0 \text{ ml of soln.}} = \frac{4.14 \text{ g}}{25.0 \text{ ml of soln.}}$$

If you do Part III, make the purpose of filtering clear to students. As much as possible of the precipitate is to be poured into and retained in the filter cone. The reason for rinsing with the filtrate is to prevent dissolving additional PbI_2. The final rinsing with ethyl alcohol removes soluble salts and aids drying.

TIMING. This experiment is to be done after the assignment and discussion of Sec. 5-2.5 in the Textbook.

EQUIPMENT NEEDED (PER PAIR)

- about 2 g NaI (dry) (see lab hint 2)
- about 4 g $Pb(NO_3)_2$
- 0.01 g balance
- 100 ml beaker
- 25 or 50 ml graduated cylinder
- 10 ml graduated cylinder
- 1 ml pipet with 0.5 ml calibration if available (see lab hint 1)
- medicine dropper
- stirring rod
- 5 13 × 100 mm test tubes and rack (see lab hint 3)
- small rubber stopper (#00) or a #3 cork

PART III (SEE LAB HINT 5)

5 ml ethanol (reagent grade, denatured)	wash bottle
100 ml beaker	drying apparatus (oven, heat lamps) (see lab hint 4)
filter paper	
funnel and support	

TIME REQUIRED. Parts I and II of this experiment require one period plus five minutes the next day. There is a stopping place after Part I. Part III requires one period (lab hint 5).

PRECAUTIONS. Observe the usual lab precautions. See *Prelab Discussion* for comments about pipet use.

LABORATORY HINTS

1. If pipets are available use them for measuring 0.5 ml and in place of the 10 ml graduate. If pipets are not available, use the instructions in the lab manual.
2. Use NaI (not KI), because the weight of 2 moles of KI (332 g) is nearly equal to that of 1 mole of $Pb(NO_3)_2$ (331 g). The student might draw the erroneous conclusion that, as a general rule, equal weights react. The salt NaI is quite hygroscopic. (Dry it in an oven, and keep in a desiccator.) Dispense it in separate 2 gram portions in order that the stock container need not be left open.
3. To aid visual comparison of the amount of precipitate, the test tubes should be of uniform diameter. Uniform tubes can be made from 12 cm lengths of 8 or 10 mm tubing closed by corks.
4. Rinsing with ethanol will probably eliminate the need for drying, but this will depend on your climatic conditions. Plan an appropriate arrangement.
5. To save time in getting quantitative results; the lab manual suggests having selected students or the teacher do Part III. If participation by the entire class seems desirable, three pairs could work together, with one student filtering the three #1 tubes together, a second student filtering the three #2 tubes together, and so on. The sixth student helps where needed or acts as "clean-up man." This plan gives each student only a single filtration and weighing; it also gives a somewhat larger quantity and decreases the uncertainty of measurement.

POSTLAB DISCUSSION. If possible collect class data on the weights of the PbI_2 precipitates before students work on the questions and exercises. This may be done as soon as they complete the weighing, in order that the general trend will be apparent to all. Emphasize the constant weight of precipitate in tubes 3–5. Use the large uncertainty of measurement (for tube 1, 0.11 g ± 0.02 g, or about 20%; for tube 2, 0.23 g ± 0.02, or about 10%; and for the other, 0.46 g ± .02, or about 5%) to explain the spread of values for tubes 1 and 2. In tube 3 the amount of PbI_2 may be skewed toward low values. This can occur because of errors in pipeting amounts of reactants. There are four possible combinations of errors, three of which lead to less PbI_2 than expected. Avoid discussing this factor before the students answer the questions, or you will give away the discovery element of the experiment.

The meaning of molarity should also be emphasized at this time. The last sentence of the answer to question 1 is for use later with Chapter 10. A question relating to this point will be included in that chapter.

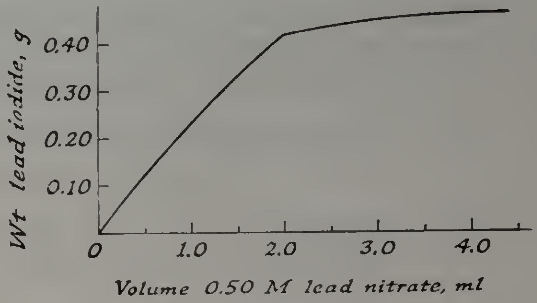
CALCULATIONS AND QUESTIONS

1. Obtain the weight of lead iodide from each test tube by subtracting the weight of one piece of filter paper from the weights recorded in III h.

Sample results, for lead iodide:

Tube	*Weight*
1	0.12 ± 0.02 g
2	0.23 ± 0.02 g
3	0.42 ± 0.02 g
4	0.45 ± 0.02 g
5	0.46 ± 0.02 g

2. Plot the data obtained in this experiment on a graph. Plot the grams of lead iodide along the ordinate and the number of milliliters of lead nitrate used along the abscissa.



Sample data from Expt. 10.

3. How do you explain the shape of the curve obtained when you connect the plotted points in the graph?

   Answer: The first part of the curve indicates a direct relation between the volume of lead nitrate used and the weight of lead iodide precipitated. Tube 2, containing twice as much lead as tube 1, had twice as much precipitate as 1; the same doubling occurred in tube 3. This relationship does not hold for tubes 4 and 5, indicating that nearly all the iodine was precipitated when 2.0 ml of lead nitrate were added, and that adding additional lead does not produce more lead iodide.

4. Calculate the number of moles of lead nitrate and of sodium iodide used in each of the five test tubes. Tabulate your answers. Two entires have been made for you.

   Answer: In tube 1, 0.5 ml of 0.5 M $Pb(NO_3)_2$ solution was used.

$$0.5 \text{ ml} \times \frac{1 \text{ liter}}{1000 \text{ ml}} \times \frac{0.5 \text{ mole}}{1 \text{ liter}} = 0.00025 \text{ mole}$$

or, if you prefer,

$$\frac{0.0125 \text{ mole used}}{25 \text{ ml}} \times 0.5 \text{ ml} = 0.00025 \text{ mole}$$

Tube	*Moles of $Pb(NO_3)_2$*	*Moles of NaI*
1	0.00025	0.0020
2	0.0005	0.0020
3	0.0010	0.0020
4	0.0015	0.0020
5	0.0020	0.0020

5. Refer to the graph, and select the combination in which there was just enough of the lead nitrate solution to react with all of the sodium iodide.

   Answer: From this sequence of questions, the student is lead to select test tube 3. You may need to point out the uncertainty of measurement and the significance of the change in direction of the curve. Tube 4 does not have $1\frac{1}{2}$ times the precipitate obtained in 3, although its weight may be slightly greater in some students' results.

6. Refer to question 4, and determine the ratio of the moles of lead nitrate to the moles of sodium iodide for the combination selected in question 5. Use this ratio to determine the formula of lead iodide.

   Answer: Since 0.0010 mole of $Pb(NO_3)_2$ and 0.0020 mole of NaI were used, the ratio is 1/2. The formula would show 1 lead ion to 2 iodide ions: PbI_2.

7. Use the weight of the precipitate obtained in the combination referred to in question 5 to calculate the number of moles of lead iodide produced in this test tube. How does this compare with the number of moles of lead nitrate and of sodium iodide used for this combination?

   Answer: Using the sample data, we obtain

$$\frac{0.42 \text{ g}}{461 \text{ g/mole}} = 0.00091 \text{ mole of lead iodide}$$

   compared to 0.0010 mole for $Pb(NO_3)_2$ and 0.0020 mole for NaI in this combination. You will want to discuss factors in the experiment which lead to a somewhat low value here.

EXPERIMENT 11 REACTIONS BETWEEN IONS IN AQUEOUS SOLUTION

PURPOSE. To introduce the idea of reacting species as contrasted with those that are merely "spectators," and to give practice in writing equations showing predominant reacting species. To permit further observations of differences of solubility. To offer a chance to develop a hypothesis and to explain some observations.

PRELAB DISCUSSION. Emphasize that the student will try combinations of these solutions and that he should develop a generalization as an explanation of his observations. In introducing it be careful not to interject your ideas—to you the experiment will seem very simple and the conclusion obvious. Students often see things in a different way and should have the experience of "thinking through" their results. Some students will need help in organizing the table indicated and in deciding how many combinations must be tested. A common error consists in showing the proportions of ions (Ba^{+2}, $2Cl^-$), the student thinking that this has something to do with the reaction. Wait until they have started to work, and then help those who are having difficulty.

TIMING. This experiment should come near the end of Chapter 5, following Sec. 5-4.2.

EQUIPMENT NEEDED

Set of six solutions as indicated in lab hint 1 for every pair or group of two or three students.

If test tubes are used, each student will need about 10 ml of each solution; if spot tests are used, each student will need about 1.5 ml of each.

Use either several 13 × 100 mm test tubes (one will do, but it is more convenient to have several), a rack, and a test tube brush (Method I) or a glass plate (any size from microscope slide to 10 × 13 cm) and a wax pencil (Method II).

TIME REQUIRED. If test tubes are used, and if they must be washed frequently, about 15 minutes will be needed. If glass plate for the spot test method is used, about 10 minutes is enough. This is the time needed to make the combinations and record the observations; it does not include time for analysis of observations or for testing other sets of solutions.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. *Selection of sets*

Several sets of reactants are listed on the next page. It is not intended that any one student work with all the sets described. Two somewhat more complicated sets have been listed, but remember that the challenge of this experiment lies in deciding on the number of tests necessary and in proposing a hypothesis and a method for testing it, rather than in having a complex set to analyze.

The set of solutions used first should be quite simple and should not include many combinations that form precipitates. Three such sample sets are included. In the first, only one pair of ions precipitates, giving $BaCrO_4$, and each other combination associated with $BaCrO_4$ as a product checks out as being soluble.

In the second set, there are two precipitates, $BaSO_4$ and $SrSO_4$, but each occurs only twice; and as before, each other combination associated with the precipitates checks out as being soluble.

In the third set, KCl, which is associated once with $Fe(OH)_3$ and once with $Co(OH)_2$, does not check out, but the student sees each of the precipitates associated with NaCl, which does check out, and there is little doubt but that he will arrive at the correct conclusion. This situation gives opportunity for a suggested "test" of the hypothesis.

In set 1, four of the fifteen possible combinations give precipitates, whereas in sets 2 and 3, six of the fifteen precipitate. There are of course numerous possible combinations. Set 1 is somewhat more difficult if $SrCl_2$ is substituted for KCl.

2. *Preparation of solutions*

The solutions should be of approximately equivalent concentrations, although considerable range is satisfactory. Check the solutions before the student uses them. If the expected precipitates do not appear in a minute or two, increase the concentrations. The weight needed to make 100 ml of solution is given after each compound.

Set 1

0.1 M $Ba(NO_3)_2$ (2.6 g)
0.1 M $BaCl_2$ (2.4 g $BaCl_2 \cdot 2H_2O$)
0.1 M Na_2CrO_4 (1.6 g)
0.1 M K_2CrO_4 (1.9 g)
0.2 M $NaNO_3$ (1.7 g)
0.2 M KCl (1.5 g)

(Four of the 15 combinations give ppts.—all are $BaCrO_4$.)

Set 2

0.1 M Na_2SO_4 (1.4 g anhydrous)
0.07 M $Al_2(SO_4)_3$ (4.7 g $Al_2(SO_4)_3 \cdot 18H_2O$)
0.1 M $Sr(NO_3)_2$ (2.1 g)
0.1 M $BaCl_2$ (2.4 g $BaCl_2 \cdot 2H_2O$)
0.1 M $Ba(NO_3)_2$ (2.6 g)
0.07 M $AlCl_3$ (1.7 g $AlCl_3 \cdot 6H_2O$)

(Six of the 15 combinations give ppts.—two are $SrSO_4$; four are $BaSO_4$.)

Set 3

0.1 M $FeCl_3$ (2.7 g $FeCl_3 \cdot 6H_2O$)
0.1 M $Co(NO_3)_2$ (2.9 g $Co(NO_3)_2 \cdot 6H_2O$)
0.1 M $CoCl_2$ (2.4 g $CoCl_2 \cdot 6H_2O$)
0.2 M NaOH (0.80 g)
0.2 M KOH (1.12 g)
0.2 M $NaNO_3$ (1.7 g)

(Six of the 15 combinations give ppts.—two are $Fe(OH)_3$; four are $Co(OH)_2$.)

3. *Two further suggestions are:*

Set 4

0.1 M $NiCl_2$ (2.4 g $NiCl_2 \cdot 6H_2O$)
0.1 M $MgCl_2$ (2.0 g $MgCl_2 \cdot 6H_2O$)
0.1 M Na_2SO_4 (as in set 2)
0.2 M NaOH (as in set 3)
0.1 M $Ba(OH)_2$ (saturated soln., 1.7 g)
0.1 M $MgSO_4$ (2.5 g $MgSO_4 \cdot 7H_2O$)

(Seven of the 15 combinations give precipitates; one combination gives two.)

Set 5

0.1 M $BaCl_2$ (as in set 1)
0.1 M $Sr(NO_3)_2$ (as in set 2)
0.1 M Na_2CrO_4 (as in set 1)
0.07 M $Al_2(SO_4)_3$ (as in set 2)
0.1 M K_2CrO_4 (as in set 1)
0.2 M $AgNO_3$ (3.4 g)

(Ten of the 15 combinations give precipitates.)

INTERPRETATION OF RESULTS

For set 3, a student's record would look like this

	6	5	4	3	2	1
SOLUTION	Na^+, NO_3^-	K^+, OH^-	Na^+, OH^-	Co^{+2}, Cl^-	Co^{+2}, NO_3^-	Fe^{+3}, Cl^-
1. Fe^{+3}, Cl^-	—	ppt	ppt	—		
2. Co^{+2}, NO_3^-	—	ppt	ppt	—		
3. Co^{+2}, Cl^-	—	ppt	ppt			
4 Na^+, OH^-	—	—				
5. K^+, OH^-	—					
6. Na^+. NO_3^-						

New combinations in which a precipitate occurred:

$Fe(OH)_3$ and KCl	KCl not eliminated; make further test
$Fe(OH)_3$ and NaCl	NaCl eliminated by results on mixing 1 and 6
$Co(OH)_2$ and KNO_3	KNO_3 eliminated by results on mixing 5 and 6
$Co(OH)_2$ and $NaNO_3$	$NaNO_3$ is soluble (solution 6)
$Co(OH)_2$ and KCl	KCl not eliminated
$Co(OH)_2$ and NaCl	NaCl eliminated above

CONCLUSIONS

1. Examine your results, and propose explanations that will account for the fact that a precipitate was observed in some cases and not in others.

Answer: Some explanations that have been suggested are:

Set 1 Ba^{+2} precipitates with SO_4^{-2}, or if the charge of each ion is 2, then a precipitate results.

Set 2 Elements in the second column of the periodic table precipitate with CrO_4^{-2}, or elements with +2 ionic charge precipitate with CrO_4^{-2}.

Set 3 Elements in the center of the periodic table precipitate with OH^-, or elements not in the first column of the periodic table precipitate with OH^-.

2. Propose a further experiment to test your ideas.

Answer: Solutions should be readily available for use in making additional checks. If possible, the student should be allowed to test his ideas.

3. Write equations to indicate what you consider to have happened in each case in which there was a reaction. Use ions to represent the species in the reacting solutions, but for those products that were precipitates write a formula. [Place *(aq)* after those species in solution and *(s)* after the precipitates.] Be sure to write the equations to show that both the atoms and the charges are conserved. For example,

$$Ag^+(aq) + NO_3^-(aq) + Na\ (aq) + Cl^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

Answer: For set 3 we have the following equations:

$$(1)\ Fe^{+3}(aq) + 3Cl^-(aq) + 3Na^+(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s) + 3Cl^-(aq) + 3Na^+(aq)$$

$$(2)\ Fe^{+3}(aq) + 3Cl^-(aq) + 3K^+(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s) + 3Cl^-(aq) + 3K^+(aq)$$

$$(3)\ Co^{+2}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s) + 2Cl^-(aq) + 2Na^+(aq)$$

$$(4)\ Co^{+2}(aq) + 2Cl^-(aq) + 2K^+(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s) + 2Cl^-(aq) + 2K^+(aq)$$

$$(5)\ Co^{+2}(aq) + 2NO_3^-(aq) + 2K^+(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s) + 2NO_3^-(aq) + 2K^+(aq)$$

$$(6)\ Co^{+2}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s) + 2NO_3^-(aq) + 2Na^+(aq)$$

4. Rewrite these equations leaving out the ions not involved. Such an equation, showing only the predominant reacting species, is called a net ionic equation.

Answer: For set 3 we have

$$Fe^{+3}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$$
$$Co^{+2}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$$

POSTLAB DISCUSSION. The main purpose of this experiment is to introduce reacting species and to use them in equations. In addition, students should understand that the differences in solubility they have observed are differences in degree, not in kind. We cannot predict what compounds will precipitate except by an accumulation of experience. There are no simple rules for prediction, but some of the trends will be discussed in Chapter 10.

Students tend to make generalizations which are too broad for the present purpose. We hope they will say something like "When Ba^{+2} and SO_4^{-2} are present a precipitate forms." If grander regularities are proposed let the student test them and discover there are no "laws of precipitation."

Be prepared for questions about why some ions have 1+ and others 2+. These should be deferred until after the nuclear atomic model is presented in Sec. 6-1.1.

Supplementary Material

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

ELECTRIC INTERACTIONS IN CHEMISTRY

A CHEM Study film

Running Time: 21 minutes

This film, prepared by Professor J. L. Hollenberg of the University of Redlands and Professor J. A. Campbell of Harvey Mudd College, illustrates the principles that opposite charges attract, like charges repel, and uncharged bodies have no electric interaction. The effect of distance on electric force is shown by a sensitive balance measuring the force between two charged spheres. The distance is varied, and the force is calculated from changes in balance readings. A graph of electric force against distance suggests the equation $Fr^2 = k$ (a constant), and the tabulated data confirm this relation. Some chemical applications of these principles are indicated by animated scenes of the migration of positive and negative ions and their mutual precipitation.

Background Discussion

FACTORS FIXING VAPOR PRESSURE

A valid discussion of vapor pressure and its change with temperature requires the use of concepts that are introduced in Chapter 9 (*Equilibrium*). It would be premature to raise them for discussion at this time. Keep the discussion on an empirical basis; experiment shows that the vapor pressure of every liquid increases as its temperature is raised. The following remarks give you the treatment that will be used in Chapter 9.

To understand why a liquid has a fixed vapor pressure (at a given temperature) and why the vapor pressure changes with temperature, let us consider the following system. A closed container has some liquid in equilibrium with its vapor. The temperature is kept constant, and there is nothing in the container except the substance we are studying.

The liquid contains a certain amount of total energy—call it $H(l)$. The gas contains a larger amount of energy, $H(g)$. These energy values might be related to stability. In any system, there is a tendency toward minimum energy (greatest stability). We see this tendency in operation in the condensation of a gas at its boiling point.

At the same time, there is a certain amount of randomness or lack of order in the liquid—call it $S(l)$—and in the gas, $S(g)$. There is another natural tendency for a system to achieve maximum randomness. This tendency is sometimes expressed in terms of the number of ways the particles can be arranged. The random arrangements are more numerous, and thus more likely. Another way to say this is that order is not achieved without effort. Once achieved, there is a tendency for order to disappear.

From these descriptions we can consider what happens when a molecule goes from the liquid state to the gaseous state. There is a change in energy (ΔH) and a change in randomness (ΔS). These changes are the differences $H(l) - H(g)$ and $S(l) - S(g)$, and they work in opposition, the condition of lowest energy corresponding to minimum randomness. The chance for randomness goes up as the particles are farther apart and have a wider distribution of energy. But these arrangements require more energy to achieve and are less stable. It turns out that equilibrium is that condition at which these two effects are in balance, i.e., $\Delta H = T\Delta S$. Temperature is included because of the dependence of randomness upon temperature.

When a liquid vaporizes, there is an increase in randomness as molecules enter the gas phase. As the pressure of the gas rises, however, the difference in randomness between liquid and gas decreases. The liquid continues to evaporate at constant temperature until this difference has been reduced enough such that $T\Delta S$ equals ΔH. No further pressure rise occurs at this temperature. When the temperature is raised, the balance between ΔH and $T\Delta S$ is upset again; now $T\Delta S$ is larger than ΔH. Further vaporization raises the gas pressure, lowering ΔS (difference in randomness), and the equality $\Delta H = T\Delta S$ is restored. Thus a rise in temperature must raise the vapor pressure.

Many teachers discuss the relationship between vapor pressure and temperature in terms of the cooling effect one observes when a liquid evaporates. The cooling of the remaining liquid is related to the escape of the more energetic molecules from the liquid, resulting in a net lowering of the temperature of the remaining liquid. Raising the temperature of the liquid increases the fraction of the molecules thus able to escape, hence the vapor pressure rises.

This treatment is all quite valid except for the conclusion. It *is* true that the more energetic molecules leave the liquid as it evaporates and that, in the nonequilibrium state that results, the liquid is somewhat cooler (this is not an equilibrium situation, because the temperature in the system is not constant throughout). It is also true that raising the temperature of the liquid increases the fraction of molecules able to escape. This will surely increase the *rate of approach* to equilibrium. It is not at all necessary on this basis that the equilibrium be shifted in favor of higher vapor pressure.

The difficulty in the argument is that kinetic observations in a system *not* at equilibrium are used to deduce conditions at equilibrium. From a kineticist's point of view, the cooling of a liquid on evaporation merely indicates that an activation energy $\Delta H^{\ddagger}$ is associated with evaporation. The lowering of the temperature gives *no* information about the sign of ΔH. If there were a 10 kcal activation energy for evaporation, the liquid would cool as it evaporated, even if the liquid and the gas had the same energy!

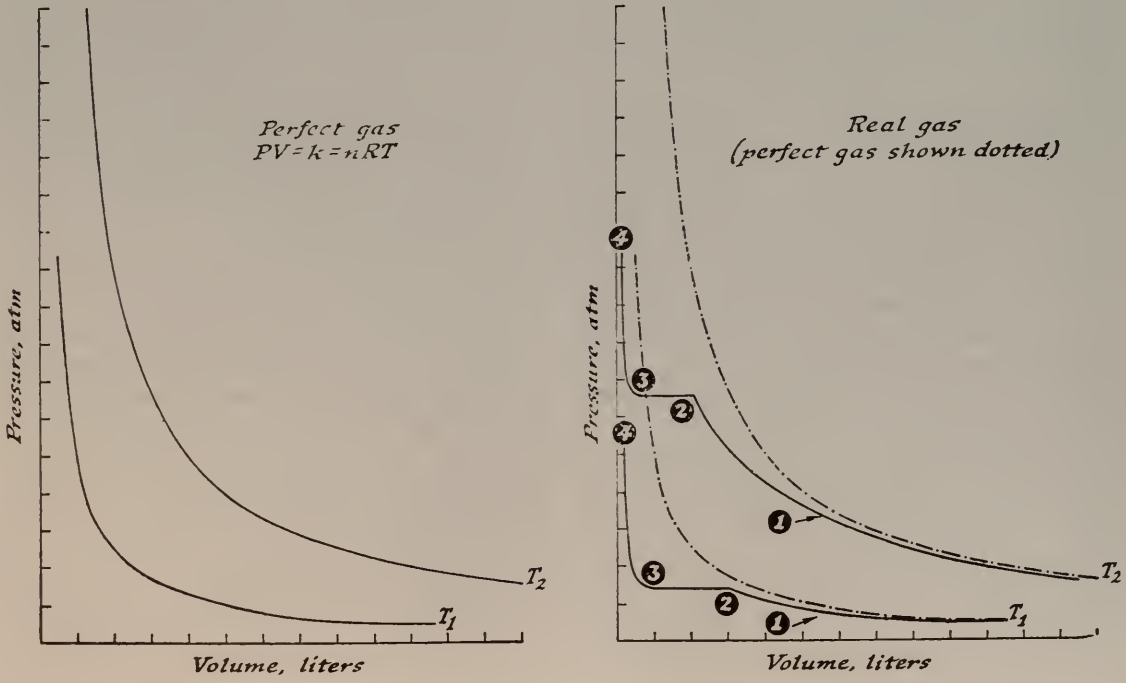
Turning to the equilibrium situation, with the temperature uniform throughout, we note that the kinetic energy distribution among molecules in the liquid phase is *identical* to the kinetic energy distribution in the gas phase. Equal temperatures imply that the K.E. distribution is the same. Hence it is not clear whether raising the temperature (and hence the fraction of molecules with enough energy to penetrate the surface) favors liquid or gas. *Both* the liquid and the gas molecules now have more high K.E. molecules.

A valid mechanistic argument can be framed, but it must be based upon the process as it occurs at equilibrium (rather than on the behavior of a nonequilibrium system such as an evaporating liquid). Such an argument misses a valuable opportunity to expose the student to the two factors that fix *all* equilibria, the tendency toward minimum energy opposed by the tendency toward maximum randomness, the latter being implemented by temperature.

It is now convenient to discuss the behavior of real gases as a modification of the PV curve for an ideal gas. If we assume relatively strong attractive forces between molecules, the processes just described give curves represented by the solid lines of Figure 5-1 (right half). The broken lines show the behavior of an ideal gas.

At point 1, deviation from the ideal curve is becoming pronounced, and at point 2, condensation of vapor begins, and continues until all of the vapor is gone (point 3). Beyond point 3,

Fig. 5-1. **Pressure versus volume** *for gases.*



attempts to reduce the volume further simply raise the pressure of the system more rapidly because the molecules are already in contact. The line from point 3 to point 4 indicates that liquids have very low compressibility, a property which we apply in a hydraulic brake system.

If we raise the temperature of our system to T_2, the kinetic theory tells us that the molecules are moving faster. It follows that the molecules must be brought closer together before the forces of intermolecular attraction will be strong enough to overcome the kinetic energy of the molecules and form a condensed phase. Such arguments suggest that at the higher temperature, T_2, the liquid phase will appear at a lower volume (higher pressure) than it did at the lower temperature, T_1. The shape of the upper curve for T_2 is then predicted by the model used, and is found experimentally.

It is gratifying to find that all of this behavior, including the rough shapes of the curves at T_1 and T_2, is suggested by a van der Waals modification of the ideal gas equation. See p. 137 for the development of the van der Waals equation from the model.

This modified equation gives one way to determine the size of molecules, since the corrective factor b can be interpreted as a measure of the molecular size. We can calculate from b the radius of a sphere whose volume equals the molecular volume. The calculated value gives an estimate of the van der Waals radius of the molecule.

Before going on we should inject a final word of caution relative to the kinetic theory of liquids. Owing to difficulties introduced by molecular size and shape, because forces of intermolecular attraction are highly specific, and because motions in the liquid state are not easy to separate and identify, the detailed quantitative study of liquids is much more difficult than that of gases. Our present-day knowledge leaves much to be desired.

There is a related situation that is sometimes confused with those described above. This is the evaporation of a liquid without the addition of heat, or, in most practical cases, the addition of some, but not enough, heat. Here we have a nonequilibrium case, and little can be learned about vapor pressure, an equilibrium property. We can explain the cooling effect with the kinetic theory, which gives us another reason for accepting that theory.

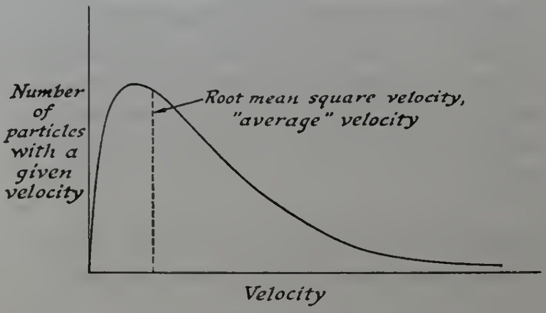


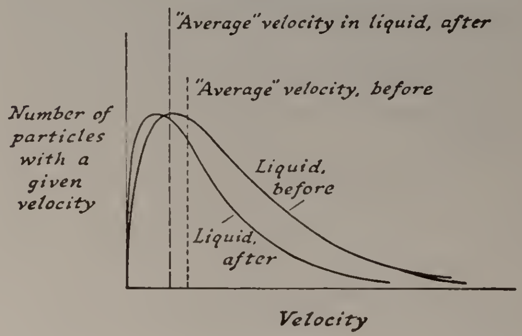
Fig. 5-2. **Distribution of molecular velocities.**

In Chapter 2 we assumed that in each collision of gas molecules the "push" was identical. Such is not the case. The student will learn in Chapter 8 that there is a distribution of velocities summarized by Maxwell's curve, as in Figure 5-2.

When a liquid evaporates, the molecules of higher velocity are more likely to go into the gas phase, converting kinetic energy into potential energy. This leaves the liquid molecules with velocities corresponding to a lower average total energy (see Figure 5-3). Most of this energy lost by the liquid goes into potential energy of the gas. The average kinetic energy of the gas molecules, however, could be raised or lowered during evaporation, depending upon the activation energy for evaporation.

Remember that this is *not* an equilibrium case

Fig. 5-3. **Velocity distribution** *before and after an evaporation during which no heat is added.*

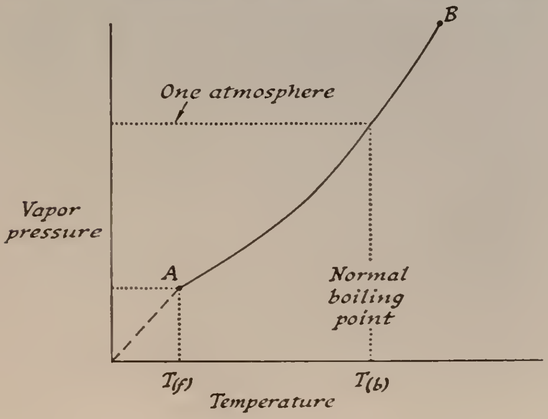


and that these remarks do not apply to an equilibrium situation such as establishing a vapor pressure in a closed system. In that case, gas and liquid are at the same temperature, hence the average kinetic energy in the two phases is the same.

VAPOR PRESSURE, BOILING POINT, AND FREEZING POINT FOR PURE LIQUIDS

The arguments just considered indicate that at a given temperature, liquid and vapor can exist in equilibrium at only a single pressure (i.e., P_1 for T_1 in Figure 5-1). Note also that a change in temperature changes the equilibrium pressure (i.e., P_2 for T_2 in Figure 5-1). We should then be able to plot the pressure of the vapor-liquid equilibrium against the temperature of the system. Such a curve is shown in Figure 5-4. It seems fairly clear that this curve should start at the freezing point, A, of the liquid. Below the freezing temperature, T_f, the substance is a solid, which likewise exists in equilibrium with the vapor above it. The solid has a measurable vapor pressure, as shown by the broken line in the figure. The vapor pressure rises as the temperature is increased. The point B corresponds to the critical conditions discussed on p. 138 and below.

Fig. 5-4. **A generalized pressure-temperature diagram.**



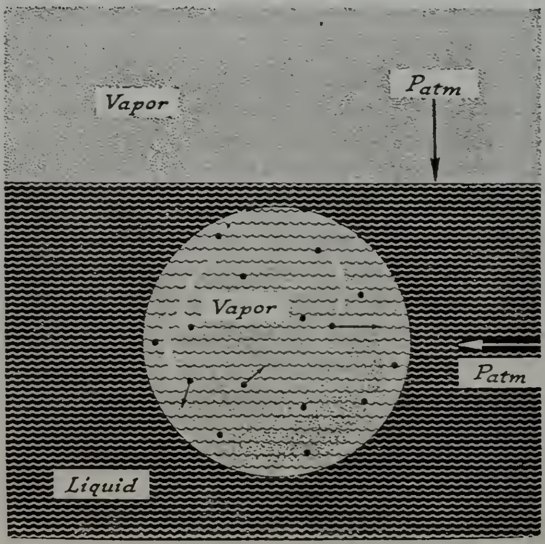


Fig. 5-5. **Bubble formation in the boiling process.**

In several places in the Textbook and in this Guide we have casually referred to the boiling point. Like the burning of the candle, the concept of boiling is a common one. Perhaps we can again profit from a closer analysis of the process. Experimentally, boiling is characterized by the formation of bubbles in the liquid. (It is best if you can lead the student to a statement of this fact in class discussion.) Bubbles then rise to the surface and break. Under what conditions can such bubbles form? To answer this question consider the situation existing inside a spherical bubble in a pure liquid, depicted in Figure 5-5. The bubble, if formed from the pure liquid, contains only gaseous molecules of the pure substance. These gaseous molecules are in rapid random motion and exert an outward pressure on the inner surface of the bubble. This outward pressure of vapor is just balanced by the inward pressure of the liquid. Since the pressure pushing inward on a bubble just below the surface is very nearly equal to the pressure of the atmosphere above the liquid, it is convenient to define the boiling point as that temperature at which the vapor pressure of the liquid is equal to the pressure above the liquid surface. At the *normal boiling point* the pressure above the surface is 760 mm (see Figure 5-5).

Another question is sometimes raised in discussions of boiling. Students occasionally wonder why the liquid doesn't all boil away at once as soon as the boiling point is reached. This is a question about rate. The above discussion provides at least two variables of importance in considering this question. Our kinetic model of a liquid shows clearly that, in boiling, the more rapidly moving molecules leave the liquid, and that heat must be added to the liquid to accelerate the slower molecules remaining in the liquid phase. Heat transfer may be a slow process. A second variable that may retard boiling is slow nucleation, or bubble formation. The results of this second factor may be dramatic!

If we return to the liquid-vapor pressure curve of Figure 5-4 another important question arises which some more interested students may appreciate. The following is not suitable for general class discussion. Does the vapor pressure-temperature curve continue indefinitely, or does it stop abruptly when some definite temperature is reached? Our kinetic model of a liquid provides a clear answer. As noted earlier, the major difference between a liquid and a vapor is in the number of molecules per unit of volume. As the temperature is raised, the liquid molecules vibrate more violently, and the liquid expands slightly; as a result, the number of molecules per unit of volume in the *liquid phase decreases slightly* as the temperature goes *up*. At the same time, an increase in temperature *increases* the number of molecules per unit of volume in the *vapor phase*, since more molecules have enough energy to overcome the intermolecular forces of attraction. At some temperature the difference between the vapor phase and liquid phase will disappear. For example, the density and surface tension of gas and liquid become the same. The liquid-vapor surface disappears, and the two cannot be detected as separate phases. The temperature at which this occurs is known as the *critical temperature* of the substance. The vapor pressure of the liquid at the critical temperature is the *critical* pressure. Our vapor pressure curve must then rise to the critical temperature and end abruptly at point *B* on Figure 5-4.

One may wonder about another facet of our example. We refer to the liquid as being under a constant pressure of 1 atmosphere, yet the vapor pressure of our liquid drops well below one atmosphere as the temperature is reduced. Molecules deep in the liquid phase cannot differentiate between pressure arising from impacts of air molecules on the liquid surface and pressure arising from impacts of molecules of our vapor. Accordingly, the bulk of the liquid behaves as though it were under a pressure of one atmosphere of pure vapor. At the liquid-vapor surface, however, the equilibrium exists only between vapor and liquid molecules; the air molecules are unimportant to the equilibrium. For this reason, we may consider the total pressure acting on the liquid as made up of the partial pressure of the vapor plus the partial pressure of the air above the system.

THE PHYSICAL PROPERTIES OF SOLUTIONS

The simple phase diagram in Figure 5-4 for a pure substance can serve as a starting point for a discussion of the physical properties of solutions. Let us assume that the pure substance of the figure is the solvent for our solution and that some of our solvent molecules are replaced by molecules of a nonvolatile solute such as sugar. The number of solvent molecules that can then escape from a given area of solution surface in unit time will be reduced. One of the prime reasons for this reduced rate of evaporation is the smaller number of solvent molecules per unit volume; the differences in intermolecular attraction caused by such a change lead to a reduction of the concentration of molecules in the vapor phase and a drop of the vapor pressure of solvent above the solution. The result is shown graphically in Figure 5-6.

The model suggests quantitatively that the vapor pressure of the solvent above the solution would be directly proportional to that fraction of the total number of molecules which is solvent. Such a relationship, known as Raoult's Law, describes with fair accuracy the behavior of a relatively large number of solutions, but there are many exceptions.

Raoult's Law can be expressed as

$$\begin{array}{c}\text{Pressure solvent}\\\text{above solution}\end{array} = \begin{array}{c}\text{Pressure pure}\\\text{solvent}\end{array}$$

$$\times \frac{\text{No. solvent molecules}}{\text{No. solvent molecules} + \text{No. solute molecules}}$$

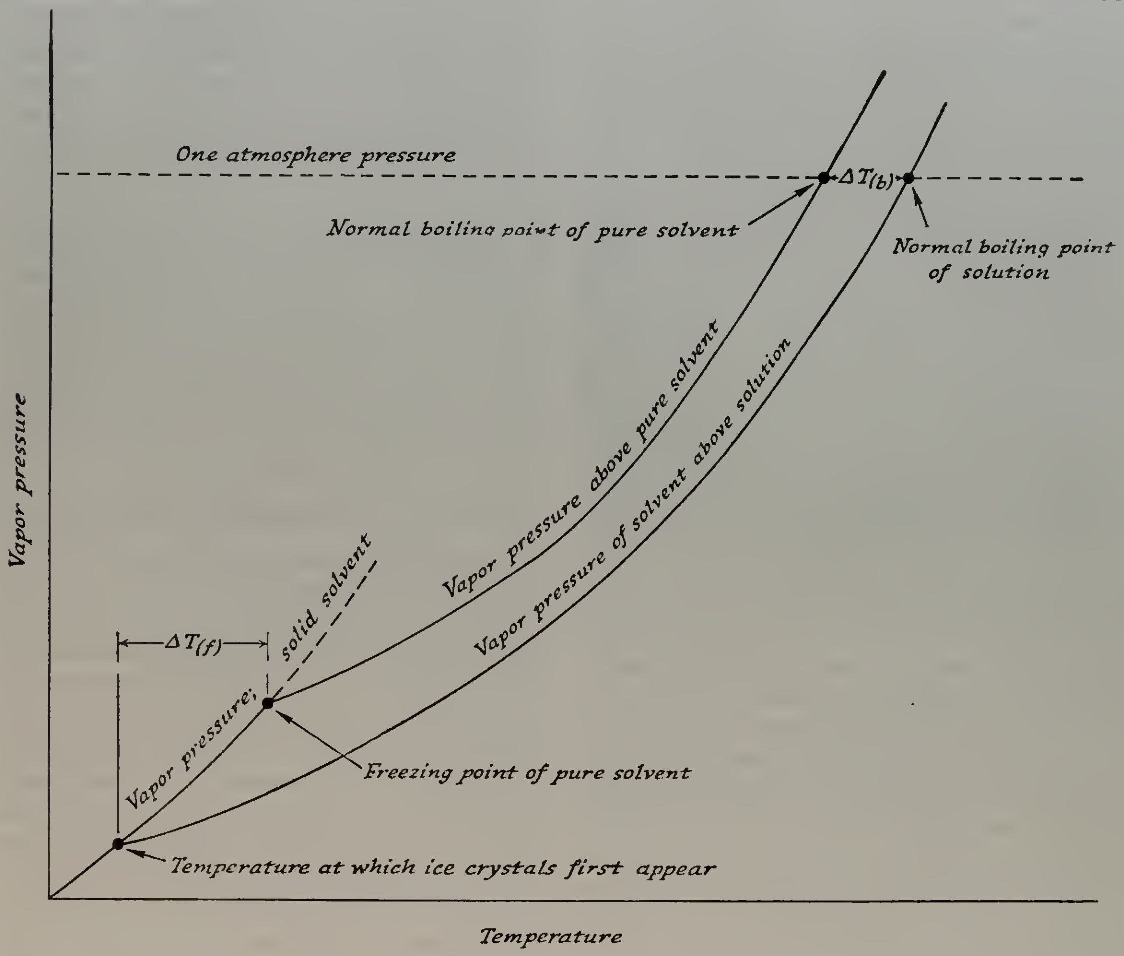


Fig. 5-6. **Liquid and solution vapor pressure versus temperature.**

or,

$$P = P^\circ \times N_1$$

where

P = vapor pressure of solvent above solution;
P° = vapor pressure of pure solvent;
N_1 = mole fraction of solvent in solution as defined above.

We note in the text that the solid phase separating from a fairly dilute aqueous solution of sugar is pure water and that the vapor phase above an aqueous solution of sugar in water is also pure water. These facts are used in our diagram: the solid-vapor equilibrium line is the same as that of pure solvent; and our solution will boil when the vapor pressure of the *solvent* above the solution is one atmosphere. The solution will freeze where the solid-vapor and liquid-vapor lines meet or at the point where both solution and solid have the same vapor pressure. If solution and solid did not have the same vapor pressure, the phase of higher vapor pressure would evaporate and condense on the phase of lower vapor pressure until both phases did have the same pressure or until one phase disappeared.

It is apparent from Figure 5-6 that the boiling point of the solution is raised by an amount ΔT_b and that its freezing point is lowered by an amount ΔT_f. Both changes result from vapor pressure changes and are thus related to the concentration of the solution. For the boiling point, the effect is direct and easily visualized, but for the freezing point, the relation to vapor pressure is less direct and demands a somewhat more detailed review of the equilibrium existing in a liquid-solid system.

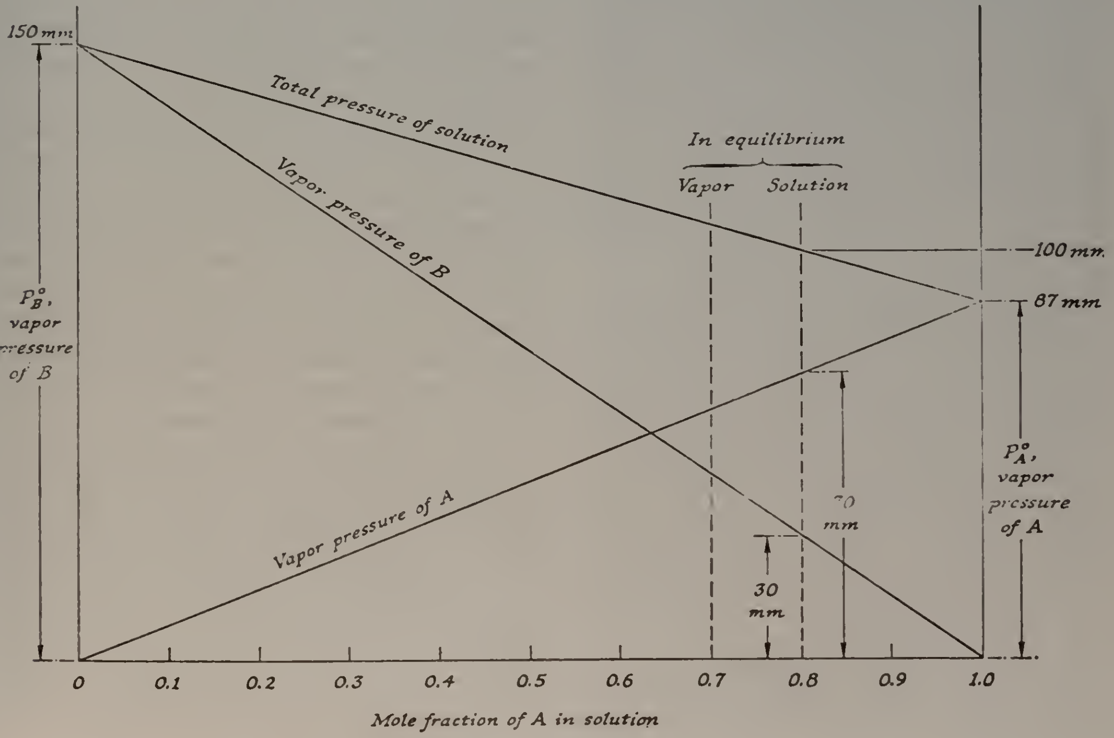
DISTILLATION

The process of distillation is one of the most widely used methods for separating components of solutions. We are now in a position to extrapolate our previous arguments and to consider the process of distillation. Suppose that we have a mixture of two liquids, *A* and *B*, both of which are volatile. The volatility of each will be reduced by the presence of the other. The vapor pressure of *A* may be plotted as a function of the mole fraction of *A* present in the mixture. If *A* obeys Raoult's Law ($P = P^\circ \times N_1$), the plot will be a straight line, as shown in Figure 5-7. The corresponding plot for the vapor pressure of *B* will be a line sloping in the other direction. The total pressure of the solution will be the sum of the two partial pressures, and is represented by the third line in Figure 5-7. To illustrate clearly and quantitatively the basis of a distillation process let us examine the composition of the vapor which is in equilibrium with a solution containing 0.8 mole fraction of *A* and 0.2 mole fraction of *B*. Our curves show that the vapor pressures are 30 mm for *B*, 70 mm for *A*, and 100 mm total. The mole fraction of *A* in the vapor is then

$$\frac{70}{30 + 70} = 0.70$$

The line labeled *vapor* shows the mole fraction composition of the vapor phase. It is obviously richer in *B*, the more volatile component, and poorer in *A*, the less volatile component. If this

Fig. 5-7. **Vapor pressure of a solution of two liquids** (*hypothetical case*).



vapor is condensed, the liquid will be richer in B than was the original. Part of the recondensed liquid could then be vaporized. Again the vapor would be richer in B, and if this vapor were condensed, a liquid still richer in B would be obtained. Repetition of this process, known as isothermal distillation, can give a product whose composition approaches more closely at each step to that of pure B.

ELECTRIC FORCES

Though most of the students enter the class "knowing" there are two kinds of charge, positive and negative, few will have been encouraged to think critically about the meaning of this statement. That is the intent of this section. A few key questions may focus and sharpen the discussion. "How many kinds of charge are there? How do you know this? How was it decided which is positive and which negative? Do you feel it is impossible for there to be a third kind of charge? Why?"

This type of discussion encourages the student to re-examine ideas he has accepted earlier without thought. The notation + and − to designate charge is already prejudicial in answering the first question. Yet it is quite conceivable that there is a third kind of charge, say C_3, with unique identifying properties. Discussion along this line prepares the student for the subsequent discussion of the nuclear atom (in the next chapter) in which it is *necessary* to postulate a new kind of force.

First, let us examine the logic, as presented in the Textbook. The evidence cited in Figures 5-3 to 5-5 is sufficient to establish that we must postulate the existence of *two* kinds of charge, at least. Postulating a single kind of charge, C_1, is insufficient because the removal of the property C_1 could then result only in the situation called "absence of charge." This is not enough, since we must also account for the behavior associated with the property C_2 ("neutralization" of C_1, repulsion of other C_2).

Having decided that two kinds of charge are needed, we can turn to the question, "Why not three or more?" The answer is that all methods of producing macroscopic electric charge produce only these two kinds, C_1 and C_2. As long as we have no evidence which contradicts the postulate that there are but two kinds of charge, it remains an acceptable model.

Having decided that a model incorporating only two kinds of charge is useful, it is convenient to associate algebraic signs with the two kinds of charge. This notational connection serves to translate the experimental observations into mathematical language, which is always a gain. The mathematical convenience is in part due to the ease with which net charge can be calculated. This is brought out in Exercise 5-6, in which the problem is handled first in words:

ten protons + eleven electrons
= (ten protons + ten electrons) + one electron
= (no charge) + one electron
= one electron charge

This contrasts with the simplicity of the algebraic form used in Exercise 5-7.

$$10(1+) + 11(1-) = +10 - 11 = -1$$

More important, though not presented to the student, is the notion that the force exerted by one charge on another is proportional to $q_1 \times q_2$, the algebraic sign automatically indicating—appropriately—attraction or repulsion.

Now let us return to the motivation for treating electric charge in this empirical fashion—the desire that the student *always* look deeply into the ideas he confronts. As remarked earlier, the + and − notation has implications that could be undesirable. Blind acceptance of the notation could furnish a barrier to recognition of the extent to which the notation goes beyond the requirements of the facts explained. Some of these implications are as follows:

(a) The minus sign and the word negative both have the meaning "a lack, a defect," as well as the mathematical operational meanings, "diminished by, with the subtraction of." Hence it is, semantically, an unfortunate choice. We intend to communicate by the expression "the electron has one unit of negative charge, −1" that the electron *possesses* a property, not that it "lacks" or has a "defect" of a property.

(b) Even the operational meaning has a connotational disadvantage. "Diminished by" implies that something is "taken away" when a body acquires negative charge. Though this may have been, historically, an intended meaning, it is hardly desirable today.

(c) The notation implies there are but two kinds of electric charge. To propose that this might not be so may seem like an empty exercise. It is not. In the very next chapter, the student will be confronted with the nuclear model of the atom, which seems to be structured in direct contradiction to the electrical behavior we are now describing. First, the electrons, though attracted to the nucleus, stay away from it. Second, the protons, which repel each other, cluster together in the nucleus. The explanation of the first paradox is that the electron has energy of motion to prevent it from "falling" into the nucleus. The second paradox concerns what is perhaps the most important property of nature that remains to be explained by the generation of students you are teaching. We must postulate a new force—a force associated with the neutron.

For heuristic benefit, let us call this property of the neutron C_3. As our understanding of the nucleus stands now, it seems clear that neutrons attract neutrons (C_3 attracts C_3) and that neutrons attract protons. This is a different set of properties than that defined by normal electrical interactions, demonstrating that the question of how we know there are but two kinds of electric charge is by no means an empty one.

This nuclear force, though not understood at all, is *not* classified as electrical in character. Why not? Presumably because the term "electrical" is associated with conventional means of producing electrical effects and, more important, electrical forces obey the inverse square dependence on distance expressed by Coulomb's Law. Nuclear forces are not readily sensed, but presumably this would not restrain us from identifying a third kind of charge. The more compelling evidence would seem to be that the force is not thought to depend upon distance as $1/r^2$. Hence it seems convenient to segregate "nuclear forces" and "coulombic forces" (electric forces) in discussing nuclear stability.

This might bring to mind the gravitational attraction. This *does* depend upon $1/r^2$, but it is *not* considered to be electrical. This is again a matter of convenience. The gravitational interaction is unlike the C_1 or C_2 interactions, and hence is classified as a new kind, say C_4. It depends upon distance as $1/r^2$, so it needn't be classified separately on that account. It is, however, operationally distinguishable; gravitational forces are many orders of magnitude smaller than electric forces, and they depend upon mass, a factor that has no importance in electrical phenomena.

It is not intended that nuclear forces be identified as a new kind of electric charge. It is intended that the student think critically about electrical phenomena and understand the meaning and limitations of the positive-negative notation.

COULOMB'S LAW

Coulomb studied the effects of charged bodies quantitatively in 1789. If one body has a charge q_1 and a second body has a charge q_2, the force (whether attracting or repelling) varies directly with the product of the quantities q_1 and q_2. The greater the product, q_1q_2, the greater the force. The force also depends upon the distance between the charged particles; it decreases with the distance between the charges.

A reasonable picture can be proposed to explain why the force varies inversely as the square of the distance. We can consider that a charged particle exerts its influence in all possible directions. The second particle can lie anywhere on the surface of an assumed sphere of radius r having the first particle at its center; the second particle "feels," or intercepts, only part of the influence of the first. If the distance r is doubled, the surface of the sphere is quadrupled (surface $= 4\pi r^2$). Then the second particle "feels" only one-fourth as much as before.

Students who have had physics may ask why the dielectric constant of the medium is not mentioned in the expression of Coulomb's Law.

It is, of course, a part of the proportionality constant in the equation. Further discussion should be reserved for after class for those students who raise the question. Emphasize that we are interested only in Coulomb's law in empty space.

It has been observed experimentally, of course, that the coulombic force depends upon the nature of the medium between the charged particles. The force between two charged objects may be lessened when a material is placed between them. The material seems to "insulate" the charges from each other. Since the dependence of force upon the charges and distance is unchanged, the entire effect of the change in medium is expressed as a change in the proportionality constant. One way of doing this is in terms of the dimensionless constant ϵ, called the dielectric constant. It is the ratio of the force in a vacuum to that in the material. In a vacuum,

$$F = \frac{-k(\text{vac})q_1q_2}{r^2}$$

In a medium m,

$$F = \frac{-k(\text{vac})q_1q_2}{\epsilon_m r^2}$$

where ϵ_m is the dielectric constant of medium m

Answers to Exercises and Problems

Ex. 5-1. The dozen or so elements that are normally found as gases include nitrogen, oxygen, fluorine, helium, neon, argon, krypton, xenon, and chlorine. Where are these placed in the periodic table (see inside front cover)?

Answer

In the upper right corner and last column to right.

Ex. 5-2. When two moles of water are evaporated, how much heat is required? One-half mole of water?

Answer

The molar heat of vaporization for water is 10 kcal. The evaporation of two moles of water requires 20 kcal; the evaporation of $\frac{1}{2}$ mole requires 5 kcal.

Ex. 5-3. What is the normal boiling point of ethyl alcohol?

Answer

78.5°C. At this temperature the vapor pressure of ethyl alcohol equals 760 mm Hg.

Ex. 5-4. Suppose a closed flask containing liquid water is connected to a vacuum pump and the pressure over the liquid is gradually lowered. If the water temperature is kept at 20°C, at what pressure will the water boil?

Answer

17.5 mm Hg, the vapor pressure of water at 20°C.

Ex. 5-5. Answer Exercise 5-4, substituting ethyl alcohol for water.

Answer

44 mm Hg, the vapor pressure of ethyl alcohol at 20°C.

Ex. 5-6. Suppose ten protons and eleven electrons are brought together. These charges, grouped together, have the same net charge as how many electrons? Remember that one proton plus one electron gives no charge.

Answer

Since one electron plus one proton equals no charge, ten protons plus ten of the eleven electrons equals no charge. There is one excess electron, hence the net charge is that of one electron.

The point of this and the following exercise is to have the student do the same problem in "words" and "algebraic symbols" to emphasize the convenience of the latter. See *Electric Forces*, p. 174.

Ex. 5-7. Write an algebraic expression to obtain the result of Exercise 5-6, using numbers with algebraic signs to represent charges.

Answer: $10(1+) + 11(1-) = 1-$.

Ex. 5-8. There was a time when atoms were said to be fundamental particles of which matter is composed. Now we describe the structure of the atom in terms of the fundamental particles we have just named, protons and electrons, plus another kind of particle called a neutron. Why are atoms no longer said to be fundamental particles? Do you expect neutrons, protons, and electrons always to be called fundamental particles?

Answer

Atoms are not now considered fundamental because they can be explained in terms of fewer, simpler particles. The present "fundamental" particles probably won't remain fundamental as nuclear structure becomes better understood. The student may not be able to give reasons for this, but by now he should be sufficiently familiar with past changes in models to anticipate further changes.

Ex. 5-9. Balance the equations for the reactions given below. For each balanced equation, sum up the charges of the reactants and compare to the sum of the charges of the products.

(a) $PbCl_2(s) \longrightarrow Pb^{+2}(aq) + Cl^-(aq)$
(b) $K_2Cr_2O_7(s) \longrightarrow K^+(aq) + Cr_2O_7^{-2}(aq)$
(c) $Cr_2O_7^{-2}(aq) + H_2O \longrightarrow CrO_4^{-2}(aq) + H^+(aq)$

Answer

(a) $PbCl_2(s) \longrightarrow Pb^{+2}(aq) + 2Cl^-(aq)$

reactants	products
0 charge	$(2+) + 2(1-)$ $= (2+) + (2-)$ $= 0$ charge

(b) $K_2Cr_2O_7(s) \longrightarrow 2K^+(aq) + Cr_2O_7^{-2}(aq)$

reactants	products
0 charge	$2(1+) + (2-)$ $= (2+) + (2-)$ $= 0$ charge

(c) $Cr_2O_7^{-2}(aq) + H_2O \longrightarrow 2CrO_4^{-2}(aq) + 2H^+(aq)$

reactants	products
$(2-) + 0 = -2$	$2(2-) + 2(1+)$ $= (4-) + (2+)$ $= -2$ charge

Pr. 1. A liquid is heated at its boiling point. Although energy is used to heat the liquid, its temperature does not rise. Explain.

Answer

The energy of the liquid is less than the energy of the gas. Hence heat must be absorbed when a liquid vaporizes. As a liquid boils, the energy put in (as heat) is used to separate the molecules of the liquid instead of to raise the temperature.

If you wish to anticipate Chapter 7, you might mention that the liquid has lower energy than the gas because the molecules attract each other. Hence the heat of vaporization increases the *potential energy* of the molecules as they enter the gas phase. It is incorrect to say that the heat of vaporization increases the kinetic energy of the molecules as they vaporize, since the liquid and vapor are at the same temperature, hence their molecules possess the *same* kinetic energy distribution.

Pr. 2. What is the maximum amount of heat that you can lose as one gram of water evaporates from your skin?

Answer

Water, as it vaporizes, absorbs 10 kcal/mole. Therefore

$$1\text{ g} \times \frac{1\text{ mole}}{18\text{ g H}_2\text{O}} = 0.056\text{ mole}$$

$$0.056\text{ mole} \times \frac{10\text{ kcal}}{\text{mole}} = 0.56\text{ kcal/g}$$

Notice that 10 kcal/mole is an average value. At 100°C, $\Delta H = 9.7$ kcal/mole; at 37°C (body temperature), it is 10.4 kcal/mole.

Pr. 3. Note in Table 5-I the correlation between the normal boiling point and heat of vaporization of a number of liquids. Suggest possible reasons for this regularity.

Answer

The boiling point goes up when there are stronger forces holding the molecules together. For the same reason, a larger amount of energy is needed to vaporize the liquid. Table 5-I is on p. 67.

Pr. 4. Which would likely cause the more severe burn, one gram of $H_2O(g)$ at 100°C or one gram of $H_2O(l)$ at 100°C?

Answer

The gas. It would give up heat as it cooled down, just as the water sample would; in addition, the gas would release the heat of liquefaction.

Pr. 5. Liquids used in rocket fuels are passed over the outer wall of the combustion chamber before being fed into the chamber itself. What advantages does this system offer?

Answer

(a) The chamber walls are cooled as the liquid vaporizes, thereby extending their life.
(b) The heat absorbed causes the liquid fuel to vaporize, which is desirable for combustion. The vapor burns more rapidly than the liquid, and potentially useful energy is not consumed in the combustion chamber to vaporize the liquid.

Pr. 6. Which of the following will require more energy?
(a) Changing a mole of liquid water into gaseous water.
(b) Decomposing, by electrolysis, one mole of water. Explain.

Answer

Note that (a) is a phase change and that (b) is a chemical reaction, characterized by larger heat effects (recall Expt. 5). In (a) water molecules are merely being separated from each other. In (b) water molecules are being separated into atoms, breaking bonds. The heats of (a) and (b) can both be obtained from the Textbook; the heat of vaporization can be found in Sec. 5-1.1, and the heat of decomposition is the opposite of the heat of formation, given in Sec. 3-1.1.

$$H_2O(l) + 10\text{ kcal} \longrightarrow H_2O(g)$$
$$H_2O(l) + 68\text{ kcal} \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

Pr. 7. Pick the liquid having the higher vapor pressure from each of the following pairs. Assume all substances are at room temperature.
(a) Mercury, water
(b) Gasoline, motor oil
(c) A perfume, honey

Answer
(a) Water
(b) Gasoline
(c) Perfume

Pr. 8. Explain why the boiling point of water is lower in Denver, Colorado (altitude, 5280 feet) than in Boston, Massachusetts (at sea level).

Answer
At the higher altitude of Denver, Colorado, atmospheric pressure is much lower (about 630 mm) than at sea level (about 760 mm). Since any liquid boils at a temperature for which its vapor pressure equals the surrounding (atmospheric) pressure, a lower vapor pressure is needed for boiling in Denver, Colorado. Since the vapor pressure of all liquids increases as the temperature is raised, a lower temperature is needed to boil water in Denver (in fact, it boils at a temperature near 95°C).

Pr. 9. Both carbon tetrachloride, CCl_4 (used in dry cleaning and in some fire extinguishers) and mercury, Hg, are liquids whose vapors are poisonous to breathe. If CCl_4 is spilled, the danger can be removed merely by airing the room overnight, but if mercury is spilled, it is necessary to pick up the liquid droplets with a "vacuum cleaner" device. Explain.

Answer
Carbon tetrachloride has a high vapor pressure (100 mm at 23°C). Hence "airing" the room overnight permits the CCl_4 to evaporate and be removed. The mercury has such a low vapor pressure (10^{-3} mm at 25°C) that it evaporates very slowly. Droplets of mercury, and the consequent danger of poisoning, would remain after many weeks of "airing" the room.

Pr. 10. Because of its excellent heat conductivity, liquid sodium has been proposed as a cooling liquid for use in nuclear power plants.
(a) Over what temperature range could sodium be used in a cooling system built to operate at one atmosphere pressure or lower?
(b) How much heat would be absorbed per kilogram of sodium to melt the solid when the cooling system is put in operation?
(c) How much heat would be absorbed per kilogram of sodium if the temperature rose too high and the sodium vaporized?
Use the data in Tables 5-I (p. 67) and 5-II (p. 69).

Answer
(a) 98–889°C. The lower temperature limit is fixed by the point at which the coolant freezes (98°C); and the upper limit, by the temperature at which the vapor pressure reaches 1 atmosphere, the boiling point (889°C).
(b) The number of moles in one kilogram is

$$\frac{1000\text{ g}}{23.0\text{ g/mole}} = 43.5\text{ moles}$$

The heat necessary to melt 43.5 moles of Na(*s*) is

$$\left(43.5\,\frac{\text{moles}}{\text{kg}}\right)\left(0.63\,\frac{\text{kcal}}{\text{mole}}\right) = 27\,\frac{\text{kcal}}{\text{kg}}$$

(c) The heat necessary to vaporize 43.5 moles of Na(*s*) is

$$\left(43.5\,\frac{\text{moles}}{\text{kg}}\right)\left(24.1\,\frac{\text{kcal}}{\text{mole}}\right) = 1050\,\frac{\text{kcal}}{\text{kg}}$$

Pr. 11. Water is a commonly used cooling agent in power plants. Repeat Problem 10 considering one kilogram of water instead of sodium. Contrast the results for these two coolants.

Answer
(a) 0°–100°C. Whereas sodium is useful over almost 800°C, water is useful over only 100°C. It is a disadvantage, however, that sodium freezes when the power plant is turned off and the temperature drops to room temperature.
(b) The number of moles in one kilogram is

$$\frac{1000\text{ g}}{18\text{ g/mole}} = 55.5\text{ moles}$$

The heat necessary to melt 55.5 moles of ice is

$$\left(55.5\,\frac{\text{moles}}{\text{kg}}\right)\left(1.44\,\frac{\text{kcal}}{\text{mole}}\right) = 80\,\frac{\text{kcal}}{\text{kg}}$$

It took only 27 kcal to melt the sodium. Notice that this heat must be put in to "start" the sodium cooling system because the sodium solidifies on "shutdown." The water would not freeze on "shutdown."

(c) The heat necessary to vaporize 55.5 moles of water is

$$\left(55.5\,\frac{\text{moles}}{\text{kg}}\right)\left(9.7\,\frac{\text{kcal}}{\text{mole}}\right) = 538\,\frac{\text{kcal}}{\text{kg}}$$

This is about one-half the heat that would be absorbed by vaporizing an equal weight of sodium.

Pr. 12. How much heat must be removed to freeze an ice tray full of water at 0°C if the ice tray holds 500 grams of water?

Answer

$$500\text{ g} \times \frac{1\text{ mole}}{18\text{ g}} = 28\text{ moles}$$

$$28\text{ moles} \times 1.44\text{ kcal/mole} = 40\text{ kcal to freeze 500 g } H_2O$$

Pr. 13. List three heterogeneous materials not given in Sec. 5-2.1.

Answer

Concrete
A piece of wood
A brick wall
A mosaic
A piece of candy with a soft center
Milk

Changing the "scale" at which observation is made can lead to interesting discussion. What appears heterogeneous close up may seem uniform from a distance. Homogenized milk can be used as an example; it appears uniform, but it actually consists of small drops of butter fat suspended in a solution.

Pr. 14. List three homogeneous materials not given in Sec. 5-2.1.

Answer

Gasoline or many other liquid solutions
Any pure compound
Honey
Glass

Pr. 15. Which of the following statements about sea water is FALSE?

(a) It boils at a higher temperature than pure water.
(b) It melts at a lower temperature than pure water.
(c) The boiling point rises as the liquid boils away.
(d) The melting point falls as the liquid freezes.
(e) The density is the same as that of pure water.

Answer: (e).

Pr. 16. How many grams of methanol, CH_3OH, must be added to 2.00 moles of H_2O to make a solution containing equal numbers of H_2O and CH_3OH molecules. How many molecules (of all kinds) does the resulting solution contain?

Answer

To obtain a solution containing equal numbers of H_2O and CH_3OH molecules, we must mix equal numbers of moles. To 2.00 moles of water we must add 2.00 moles of CH_3OH. The molecular weight of CH_3OH is 32.0, so 64.0 g contain 2.00 moles.

The solution contains 4.00 moles, hence

$$(4.00) \times (6.02 \times 10^{23}) = 2.41 \times 10^{24}\text{ molecules}$$

Pr. 17. How many grams of ammonium chloride, NH_4Cl, are present in 0.30 liter of a 0.40 *M* NH_4Cl solution? *Answer:* 6.4 grams.

Answer

$$(0.30\text{ liter})(0.40\text{ mole/liter}) = 0.12\text{ mole } NH_4Cl$$
$$(0.12\text{ mole})(53.5\text{ g/mole}) = 6.4\text{ g } NH_4Cl$$

Pr. 18. Write directions for preparing the following aqueous solutions:

(a) 1.0 liter of 1.0 *M* lead nitrate, $Pb(NO_3)_2$, solution.
(b) 2.0 liters of 0.50 *M* ammonium chloride, NH_4Cl, solution.
(c) 0.50 liter of 2.0 *M* potassium chromate, K_2CrO_4, solution.

Answer

(a) (1.0 liter)(1.0 mole/liter) = 1.0 mole $Pb(NO_3)_2$ needed. Therefore, dissolve 331 g of $Pb(NO_3)_2$ in sufficient water to make the final volume equal to 1.0 liter.

(b) (2.0 liters)(0.50 mole/liter) = 1.0 mole NH_4Cl needed. Therefore, dissolve 54 g of NH_4Cl in sufficient water to make the final volume equal to 2.0 liters.

(c) (0.50 liter)(2.0 moles/liter) = 1.0 mole K_2CrO_4 needed. Therefore, dissolve 194 g of K_2CrO_4 in sufficient water to make the final volume equal to 0.50 liter.

Pr. 19. How many liters of 0.250 *M* K_2CrO_4 solution contain 38.8 grams of K_2CrO_4?

Answer

$$38.8\text{ g} \times \frac{1}{194\text{ g/mole}} = 0.200\text{ mole } K_2CrO_4$$

$$0.200\text{ mole} \times \frac{1\text{ liter}}{0.250\text{ mole}} = 0.800\text{ liter}$$

Pr. 20. List three properties of a solution you would expect to vary as the concentration of the solute varies.

Answer

(a) Density
(b) Boiling point
(c) Viscosity
(d) Color in some cases
(e) Freezing point
(f) Chemical action

Pr. 21. Give two forces other than electric that are felt at a distance.

Answer

Gravitational
Magnetic

Pr. 22. What would you expect to observe if one electrometer sphere were charged by your hair and the other by the comb used to comb your hair?

Answer

They would be attracted just as the comb attracted your hair.

Pr. 23. Why do scientists claim there are only two kinds of electric charge?

Answer

No others have been found. This is discussed on p. 174.

Pr. 24. It is known that electric charges attract or repel each other with a force that is inversely proportional to the square of the distance between them. If two spheres like those in the electrometer (Figure 5-7) are negatively charged, what would be the change in the force of repulsion if the distance between them were increased to four times the original distance?

Answer

As the spheres move apart, the force of repulsion decreases. The quantitative dependence is proportional to $1/r^2$, so if r changes by 4, the force decreases by the factor $1/4^2 = \frac{1}{16}$.

Pr. 25. Why do two electrically neutral objects with mass attract each other?

Answer

The attraction of objects with mass is a fundamental property of matter. There is no model to explain this. The answer "Because of gravity" of course explains nothing; it is just the name of the mystery.

Pr. 26. Each of the following ionic solids dissolves in water to form conducting solutions. Write equations for each reaction.

(a) potassium chloride, KCl.
(b) sodium nitrate, $NaNO_3$.
(c) calcium bromide, $CaBr_2$.
Answer:
$CaBr_2(s) \longrightarrow Ca^{+2}(aq) + 2Br^-(aq)$.
(d) lithium iodide, LiI.

Answer

(a) $KCl(s) = K^+(aq) + Cl^-(aq)$
(b) $NaNO_3(s) = Na^+(aq) + NO_3^-(aq)$
(c) $CaBr_2(s) = Ca^{+2}(aq) + 2Br^-(aq)$
(d) $LiI(s) = Li^+(aq) + I^-(aq)$

Pr. 27. A chloride of iron called ferric chloride, $FeCl_3$, dissolves in water to form a conducting solution containing ferric ions, Fe^{+3}, and chloride ions, Cl^-.

(a) Write the equation for this reaction.
(b) If 0.10 mole of $FeCl_3$ is dissolved in 1.0 liter of water, what is the concentration of ferric ion and of chloride ion?

Answer: concentration of $Fe^{+3} = 0.10\ M$
concentration of $Cl^- = 0.30\ M$

Answer

(a) $FeCl_3(s) \longrightarrow Fe^{+3}(aq) + 3Cl^-(aq)$
(b) 0.10 mole of $FeCl_3$ gives 0.10 mole of Fe^{+3} ions and 0.30 mole of Cl^- ions. Hence, the concentrations are:

$$[Fe^{+3}] = \frac{0.10\text{ mole}}{1.0\text{ liters}} = 0.10\ M$$

$$[Cl^-] = \frac{0.30\text{ mole}}{1.0\text{ liters}} = 0.30\ M$$

Pr. 28. The salt ammonium sulfate, $(NH_4)_2SO_4$, dissolves in water to form a conducting solution containing ammonium ions, NH_4^+, and sulfate ions, SO_4^{-2}.

(a) Write the balanced equation for the reaction when this ionic solid dissolves in water.
(b) Verify the conservation of charge by comparing the charge of the reactant to the sum of the charges of the products.
(c) Suppose 1.32 grams of ammonium sulfate is dissolved in 0.500 liter of water. Calculate the concentrations of $NH_4^+(aq)$ and $SO_4^{-2}(aq)$.

Answer

(a) $$(NH_4)_2SO_4(s) \longrightarrow 2NH_4^+(aq) + SO_4^{-2}(aq)$$

(b) reactant — products

0 charge — $2(1+) + (2-) = (2+) + (2-) = 0$

(c) The number of moles in 1.32 g of $(NH_4)_2SO_4$ is $\dfrac{1.32\text{ g}}{132\text{ g/mole}} = 0.0100$ mole

moles $NH_4^+ = 2(0.0100) = 0.0200$ mole
moles $SO_4^{-2} = 0.0100$ mole

concentration NH_4^+

$$= [NH_4^+] = \frac{0.0200\text{ mole}}{0.500\text{ liter}} = 0.0400\ M$$

concentration SO_4^{-2}

$$= [SO_4^{-2}] = \frac{0.0100\text{ mole}}{0.500\text{ liter}} = 0.0200\ M$$

Pr. 29. 1.00 liter of solution contains 0.100 mole of ferric chloride, $FeCl_3$, and 0.100 mole of ammonium chloride, NH_4Cl. Calculate the concentrations of Fe^{+3}, Cl^-, and NH_4^+ ions.

Answer: conc. $Fe^{+3} = 0.100\ M$
conc. $NH_4^+ = 0.100\ M$
conc. $Cl^- = 0.400\ M$

Answer

$$FeCl_3(s) \longrightarrow Fe^{+3}(aq) + 3Cl^-(aq)$$
$$NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

From 0.100 mole of $FeCl_3$, we obtain 0.100 mole of Fe^{+3} ions and 0.300 mole of Cl^- ions. From 0.100 mole of NH_4Cl, we obtain 0.100 mole of NH_4^+ ions and 0.100 mole of Cl^- ions. Hence

$$[Fe^{+3}] = \frac{0.100\text{ mole}}{1.00\text{ liter}} = 0.100\ M$$

$$[NH_4^+] = \frac{0.100\text{ mole}}{1.00\text{ liter}} = 0.100\ M$$

$$[Cl^-] = \frac{0.300 + 0.100\text{ mole}}{1.00\text{ liter}} = 0.400\ M$$

Pr. 30. In Expt. 10 you mixed lead nitrate and sodium iodide. Write an equation for the reaction that occurred. Show only the predominant reacting species.

Answer

$$Pb^{+2}(aq) + 2I^-(aq) = PbI_2(s)$$

Pr. 31. Write equations for the reactions between aqueous bromide ions and:
(a) aqueous lead ions
(b) aqueous silver ions
Both lead bromide, $PbBr_2$, and silver bromide, AgBr, are only slightly soluble.

Answer

(a) $Pb^{+2}(aq) + 2Br^-(aq) = PbBr_2(s)$
(b) $Ag^+(aq) + Br^-(aq) = AgBr(s)$

Pr. 32. When solutions of barium chloride, $BaCl_2$, and potassium chromate, K_2CrO_4, are mixed, the following reaction occurs:

$$2K^+(aq) + CrO_4^{-2}(aq) + Ba^{+2}(aq) + 2Cl^-(aq) \longrightarrow BaCrO_4(s) + 2K^+(aq) + 2Cl^-(aq)$$

(a) Show how charge is conserved.
(b) Rewrite the equation showing predominant reacting species only.
(c) Suppose 1.00 liter of 0.500 M $BaCl_2$ is mixed with 1.00 liter of 0.200 M K_2CrO_4. Assuming $BaCrO_4$ has negligible solubility, calculate the concentrations of all ions present when precipitation stops.

Answer: conc. $K^+ = 0.200\ M$
conc. $Cl^- = 0.500\ M$
conc. CrO_4^{-2} = negligible
conc. $Ba^{+2} = 0.150\ M$

Answer

Emphasize net ionic equations and balance of charge.

(a) The sum of the electric charges among the reactants is:

$$\begin{array}{ccccccc} 2K^+(aq) & + & CrO_4^{-2}(aq) & + & Ba^{+2}(aq) & + & 2Cl^-(aq) \\ (2+) & + & (2-) & + & (2+) & + & (2-) \end{array} = 0$$

The sum of the electric charges among the products is:

$$\begin{array}{ccccc} BaCrO_4(s) & + & 2K^+(aq) & + & 2Cl^-(aq) \\ (0) & + & (2+) & + & (2-) \end{array} = 0$$

Summing these charges, we find that since $0 = 0$, charge has been conserved.

(b) $CrO_4^{-2}(aq) + Ba^{+2}(aq) = BaCrO_4(s)$

(c) 0.500 M $BaCl_2$ contains 0.500 M Ba^{+2} and 1.00 M Cl^-.
0.200 M K_2CrO_4 contains 0.400 M K^+ and 0.200 M CrO_4^{-2}.

When the two solutions are mixed, the volume is doubled, so the concentrations of Cl^- and K^+ are halved.

$$[K^+] = 0.200\ M$$
$$[Cl^-] = 0.500\ M$$

In addition, the reaction

$$Ba^{+2}(aq) + CrO_4^{-2}(aq) \longrightarrow BaCrO_4(s)$$

will occur as long as both Ba^{+2} and CrO_4^{-2} remain (assuming negligible solubility of $BaCrO_4$). Sincc there is an excess of Ba^{+2}, virtually all of the CrO_4^{-2} will be consumed.

$$[CrO_4^{-2}] = \text{negligible}$$

The solution originally contained 0.500 mole of Ba^{+2} but 0.200 mole are precipitated by the CrO_4^{-2}. The remaining 0.300 mole of Ba^{+2} is dissolved in 2.00 liters, hence

$$[Ba^{+2}] = \frac{0.300\text{ mole}}{2.00\text{ liters}} = 0.150\ M$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1 and 2 refer to an experiment in which solid copper is heated to melting.

$$3.11\text{ kcal} + \text{Cu}(s) \longrightarrow \text{Cu}(l) \quad \text{m.p.} = 1083°\text{C}$$

The liquid copper is heated until it is changed into vapor.

$$72.8\text{ kcal} + \text{Cu}(l) \longrightarrow \text{Cu}(g) \quad \text{b.p.} = 2582°\text{C}$$

1. How much heat is required to melt 6.35 g of Cu?

   Answer: 311 cal.

2. How much heat is required to vaporize 6.35 g of Cu?

   Answer: 7280 cal.

   Consider the system described below in answering questions 3–9.

   A flask is half full of 1.00 *M* sodium carbonate, Na_2CO_3, solution with solid water (ice) floating in the solution. The system has been standing long enough for equilibrium to have become established. The flask is stoppered.

3. How many phases are present in the entire system? Describe them. (Neglect the flask and stopper.)

   Answer

   Three. They are (1) the gas phase above the liquid; (2) the solid water; and (3) the salt solution.

4. Which of the phases present is a pure substance?

   Answer: Solid water.

5. How many grams of Na_2CO_3 are dissolved in 500 ml of the 1.00 *M* solution?

   Answer

   A 1.00 *M* solution of Na_2CO_3 contains 106 g/liter.

   $$\frac{106\text{ g}}{\text{liter}} \times 0.5\text{ liter} = 53\text{ g}$$

6. The solution is heated until it begins to boil. The atmospheric pressure is 760 mm of Hg. Will the boiling temperature be 100°C, higher, or lower than 100°C?

   Answer

   It will be higher than 100°C (see Figure 5-4 on p. 70 of the Textbook).

7. Describe a method by which the components of the solution may be separated.

   Answer

   Student description. Distillation would be best.

8. When $Na_2CO_3(s)$ dissolves in water, sodium ions, $Na^+(aq)$, and carbonate ions, $CO_3^{-2}(aq)$, are present in the solution. Write an equation to represent this reaction.

   Answer

   $$Na_2CO_3(s) \longrightarrow 2Na^+(aq) + CO_3^{-2}(aq)$$

9. Would you expect the sodium carbonate solution to be a good conductor of electricity? Why?

   Answer

   Yes. The charged particles (ions) act as charge carriers in solution, thereby completing the circuit between the immersed electrodes.

10. If 40 grams of calcium bromide, $CaBr_2$, are dissolved in 100 ml of aqueous solution (total volume of salt and water is 100 ml), what is the concentration of the solution in moles/liter?

    Answer

    $$\frac{40\text{ g}/0.1\text{ liter}}{200\text{ g/mole}} = 2\text{ moles/liter or } 2\ M$$

The next three questions refer to this experiment.

A heavy wall flask is partially evacuated to 500 mm Hg pressure of air. A small amount of benzene is introduced into the flask in order that some liquid will remain after equilibrium has been established. The vapor pressure of benzene at room temperature, 21°C, is about 80 mm Hg.

11. What will the total pressure in the flask be at equilibrium at 21°C?

    Answer: 580 mm Hg.

12. If a little more benzene (negligible volume change) is added to the flask, how will this affect the total pressure of the system?

    Answer
    The total pressure of the system will remain essentially unchanged.

13. If the temperature of the system is increased, what will happen to the pressure? Why?

    Answer
    It will increase because the air pressure and vapor pressure increase on heating.

14. Imagine two positively charged ions of 1+ charge each are held 2 Å apart. Two other negatively charged ions of 1− charge each are held 3 Å apart.

    What is the nature of the force between the 1+ ions (repulsion or attraction)?

    Answer: Repulsion.

15. What is the nature of the force between the 1− ions (repulsion or attraction)?

    Answer: Repulsion.

16. How does the magnitude of the electrostatic force exerted between ions of the first pair compare to that between the ions of the second pair?
    (1) The force in the first pair is greater than that in the second pair.
    (2) The force in the second pair is greater than that in the first pair.
    (3) The same force for either pair.

    Answer
    (1) The force in the first pair is greater than that in the second pair.

17. A few drops of 0.1 *M* $FeCl_3$ are mixed with a few drops of 0.1 *M* KOH (which gives K^+ and OH^-). The mixture produces a precipitate. When a few drops of the $FeCl_3$ solution are mixed with a few drops of KNO_3 solution, no precipitate forms. Write the net ionic equation representing the reaction which occurred between the $FeCl_3$ and KOH solutions.

    Answer

    $Fe^{+3}(aq) + 3OH^-(aq) = Fe(OH)_3(s)$

CHAPTER

6

STRUCTURE OF THE ATOM AND THE PERIODIC TABLE

Intent and Approach

Chapter 6 is an introduction to atomic structure and the periodic table. As the course advances, Chapters 14, 15, 19, 20, 21, and 22 will add much more information about the table and treat it in depth. This chapter is confined to a study of experimental facts; trends in these facts are pointed out, but the effort to explain them and correlate them with structural theory is just barely started.

This chapter describes the nuclear atom to show how the elements differ in atomic structure. After that the details of periodic properties are given by demonstration. Then the table is discussed as an expression of "regularity." This approach convinces the students of the need for some sort of system for organizing information. The periodic table does this for a tremendous number of chemical facts. The electron structure of the inert gases is used as a basis for organizing the regularities that occur in elements and, later, in compounds.

In this chapter the student will be exposed to many concepts and chemical facts. You must exercise care in order that neither you nor the student will feel buried by the flood. At this stage, center the student's attention on the chemistry which most pointedly displays the family relationships and periodicity. Remember that several later chapters will also deal with the periodic table.

Outline

1. The introduction to this chapter points out the tremendous variety in chemicals and in their properties.
2. The nuclear atom (6-1.1) is discussed as a model.
3. The parts of the atom are discussed, and their mass (6-1.2) and size (6-1.3) revealed.
4. Atomic number (6-1.4) is established as the property that identifies the element and its chemistry.
5. Isotopes are described (6-1.5).
6. The inert gases are the first family of elements discussed as the group of elements around which the table is constructed. Their boiling points, melting points, and atomic volume are discussed as pertinent properties (6-2.1–6-2.4).
7. The alkali metals, as a group of elements next to the inert gases but having one more electron, are considered via the same properties as the inert gases (6-3.1). Systematic variation from inert gas behavior is noted. The chemistry of the alkalies is also discussed through their reactions with chlorine and water (6-3.2).
8. The halogens are considered next as the group adjacent to the inert gases and having one less electron. Again, pertinent properties and reactions are discussed and systematic variation noted, particularly for halide ions (6-4.1–6-4.3).

9. Hydrogen, as a family by itself, is shown to be somewhat like the alkali metals and also like the halogens. It has a unique position (6-5.1–6-5.2).
10. The third-row elements are then considered and some pertinent properties discussed (6-6.1). A major emphasis is placed on compound formation and the pattern in the formulas. Hydrides, chlorides, and oxides are used as examples (6-6.2).
11. The periodic table is briefly summarized (6-7).

New Concepts

1. The structure of the nuclear atom is discussed.
2. The periodic arrangement of elements emerges as a regularity.
3. The inert gases are chemically distinctive because they have relatively little chemical activity.
4. Other elements tend to form the electron arrangement of the inert gases, and approach inert gas stability.

Development

INTRODUCTION

This chapter should be introduced by emphasizing the tremendous variety exhibited by the elements. One form of the variety lies in the range of melting points, from a few degrees Kelvin to above 1000°K. Such ranges are represented by the specific elements studied in this chapter. Another varying property is chemical reactivity. The elements considered in this chapter also illustrate a great range of this property.

There are about 100 elements, most of them capable of reaction, and there are about 100,000 *inorganic* compounds known. To remember several dozen facts about even a fraction of these is impossible. System and order must be discovered and used.

To develop this idea you might exhibit quite a sizeable number of elements and compounds from the stock room. Make the exhibit haphazard, so that no particular order is evident, and suggest to students what a job it would be for them if you started ticking off the properties of each element and saying that they were responsible for learning them all.

If you use elements only, then you can start a lively discussion by asking the students to group the materials. You may get a metal-nonmetal classification, a ranking by color, density or hardness, or some other property. This exercise allows you to emphasize that the table permits the correlation of many experimental facts. Later in the semester we will be involved in explaining some of these properties.

STRUCTURE OF THE ATOM (6-1)

A Model: The Nuclear Atom (6-1.1)

At this stage of the course, only a general description of the atom should be given. Such a description might be summarized as follows. An atom is a small particle made up of a very small nucleus (containing neutrons and protons) surrounded at relatively great distances by electrons (same number as protons). The reasons for this approach are (1) no further description is needed at this time, (2) Chapters 15 and 16 expand the topic greatly, and (3) we wish to avoid the Bohr planetary model of the atom. The planetary atom is known to be incorrect in many respects. It gives erroneous energy levels

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
S 6-1/6-1.5 (pp. 86–90)	1	Discussion		1, 4, 8	2, 3, 5, 9–11	6, 7	The Nuclear Atom
S 6-2/6-2.4 (pp. 90–93)	2	Discussion Film: CHEMICAL FAMILIES		13	12, 14, 15		Periodic Table, Inert Gases
S 6-3/6-3.2 (pp. 93–96)	3	Discussion*	1	16	17	18	Alkali Metals
S 6-4/6-4.3 (pp. 96–99)	4	Discussion*		19, 22	20, 21		Halogens
S 6-5/6-5.2 (pp. 99–101)	5	Discussion*				23	Hydrogen
S 6-6/6-7 (pp. 101–104)	6	Discussion*		24	25–27, 29, 30	28, 31	Third-row Elements
	7	Review, Quiz					

* Parts of the film may be shown again.

for all atoms having two or more electrons. Even for the hydrogen atom, it suggests the electron has a trajectory, a conclusion which is not supported by quantum mechanics.

Chemists and physicists, who use the atomic theory most, are keenly aware of the parts of the theory that are firmly grounded and the parts that are tentative. In teaching the theory *you should make the same distinctions*. For instance, the existence of a very small, dense nucleus is firmly based upon experiment. Any description of "where an electron is" is not. The nature of the forces which hold the nucleus together, despite the coulombic repulsion, is also not understood. If asked why the nucleus remains intact, you can answer correctly by saying that since it does, there must be other forces (attractive) which dominate the coulombic forces, but they are not understood.

The following sections describe aspects of the main concept of the nuclear atom.

The Mass of an Atom and Its Parts (6-1.2)

The Sizes of Atoms (6-1.3)

Atomic Number (6-1.4)

Mass Number and Isotopes (6-1.5)

The *Background Discussion* contains relevant material.

THE SIMPLEST CHEMICAL FAMILY—THE INERT GASES (6-2)

Take up the inert gases first. This is not the historical order of development, but it provides a key group to start with and gives a good point of departure for the brief account of electron arrangement given here.

In discussing the inert gases, emphasize the fact that properties of a group are being considered rather than properties of a single element. A group is shown as a column in the form of periodic table that we use.

The inert gases, having almost no chemistry, being colorless gases, and also not being readily available in high school laboratories, are a little hard to put before the student in a live demonstration. However, neon signs are familiar to all; some incandescent bulbs contain argon; and a variety of gas discharge tubes are often a part of a school's complement of physics equipment. You may choose to utilize these facts to convey the reality of the inert gases to your students.

Since the inert gases have almost no chemistry, the only properties to be mentioned are physical properties. The Textbook, however, covers these properties adequately, and no classroom discussion should be needed. Merely point out that the physical properties of the inert gases do not identify the inert gases as a family. The real uniqueness of the inert gases is their slight chemical reactivity. Note that interpolation is not proper in a diagram such as Figure 6-3.

The final look at the inert gases should be directed at the electron arrangements of each. The number of electrons is even in all inert gases; there is a pattern—a regularity—to the differences in the number of electrons these gases possess. Compare the electron arrangement of argon with that of sodium and chlorine. In sodium chloride, there is an even number of electrons; both sodium and chlorine ions are like inert gases. The point is that chemical reaction leads to the imitation of inert gases.

The very recent discovery of the first compounds of inert gases [N. Bartlett, "Xenon hexafluoroplatinate (V)," *Proceedings of the Chemical Society* (London), 218 (1962); C. L. Chernick, et al., "Fluorine compounds of xenon and radon," *Science*, 138, 136–138 (1962)] can be used to illustrate several points. First, it is a beautiful example of the way in which new experimental discoveries can alter a well-established theory. Second, there are still exciting things to be found—some of them relatively simple. Third, some new ideas of bonding will probably result. Even so, the new results do not vitiate the remarks in the Textbook. The inert gases *are* quite inert and do act as a unifying group for the periodic table.

The work reviewed by the second paper cited above shows that Xe and F_2 react in one hour, at about 400°C to give XeF_4 (and, after photolysis, XeF_2), a colorless solid melting near 90°C. It crystallizes in small cubes and looks like NaCl. Preliminary infrared and X-ray results imply it has a square planar, not a tetrahedral, structure. Radon forms similar compounds. Note that reactions with fluorine are to be undertaken only by those with some knowledge of the dangers. These new compounds are not suitable for study by beginning students.

THE ALKALIES (6-3)

Again, emphasize to the student that he is studying a group of elements, and thus systematizing his accumulating knowledge of chemistry. This group of elements has one more electron than the nearest inert gas. These elements achieve the inert gas configuration by losing one electron to form positive ions.

Point out their characteristics as metals, and then concentrate on the properties listed in Table 6-V of the Textbook. It is again best for you to prepare charts in graphic form of the tabulated data unless you feel that students should prepare their own graphs for this group of elements.

To answer the question of the opposite trends for melting point in alkali metals as contrasted with inert gases, suggest a difference in "bonding," and postpone giving a specific answer until Chapter 17. Very briefly, the answer follows these lines. The inert gas atoms of higher atomic number have more electrons and are larger. These larger atoms develop greater attraction and have higher melting points. The alkali metal atoms also become larger and have more electrons as atomic number goes up. But the important number of valence electrons (one in this case) does not increase; the bonding strength does decrease, however, because other factors (atomic size) change.

Unlike the inert gases, the alkali metals exhibit a very observable chemistry. Sodium may be used as representative in a demonstration, though it surely won't be needed if the film CHEMICAL FAMILIES is shown.

(a) Cut two small pieces of sodium metal (smaller than a pea) such that clean surfaces are exposed. Place one piece in a bottle full of air or oxygen gas. Drop the second piece into a bottle of *dry* chlorine gas and let it stand. Observe the rate at which the white reaction products form.

(b) Cut a third small piece of sodium metal (less than half the size of a pea). Work behind a glass plate for protection against spattering. Drop the sodium in pure water. Observe the rate of the reaction.

The reaction of sodium and chlorine is described in *Tested Demonstrations* (p. 58).

Go on to discuss the reaction of the alkali metals with chlorine and water, both of which are demonstrated in the film CHEMICAL FAMILIES. All of these reactions produce highly stable, inert gas-like ions from the alkali metal atoms. Summarize the discussion of the alkali metals by contrasting the reactivity of the atoms with the stability of the ions.

THE HALOGENS (6-4)

Point out that a neutral atom for any element in this group is just one short of having the electron number of the nearest inert gas. It would be perfectly natural to expect these elements to enter reactions that would lead to the acquisition of electrons. In fact, the reaction of sodium and chlorine cited for the alkalies already says as much.

However, these elements already exist as diatomic molecules, which gives them some of the inert gas stability as elements. Point out that a concept of shared electrons suggests a molecular structure in which the two atoms of the molecule have the inert gas number of electrons. The existence of such molecules also leads to particular physical properties.

A student may wonder why a diatomic halogen molecule should react, since it already "has" an inert, gas-like electronic arrangement. At this stage the best answer is that the diatomic molecule is only one such arrangement and that, from the experimental evidence given by the reaction of sodium with chlorine, others are possible. Emphasize that the tendency toward the inert gas arrangement is shown by all these reactions.

This section introduces the covalent bond, just as the last section introduced the ionic bond. Some students may be inquisitive about "what is a bond." Don't try to give a full answer, but you can indicate (in anticipation of Chapter 15) that the bond results from the especially attractive position of electrons between atomic nuclei and that different types of bonds come from different positioning of the electrons.

Examination of the trends in Textbook Table 6-VI shows that the halogens resemble the inert gases. Melting points and boiling points are systematically higher than the inert gases, yet low enough to suggest weak intermolecular forces. The fact that the liquid phase exists over short temperature ranges suggests a small energy difference between solid, liquid, and gas phases. The increase in atomic volume is evident.

As do the alkali metals, the halogens show definite chemical reactivity. They pick up electrons to gain a configuration like that of the inert gases in terms of stability. You may wish to demonstrate the production of Cl_2, Br_2, and I_2 and give some examples of their reactions to supplement the chemistry shown in the film CHEMICAL FAMILIES. *Do not use* potassium—it detonates with Br_2 and I_2.

All the halogens attract electrons, and, in water solution, their tendency to form ions decreases from fluorine to iodine. Later (Chapter 19) you can give some of the details of the postulated processes involved.

Electrons can be shared between atoms of different elements, forming relatively stable compounds. Hydrogen halides are illustrative of this. As dry gases, they are mostly covalent molecules. When put in water, they react with water, giving ions.

HYDROGEN—A FAMILY BY ITSELF (6-5)

The properties cited in the section under this title are used to show that hydrogen is unique. It should be included in neither the alkali nor the halogen group, because reliable predictions cannot be made from such a grouping. This conclusion should cause no disturbance. Hydrogen doesn't *have* to fit into one of the families. The periodic table only states what regularities *do* exist among the elements. We must let experimental facts tell us what hydrogen "should" do.

THE THIRD-ROW ELEMENTS (6-6)

Up to this point, Chapter 6 has focused on three well-defined vertical columns in the table. The properties of the elements in these three columns have been made quite evident. The question still remains, "How about the other vertical groups of the table?" Rather than study each group in a manner similar to that used for the inert gases, the alkalies, and the halogens, the third-row elements are chosen as representatives of their particular groups, and the emphasis is placed on horizontal changes in properties. The same properties as considered for the three groups are enumerated in Table 6-VIII of the Textbook.

The pattern of compound formation is given in Table 6-IX (Textbook). On the basis of the idea that hydrogen must gain or share one more electron to be like helium, students can draw an inference as to how far from an inert gas form each element is when in the elementary state. Chlorine is also a known element in the sense that it needs to gain one electron to resemble argon. You might ask students whether the formulas of the chlorides are consistent with those of the hydrides. They are, in general. The same judgment can be asked for with respect to the oxides. Remember that some of the formulas shown are empirical, others molecular. You can touch lightly on nomenclature by asking for the names of some of the compounds in Table 6-IX (Textbook).

THE PERIODIC TABLE (6-7)

The Textbook very briefly describes some of the history of the thinking that gave rise to the table. This is all the history that is needed. Anyone particularly interested can be directed to Mendeleev's original paper (in English) in the *World of Mathematics*, Vol. II, pp. 913–918; Editor, J. R. Newman, Simon and Schuster, 1956.

To summarize the chapter, try reviewing the student's acquaintance with the elements. Emphasize to the student that he can now claim an ordered knowledge about the properties of twenty elements and some of their compounds. Further, their ordered acquaintance forms the basis for some fairly good guesses about the properties of other elements and their compounds.

Supplementary Material

Books

H. N. Alyea and F. B. Dutton, *Tested Demonstrations in Chemistry*, Journal of Chemical Education, Easton, Pa. (1960).

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

CHEMICAL FAMILIES

A CHEM Study film

Running Time: 22 minutes

This film, made in collaboration with Drs. J. A. Campbell and J. L. Hollenberg, provides direct experimental support for this chapter. It was produced because the absence of chemistry of the inert gases is inherently difficult to demonstrate convincingly and because the chemistry of the alkali metals and the halogens is hazardous. Some of the content of the film is susceptible to classroom demonstration, but, owing to the excellent, close-up color views provided by the film, the demonstration is probably less effective.

Samples of most of the elements are shown, and the great differences among them are demonstrated. Ordering is begun by segregating metals and nonmetals on the basis of electrical conductivity. Then the gases are further subdivided according to reactivity, thus singling out the inert gas family. Thereafter, the film focuses on actual laboratory demonstrations of the chemistry of the alkalies and the halogens, following closely the development in the Textbook.

Background Discussion

SUBATOMIC PARTICLES

These details of how the particles were characterized are for your use only. Do not elaborate greatly on the Textbook here. We have already considered two charged particles, the electron and the proton. These have masses smaller than that of the lightest atom, the hydrogen atom. Deflection experiments (discussed in this guide for Chapter 14) show that the mass of slow-moving (charge 1−) electrons is $\frac{1}{1840}$ that of the hydrogen atom. The mass of the proton (charge 1+) is substantially equal to the mass of the hydrogen atom. The difference is the mass of an electron. Thus the mass of the hydrogen atom is equal to the combined masses of one proton and one electron.

No negatively charged particle lighter than the electron has been discovered. In 1932, C. A. Anderson, an American physicist, discovered a transitory, positively-charged particle having the same mass as the electron. This particle, usually called the positron, but sometimes the positive electron, exists independently only for very short periods of time. Since, in chemistry, we are interested in more stable particles, we shall not need to consider the positron here. A number of other particles, called mesons, also are formed in bombardment reactions involving very high energy. Mesons have masses between that of the electron and that of the proton; some have no charge, and others have a charge of 1− or 1+. The mean lifetime of a meson is only about 10^{-6} second. Mesons, like the positron, play no significant role in chemistry.

Another particle, discovered in 1932 by James Chadwick, an English physicist, is important to us. It is the *neutron*, a neutral particle having approximately the same mass as the proton. It is hard to detect and control (because it has no charge). Its mass is made evident by the effect it produces when it collides with atoms.

THE NUCLEAR ATOM

The nuclear theory of the atom was proposed by E. Rutherford in 1911 on the basis of the scattering experiment described in Chapter 14. Rutherford's explanation of his scattering data was that the mass of the atom and all the positive charge of an atom is concentrated in a tiny nucleus and that electrons occupy the space in the atom around the nucleus.

This theory laid the basis for modern atomic structure. It leaves open several questions:

1. What is the internal structure of the nucleus?
2. How are the electrons arranged around the nucleus?
3. How do the atoms of different elements differ in structure?

The first question is still unanswered, and is the subject of intensive research by nuclear scientists. At present we employ certain rules which lead to the observed charges and masses of nuclei. We are much less certain about the structure of the nucleus than about other details of atomic structure.

The second question will be considered throughout the rest of the course (especially Chapter 15). It is very closely tied to chemistry. We shall now consider the third question.

ISOTOPES

Different forms of an element were first recognized in the products from radioactive disintegration of atoms. The British chemist F. Soddy, in 1913, called the different forms isotopes (isotopes occupy the same place, chemically, in the periodic table).

The separation of isotopes was first accomplished in the same year, when J. J. Thomson found that neon gas contained two kinds of atoms having masses 20 and 22. He found no atoms having masses 20.2, the average weight of the atoms. All other elements whose atomic weights depart substantially from whole numbers consist of a mixture of two or more kinds of atoms. All the isotopic atoms have the same nuclear charge; they differ in mass number. The element neon consists mainly of two isotopes, neon-20 (^{20}Ne) and neon-22 (^{22}Ne). The mass numbers are used to identify the different species of atoms in an element.

Thus we see that it is the atomic number rather than the mass that identifies an element. The atomic number characterizes an element precisely; the mass of the atom does not.

Some elements—for example, fluorine, sodium, aluminum, phosphorus, all of which are odd-numbered elements—have only one naturally occurring nuclear species. Most elements have two or more naturally occurring isotopes; tin has ten. About 300 naturally occurring nuclear species are known for the first 92 elements, and more than 1000 have been made in nuclear bombardment reactions. Isotopic species have been made and identified for all the elements.

ELECTRONS IN ATOMS

Because all the atoms of an element have the same nuclear charge, they must have the same number of electrons in the neutral atom. These electrons surround the nucleus in a manner which in some aspects, but not all, resembles an electron cloud. It is the electron cloud of an atom that is primarily responsible for the chemical behavior of the atom. Chapters 15, 16, and 17 cover this in detail.

Different isotopes of an element have essentially the same chemical properties because their nuclei have the same charge and their electron clouds have identical form. The isotopes differ only in those properties that are related to the mass of the atom.

The electrons of an atom are arranged in a series of orbitals in such a way that the inner orbitals are filled. The electrons outside the filled orbitals are the ones that interact most strongly when two atoms are brought together. These outer electrons are called *valence electrons*. They will be discussed and correlated with chemical behavior in later chapters.

THE FORM OF THE PERIODIC TABLE

A great many forms of the periodic table have been published, employing concentric circles, stair-steps, and helical arrangements. Each physical arrangement has advantages for displaying the regularity of a particular property, but the *long form* used in this course was selected because it best fits the needs of most practicing chemists.

The table is arranged into *rows* and *columns*. The first row contains 2 elements; the second row, 8; the third row, 8; the fourth row, 18; the fifth row, 18; the sixth row, 32; and the seventh row is incomplete. The nuclei of the atoms of the seventh-row elements are unstable. None of the elements beyond uranium, number 92, occurs naturally in recoverable quantities.

The elements in a single vertical column of the table constitute a *chemical group*, or *family*. Some groups, or families, are given names; for example, the alkali elements and the halogen family. Sometimes the groups are identified by a *group number*, as shown on your wall chart of the periodic table. Unfortunately, different systems of numbering are in common use. To avoid misunderstanding, name the families rather than number them.

THE RULE OF EIGHT

In traditional high school chemistry courses a major emphasis in chemical bonding has been given to the "rule of eight." Table 6-IV of the Textbook reveals, however, that this rule, based on the presence of eight electrons in the outer energy levels, may work for the second and third rows of the periodic table, but not for hydrogen in the first row or for the elements beyond argon. Indeed, we find that the rule of eight does not hold for some compounds in the second and third rows, such as phosphorus pentachloride (PCl_5), and for such compounds as sulfur tetrachloride (SCl_4) or sulfur hexafluoride (SF_6). Do not teach this rule. Wait for orbital and other representations (Chapter 15). Instead, stress the special stability of the inert gas population.

A fuller discussion of chemical bonding will occur in later chapters. For the present, we shall restrict ourselves to interpretations of bonding which have rather general application. In a number of introductory courses, ionic bonding has been given undue emphasis. We shall limit our application of this concept to substances in which the presence of ions is clearly indicated. Both ionic and covalent bonding will be discussed in terms of electrons attracted to two positive nuclei.

SOME TRENDS IN THE FOURTH-ROW ELEMENTS

The next row of elements (taking out the transition elements) follows the same trends the Textbook discusses for row three (Sec. 6-6.1). See Table 6-I (below), and use parts of it to reinforce the organization achieved by the periodic table. Pay particular attention to the chemical trends. As you can see from this table, and Textbook Table 6-IX (p. 102), there is often more than one oxide (or halide) for a given element. This is especially prevalent in the right portion of the table. Keep the discussion limited here so as not to confuse the student with too many exceptions. Nitrogen oxides are a prime example, N_2O, NO, N_2O_3, NO_2, and N_2O_5 all being known. Judicious selection has been used in the tables.

Table 6-I. **Some Properties of Elements in the Fourth (Short) Row of the Periodic Table**

	K	Ca	Ga	Ge	As	Se (gray)	Br	Kr
Hydrides	KH	CaH_2	$(GaH_3)_2$*	GeH_4	AsH_3	SeH_2	BrH	—
Chlorides	KCl	$CaCl_2$	$GaCl_3$	$GeCl_4$ $(GeCl_2)$	$AsCl_3$	Se_2Cl_2	BrCl	—
Oxides	K_2O†	CaO	Ga_2O_3	GeO_2 (GeO)	As_2O_3** As_2O_5	SeO_2	Br_2O	

[*] Compounds in parentheses are known but are not common.

[†] These oxides can be formed, but in a normal reaction between metal and oxygen, the products are KO_2 and RbO_2. They are called hyperoxides. They have the NaCl-type crystal lattice, in which each chlorine atom is replaced by an O_2 group.

[**] Molecular weight determinations show this to really be As_4O_6 in the vapor phase below about 800°C.

Answers to Exercises and Problems

Ex. 6-1. Write the equations for the reactions between water and: lithium, potassium, rubidium, cesium.

Answer

$$2Li(s) + 2H_2O = 2Li^+(aq) + 2OH^-(aq) + H_2(g) + \text{energy}$$

$$2K(s) + 2H_2O = 2K^+(aq) + 2OH^-(aq) + H_2(g) + \text{energy}$$

$$2Rb(s) + 2H_2O = 2Rb^+(aq) + 2OH^-(aq) + H_2(g) + \text{energy}$$

$$2Cs(s) + 2H_2O = 2Cs^+(aq) + 2OH^-(aq) + H_2(g) + \text{energy}$$

Pr. 1. For which of the following processes will energy be absorbed?

(a) Separating an electron from an electron.
(b) Separating an electron from a proton.
(c) Separating a proton from a proton.
(d) Removing an electron from a neutral atom.

Answer

Processes (b) and (d). The release of energy when the fluorine atom acquires an electron can be regarded as an example of the reverse of (b).

Pr. 2. Which of the following statements is FALSE? The atoms of oxygen differ from the atoms of every other element in the following ways:

(a) the nuclei of oxygen atoms have a different number of protons than the nuclei of any other element;
(b) atoms of oxygen have a higher ratio of neutrons to protons than the atoms of any other element;
(c) neutral atoms of oxygen have a different number of electrons than neutral atoms of any other element;
(d) atoms of oxygen have different chemical behavior than atoms of any other element.

Answer: (b).

Pr. 3. For *every* atom, less energy is needed to remove one electron from the neutral atom than is needed to remove another electron from the resulting ion. Explain.

Answer

The first electron removed from a neutral atom leaves an ion with 1+ charge. Hence, work must be done to overcome the attraction between the negative electron and the resulting 1+ ionic charge. The second electron leaves an ion with 2+ charge. Hence, a larger amount of work must be done to overcome the additional attraction between the negative electron and the resulting 2+ ionic charge.

Pr. 4. List the number and kind of fundamental particles found in a neutral lithium atom that has a nucleus with a nuclear charge three times that of a hydrogen nucleus and with seven times the mass.

Answer

$3p$, $4n$, $3e^-$ (given in table).

Don't represent the electrons as orbiting around the nucleus. This picture is not consistent with modern quantum theory, and is not used in this course. Chapters 14–17 will cover the structure of atoms.

Pr. 5. The nucleus of an aluminum atom has a diameter of about 2×10^{-13} cm. The atom has an average diameter of about 3×10^{-8} cm. Calculate the ratio of the diameters.

Answer

If we let d = the diameter of the nucleus = 2×10^{-13} cm and D = the diameter of the atom = 3×10^{-8} cm, then the ratio is

$$\frac{d}{D} = \frac{2 \times 10^{-13}}{3 \times 10^{-8}} = \frac{2}{3} \times 10^{-5} = 0.7 \times 10^{-5}$$

This expresses the fact that the nucleus is about 1/100,000 as large (in diameter) as the atom. The student may calculate the ratio $D/d = 1.5 \times 10^5$, which is just the other way of looking at it—the atom is about 100,000 times as large as the nucleus.

Pr. 6. Suppose a copper atom is thought of as occupying a sphere 2.6×10^{-8} cm in diameter. If a spherical model of the copper atom is made with a 5.2 cm diameter, how much of an enlargement is this?

Answer

$$\frac{5.2\ \text{cm}}{2.6 \times 10^{-8}\ \text{cm}} = 2.0 \times 10^8$$

The enlargement factor is 200 million.

Pr. 7. Suppose an atom is likened to bees flying around their beehive. The beehive would be compared to the nucleus and the bees roving about the countryside would be compared to the electrons of the atom.

(a) If the radius of the beehive is 25 cm, what would be the average radius of the flight of the bees to maintain proper scale with the atom? Express your answer in kilometers.
(b) At any instant, where is the concentration of bees apt to be highest?
(c) Describe qualitatively the distribution of bees around the hive as a function of direction and of distance.

Answer

(a) The nucleus and the atom differ in radius by a factor of about 10^5. If the radius of the beehive is 25 cm, the radius of flight must average $25 \times 10^5 = 2.5 \times 10^6$ cm. This equals 2.5×10^4 m = 25 km. Notice that 25 km is about 15 miles (1.609 km = 1 mile).
(b) The concentration of bees is likely to be highest near the hive, the center of the bees' activities.
(c) If the clover fields are uniformly placed around the hive, the distribution of bees will be the same in any direction as you move away from the hive. The concentration of bees will be highest at the hive and will decrease steadily as distance from the hive increases. Notice there is no boundary to the bees' flight. Some bees will fly much farther from the hive than the average flight.

This is a much better analogy to the structure of the atom than are the "hard-sphere" styrofoam models or the planetary model.

Pr. 8. Helium, as found in nature, consists of two isotopes. Most of the atoms have a mass number 4 but a few have a mass number 3. For each isotope, indicate the:

(a) atomic number;
(b) number of protons;
(c) number of neutrons;
(d) mass number;
(e) nuclear charge.

Answer

	Helium 4	*Helium 3*
Atomic Number	2	2
Number of Protons	2	2
Number of Neutrons	2	1
Mass Number	4	3
Nuclear Charge	2+	2+

Pr. 9. Fill in the blanks of the following table:

ELEMENT	ATOMIC NO.	*Particles Per Atom*			MASS NUMBER
		PROTONS	ELECTRONS	NEUTRONS	
Aluminum (Al)	13				27
Beryllium (Be)		4			9
Bismuth (Bi)	83				209
Calcium (Ca)			20	20	
Carbon (C)		6		6	
Fluorine (F)			9		19
Phosphorus (P)	15			16	
Iodine (I)			53		127

Answer

ELEMENT	ATOMIC NO.	*Particles Per Atom*			MASS NUMBER
		PROTONS	ELECTRONS	NEUTRONS	
Aluminum (Al)		13	13	14	
Beryllium (Be)	4		4	5	
Bismuth (Bi)		83	83	126	
Calcium (Ca)	20	20			40
Carbon (C)	6		6		12
Fluorine (F)	9	9		10	
Phosphorus (P)		15	15		31
Iodine (I)	53	53		74	

Pr. 10 How do isotopes of one element differ from each other? How are they the same?

Answer

They differ in weight and in number of neutrons. They have the same number of protons and electrons, and their chemical behavior is the same.

Pr. 11. How much would 0.754 mole of chlorine-35 atoms weigh? How much would 0.246 mole of chlorine-37 atoms weigh? What is the weight of a mole of "average" atoms in a mixture of the above samples? What is the atomic weight of the naturally occurring mixture of these two isotopes of chlorine?

Answer

$$0.754 \text{ mole} \times \frac{35 \text{ g}}{\text{mole}} = 26.40 \text{ g}$$

$$0.246 \text{ mole} \times \frac{37 \text{ g}}{\text{mole}} = 9.10 \text{ g}$$

Adding these two equations gives

$$\begin{aligned} 1.000 \text{ mole} &= 35.50 \text{ g} \\ 1 \text{ mole} &= 35.5 \text{ g} \end{aligned}$$

Atomic weight of "average" atom = 35.5 g/mole.

Pr. 12. What is the significance of the trends in the boiling points and melting points of the inert gases in terms of attractions among the atoms?

Answer

Both the melting points and boiling points increase from helium to radon. The attractive forces must be increasing as we move down in the periodic table.

Pr. 13. Why is argon used in many electric light bulbs?

Answer

Argon is used because it is inert and does not react with the tungsten. Thus, the presence of argon insures a longer life for the electric light bulb. In addition, the presence of a gas makes it possible for the filament to lose more heat, hence remain cooler.

Pr. 14. Calculate the ratio of the number of electrons in a neutral xenon atom to the number in a neutral neon atom. Compare this number to the ratio of the atomic volumes of these two elements. On the basis of these two ratios, discuss the effect of electron-electron repulsions and electron-nuclear attractions on atomic size.

Answer

The atomic numbers of xenon and neon are respectively, 54 and 10. Hence there are 54/10 = 5.4 times as many electrons in a neutral xenon atom as in a neutral neon atom. The ratio of the atomic volumes is lower, xenon being larger than neon by a factor of 42.9/16.8 = 2.55.

This shows that the atomic volume does not grow in proportion to the number of electrons, as would be expected, because the electrons repel each other, tending to stay apart. Apparently this is opposed by the effect of the higher nuclear charge of xenon. The xenon nucleus, with a nuclear charge of 54+, attracts the electrons more strongly than does the neon nucleus, with a charge of only 10+. This effect tends to reduce the size of the xenon atom, providing an explanation of the lower ratio of atomic volumes (2.55) as compared to the number of electrons (5.4).

Pr. 15. The molar heats of vaporization of the inert gases (in kcal/mole) are: He, 0.020; Ne, 0.405; Ar, 1.59; Kr, 2.16; Xe, 3.02; Rn, 3.92. Using the data in Table 6-III (p. 91), plot the boiling points (vertical axis) against the heats of vaporization (horizontal axis). Suggest a generalization based upon a simple curve passing near the plotted points. Write an equation for the straight line passing through the origin (that is, through zero) and through the point for radon.

Answer

A generalization: The boiling points, expressed in absolute temperatures, of the inert gases increase directly as the heat of vaporization. A general equation for a straight line through points (x_1, y_1) and the origin is

$$\frac{y}{y_1} = \frac{x}{x_1}$$

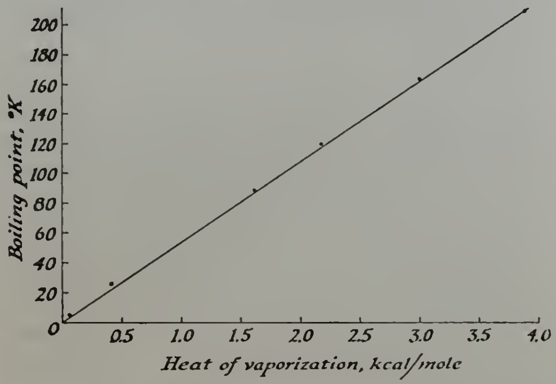
where x is the heat of vaporization and y is the boiling point.

For radon

$$x_1 = 3.92$$

and, at point 1,

$$y_1 = 211\text{°K}$$



Relation between boiling point and heat of vaporization *for the inert gases.*

Substituting, we obtain

$$\frac{y}{211} = \frac{x}{3.92}$$

$$y = 53.9x$$

Pr. 16. Lithium forms the following compounds: lithium oxide, Li_2O; lithium hydroxide, LiOH; lithium sulfide, Li_2S. Name and write the formulas of the corresponding sodium and potassium compounds.

Answer

Sodium oxide	Na_2O	Potassium oxide	K_2O
Sodium hydroxide	NaOH	Potassium hydroxide	KOH
Sodium sulfide	Na_2S	Potassium sulfide	K_2S

Pr. 17. An alkali element produces ions having the same electron population as atoms of the preceding inert gas. In what ways do these ions differ from the inert gases? In what ways are they alike?

Answer

An ion of an alkali element differs from an atom of the preceding inert gas element in that (1) the ion has a 1+ charge, and the inert gas atom has no charge, (2) the atomic number and nuclear charge of the ion are one unit greater.

The ion of the alkali element is like the atom of the preceding inert gas element in that both possess the same number of electrons and are relatively stable.

Pr. 18. There is a large difference between the energy needed to remove an electron from a neutral, gaseous sodium atom and a neutral, gaseous neon atom:

$$Na(g) + 118.4 \text{ kcal} = Na^+(g) + e^-$$
$$Ne(g) + 497.0 \text{ kcal} = Ne^+(g) + e^-$$

Explain how these energies are consistent with the proposal that the electron arrangements of the inert gases are specially stable.

Answer

It takes much less energy to remove an electron from a sodium atom to form the 10 electron arrangement of Na^+ (which is the same as Ne) than it does to remove an electron from the 10 electron arrangement of Ne. This is readily understood in terms of a special stability of the 10 electron arrangement. It takes relatively little energy to form the stable arrangement, but it takes a relatively high energy to disrupt it.

Pr. 19. Refer to the halogen column in the periodic table. How many electrons must each halogen atom gain to have an electron population equal that of an atom of the adjacent inert gas? What property does this population impart to each ion?

Answer

Each halogen atom gains one electron to attain the electron population of an atom of the inert gas adjacent to it. This population imparts the property of stability (inertness) to the ion, but the ionic charge causes it to repel other negatively charged ions and attract positively charged ions.

Pr. 20. How do the trends in physical properties for the halogens compare with those for the inert gases? Compare boiling points, melting points, and atomic volumes.

Answer

Consider that we are moving down (to higher atomic number) in each column. All these properties increase for both groups of elements. Each halogen has a higher boiling point and a higher melting point than its neighboring inert gas, but a smaller atomic volume.

Pr. 21. Use your knowledge of the usefulness of the periodic table to fill in the blank spaces in Table 6-VI, p. 97, under Astatine. List some chemical reactions expected for astatine.

Answer

	Astatine	
Atomic weight	216	(average of Po and Rn)
Molecular formula	At_2	(analogy to Cl_2, etc.)
Boiling point	300–400°C	(extrapolation of other members)
Melting point	200–300°C	(extrapolation of other members)
Atomic volume	above 26 ml/mole	(extrapolation of other members)

$$\begin{aligned} &Na(s) + \tfrac{1}{2}At_2(g) \longrightarrow NaAt(s) + \text{energy} \\ &H_2(g) + At_2(g) \longrightarrow 2HAt(g) \\ &HAt(g) + \text{water} \longrightarrow H^+(aq) + At^-(aq) \end{aligned}$$

Pr. 22. Chlorine is commonly used as a germicide in swimming pools. When chlorine dissolves in water, it reacts to form hypochlorous acid, HOCl, as follows:

$$Cl_2 + H_2O \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)$$

Predict what happens when bromine, Br_2, dissolves in water. Write the equation for the reaction.

Answer

Assuming similar chemistry, we would expect bromine to react, forming hypobromous acid, HOBr.

$$Br_2 + H_2O \rightleftharpoons HOBr(aq) + H^+(aq) + Br^-(aq)$$

Pr. 23. Zinc metal dissolves in a solution of gaseous chlorine in water as follows:

$$Zn(s) + Cl_2(aq) \longrightarrow Zn^{+2}(aq) + 2Cl^-(aq)$$

Zinc does not dissolve in a solution of gaseous hydrogen in water, but it *does* dissolve in an aqueous solution of hydrogen chloride:

$$Zn(s) + 2H^+(aq) + 2Cl^-(aq) \longrightarrow Zn^{+2}(aq) + H_2(g) + 2Cl^-(aq)$$

Recognizing that zinc metal must release electrons to form $Zn^{+2}(aq)$, explain how these reactions demonstrate that gaseous hydrogen does not behave like a halogen.

Answer

As zinc metal dissolves to form $Zn^{+2}(aq)$, it must release electrons. Chlorine will accept the electrons, forming the stable Cl^- ion. Hydrogen *will not* accept the electrons, which shows that hydrogen does not tend to form negative ions, as do the halogens. Instead, $H^+(aq)$ will accept the electrons to *form* $H_2(g)$.

Pr. 24. Write the molecular formulas of the hydrogen compounds of the second-row elements, Li, Be, B, C, N, O, F, Ne. Indicate, for each compound, the H/M ratio.

Answer

LiH,	BeH_2,	BH_3,	CH_4,	NH_3,	H_2O,	HF,
1/1	2/1	3/1	4/1	3/1	2/1	1/1

Neon, being inert, forms no compounds with hydrogen. The compound BH_3 has not been isolated, but B_2H_6 is well known, with the same H/B ratio, 3.

Pr. 25. Indicate the electron rearrangement (gain or loss) in each kind of atom assuming it attains inert gas-like electron structure in the following reactions.

(a) $2Rb + Br_2 \longrightarrow 2RbBr$
(b) $2Cs + I_2 \longrightarrow 2CsI$
(c) $Mg + S \longrightarrow MgS$
(d) $2Ba + O_2 \longrightarrow 2BaO$

Answer

Kind of Atom	*Number of Electrons* *As Reactant*	*As Product*	
Rb	37	36	loses 1
Br	35	36	gains 1
Cs	55	54	loses 1
I	53	54	gains 1
Mg	12	10	loses 2
S	16	18	gains 2
Ba	56	54	loses 2
O	8	10	gains 2

The state of the reactants and products has been neglected in the equations, since the main point here is the number of electrons. You may wish to have your students add *(s)*, *(l)* and *(g)*.

Pr. 26. Which of the following is NOT a correct formula for a substance at normal laboratory conditions?

(a) $H_2S(g)$
(b) $CaCl_2(s)$

(c) He(*g*)
(d) NaNe(*s*)
(e) $Al_2O_3(s)$

Answer: (d).

Pr. 27. Magnesium metal burns in air, emitting enough light to be useful as a flare, and forming clouds of white smoke. Write the equation for the reaction. What is the composition of the smoke?

Answer

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

The smoke consists of small particles of solid magnesium oxide, MgO.

Pr. 28. Use the formulas for magnesium oxide, MgO, and magnesium chloride, $MgCl_2$, together with the periodic table to decide that magnesium ions have the same number of electrons as each of the following, EXCEPT

(a) neon atoms, Ne;
(b) sodium ions, Na^+;
(c) fluoride ions, F^-;
(d) oxide ions, O^{-2};
(e) calcium ions, Ca^{+2}.

Answer: (e).

Pr. 29. Sodium metal reacts with water to form sodium ions (Na^+), hydroxide ions (OH^-), and hydrogen gas (H_2) as follows:

$$2Na(s) + 2H_2O \longrightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$

Assuming calcium metal reacts in a similar way, write the equation for the analogous reaction between calcium and water. Remember that calcium is in the second column of the periodic table and sodium is in the first.

Answer

$$Ca(s) + 2H_2O \longrightarrow Ca^{+2}(aq) + 2OH^-(aq) + H_2(g)$$

Pr. 30. Use Table 6-IX, p. 102, and the periodic table to write possible formulas for the following compounds:

(a) a hydride of barium, element 56;
(b) a chloride of germanium, element 32;
(c) an oxide of indium, element 49;
(d) an oxide of cesium, element 55;
(e) a fluoride of tin, element 50.

Answer

(a) BaH_2; analogue, MgH_2.
(b) $GeCl_4$; analogue, $SiCl_4$.
(c) In_2O_3; analogue, Al_2O_3.
(d) Cs_2O; analogue, Na_2O.
(e) SnF_4; analogue, $SiCl_4$ (Sn like Si, F like Cl).

Pr. 31. All of the isotopes of the element with atomic number 87 are radioactive. Hence, it is not found in nature. Yet, prior to its preparation by nuclear bombardment, chemists were confident they knew the chemical reactions this element would show. Explain. What predictions about this element would you make?

Answer

Because its nuclear charge is one greater than the inert gas radon, chemists were confident that element 87 would belong to the alkali metal family and that its chemistry could therefore be predicted on the basis of the known chemistry of the family.

Predicted properties
Boiling point: Because of the slight deviation of cesium from the decreasing trend, one can predict only a probable range, 900–1000°K.
Melting point: Below cesium, 250–300°K.
Atomic volume (solid): Above cesium, above 70 ml/mole.
Some probable reactions are:

$$Fr(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow FrCl(s) + \text{energy}$$

$$2Fr(s) + 2H_2O(l) \longrightarrow 2Fr^+(aq) + 2OH^-(aq) + H_2(g) + \text{energy}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Use Tables 6-VIII and 6-IX on pp. 101 and 102 of your Textbook to answer the following four questions regarding the elements in the third row of the periodic table.

1. Which elements are gases at room temperature, 25°C?

   Answer: Cl and Ar.

2. Which elements are liquids at 100°C?

   Answer: Na and P.

3. Which element has a neutral atom with the greatest number of electrons?

   Answer: Ar.

4. Give the formulas of two nonmetal ions that have the same number of electrons as a neutral argon atom.

   Answer: S^{-2}, Cl^{-}.

5. Positive ions are formed from neutral atoms by the loss of

   (1) neutrons;
   (2) nuclear charge;
   (3) protons;
   (4) electrons;
   (5) energy.

   Answer: (4).

6. Give the formula of three metal ions that have the same number of electrons as the inert gas neon.

   Answer: Na^{+}, Mg^{+2}, Al^{+3}.

7. Predict the formulas for the bromides and sulfides of the elements in the third row of the periodic table.

   Answer
   $NaBr$, $MgBr_2$, Al_2Br_6, $SiBr_4$, PBr_5, S_2Br_2, $ClBr$, Na_2S, MgS, Al_2S_3, SiS_2, P_4S_{10}, S_8, Cl_2S_7 or Cl_2S.

8. Predict which elements of the third row would be good conductors of electricity in the solid state.

   Answer: Na, Mg, Al.

9. Which of the following properties are different for neutral atoms of two isotopes of the same element?

   (1) atomic number;
   (2) mass;
   (3) number of electrons;
   (4) general chemical reactions.

   Answer: (2).

10. What is wrong with the statement, "Atoms of element *X* have 8.5+ nuclear charge"?

    Answer
    Nuclear charge is measured in fundamental units of charge, and occurs only in unit amounts. We cannot have half a unit charge.

11. Complete the following table for two naturally occurring isotopes, both of element *X*.

Atomic Mass	*Atomic Number*	*No. of Protons*	*No. of Neutrons*	*No. of Electrons in Neutral Atom*	*Positive Charge on Nucleus*
12	6				
13					

Answer

Atomic Mass	*Atomic Number*	*No. of Protons*	*No. of Neutrons*	*No. of Electrons in Neutral Atom*	*Positive Charge on Nucleus*
12	6	6	6	6	6
13	6	6	7	6	6

The following information concerning five *consecutive* elements in the periodic table was collected as a result of several experiments. The letters used have been assigned arbitrarily.

Element *A* reacts vigorously with water to liberate a gas which ignites and burns. It also reacts with methanol, CH_3OH, to produce the same combustible gas.

Element *B* is highly unreactive and is used as an inert atmosphere in light bulbs. It is a monatomic gas.

Element *C* exists in the gaseous state at room temperature as a diatomic molecule. It reacts with element *A* to form a stable compound having the empirical formula *AC*. The solid compound *AC* does not conduct electricity, but its aqueous solution does.

Element *D* reacts with element *C* to form a compound having the empirical formula DC_2. Its aqueous solution is a good conductor of electricity. Element *D* has a higher melting point and a higher boiling point than element *A*. It reacts slowly with water but more vigorously with dilute hydrochloric acid to liberate a combustible gas.

Element *E* exists at room temperature as a molecular solid. It reacts with element *D* to form a compound having the empirical formula *ED*. Element *E* burns in the air to form a gas having the formula EO_2. At STP, 22.4 liters of this gas weigh about 64 grams.

12. Study the information carefully so that you can identify the elements and arrange them in order of increasing atomic number. (The order is not *A*, *B*, *C*, *D*, *E*.)

    Answer
    E, *C*, *B*, *A*, *D* are the elements S, Cl, Ar, K, Ca, whose atomic numbers are 16, 17, 18, 19, 20.

13. Write the equations for the following reactions:

    (1) Rb with Br;
    (2) Rb with water;
    (3) Sr with Br;
    (4) Br with hydrogen gas.

    Answer
    (1) $2Rb(s) + Br_2(l) = 2RbCl(s)$
    (2) $2Rb(s) + 2H_2O(l)$
    $= 2Rb^+(aq) + 2OH^-(aq) + H_2(g)$
    (3) $Sr(s) + Br_2(l) = SrBr_2(s)$
    (4) $Br_2(l) + H_2(g) = 2HBr(g)$

14. Which of the following statements is FALSE?
    Elements in the first column of the periodic table

    (1) are called alkali metals;
    (2) have mobile electrons;
    (3) have one electron less than an inert gas configuration;
    (4) have decreasing melting points as the atomic number goes up;
    (5) react vigorously with chlorine.

    Answer: (3).

CHAPTER
7

ENERGY EFFECTS IN CHEMICAL REACTIONS

Intent and Approach

In presenting this material, introduce the idea that energy changes are an integral part of chemical reactions; then let the experiment provide the basis for student "discovery" of the additivity relation. Finally, explain that many repeated measurements, of the kind the student has performed, support the "law" of additivity. He will remember his experiment and will use his specific experience as a basis for his understanding of the law. Avoid the reverse, authoritarian rule that "Because energy is conserved, the sum of reaction heats No. 1 and No. 2 must equal No. 3."

Outline

1. Use of equations involving formation of water gas to emphasize the difference in reaction heats for different reactions (7-1).
2. The water gas example is used to develop an operational definition of heat content, H (7-1.1) and to show the additivity of reaction heats ΔH (7-1.2).
3. The measurement of heat is disclosed in terms of calorimetry (7-1.3).
4. Section 7-1.4 describes the use of ΔH values to predict the heat of a reaction.
5. The conservation of kinetic energy (7-2.1) and potential energy (7-2.2) are introduced.
6. Chemical energy is one type of stored energy (7-2.3).
7. The Law of Conservation of Energy is presented (7-2.4).
8. Types of energy associated with molecules are discussed—kinetic, chemical, and nuclear (7-3.1).
9. The macroscopic effects of warming are described in terms of the energy types (7-3.2).
10. The magnitude of nuclear reaction energy; symbols used in writing nuclear equations; and fission, fusion, and mass-energy relationships are introduced (7-4).

New Concepts

1. Chemical reactions involve energy.
2. Additivity Law of Reaction Heats.
3. Types of energy and the Law of Conservation of Energy.
4. Chemical energy is stored in molecules.
5. Heat content of chemical compounds, heat of reaction, ΔH.
6. Relative magnitudes of energies involved in phase changes, chemical changes, and nuclear changes.

Schedule and Related Material

Assignment Prior to Period	Period	Class Work	Ex.	Problems EASY	Problems MEDIUM	Problems HARD	Topic
Expt. 12*		This experiment is really an introduction to reactions. It should be done before Chapter 7 but it will be used in several chapters.					
S 7-1/7-1.1 (pp. 108–110) Expt. 13	1	Expt. 13*		1–3			Reaction Heat, Heat Content, "Discovery" of Additive Law
S 7-1.2/7-1.4 (pp. 111–113)	2	Discussion Expt. 13	1–3	4, 5	6, 8, 10†, 12	7, 9, 11, 13, 14	Use of Additivity Law
S 7-2/7-2.2 (pp. 114–115)	3	Discussion					Kinetic and Potential Energy
S 7-2.3/7-2.4 (pp. 115–117)	4	Discussion			15, 16	17	Chemical Energy, Conservation
S 7-3/7-3.2 (pp. 118–119)	5	Discussion Films, VIBRATION OF MOLECULES and MOLECULAR MOTIONS			18, 19		Molecular Energy
S 7-4/7-4.1 (pp. 120–121)	6	Discussion	4		20	21–23	Nuclear Energy
	7	Review					
	8	Test on Ch. 5–7					

Note: Experiment 14 (Chapter 8) requires solutions made the day before.

* Experiments 12 and 13 require extensive preparation.

† Boldface indicates problems whose answers are given in the Textbook.

Development

Expt. 12, A STUDY OF REACTIONS, fits here. See p. 215 for guide.

This experiment is given mainly to provide a backlog of experience with reactions. This experience will be used in the next several chapters.

HEAT AND CHEMICAL REACTIONS (7-1)

The idea that chemical reactions can produce heat should not be new to the student. He may recall the burning of wood, his own body's combustion of food, the car engine heating up, and so on. Since the reproducible, quantitative aspect may not be in his thinking, it is unlikely that he will be able to give examples of reactions which absorb energy. To find examples for class use look up the terms heat of formation, heat of combustion, heat of reaction, etc. in a handbook, or see the section on thermochemistry in a physical chemistry text. Of course he already knows from his own experiments that some chemical reactions produce heat (in Expt. 5—combustion of candle wax) and that some phase changes absorb heat (in Expt. 5—heat of melting). Experiment 12 showed some examples of both exo- and endothermic heat effects from reaction and solution.

This is a good place to emphasize why we write (s), (l), (g), or (aq) after the symbols of compounds. Ask for a class discussion on what difference in heat effects would be expected for the reactions

$$\begin{array}{lll}
C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) & \Delta H & = -26.4\text{ kcal} \\
\underline{\qquad\quad H_2O(g) \longrightarrow \frac{1}{2}O_2(g) + H_2(g)} & \underline{\Delta H} & \underline{= +57.8\text{ kcal}} \\
C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) & \Delta H_1 & = +31.4\text{ kcal}
\end{array} \qquad (1)$$

$$\begin{array}{lll}
C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) & \Delta H & = -26.4\text{ kcal} \\
\underline{\qquad\quad H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + H_2(g)} & \underline{\Delta H} & \underline{= +68.3\text{ kcal}} \\
C(s) + H_2O(l) \longrightarrow CO(g) + H_2(g) & \Delta H_2 & = +41.9\text{ kcal}
\end{array} \qquad (2)$$

The additional 10.5 kcal absorbed in reaction (2) is equal to the heat of vaporization of liquid water at 25°C.

A possibility exists for the confusion of symbols: H denotes heat content, and H represents one atom of hydrogen. We use H (heat content) only to establish the idea; in practice it is ΔH that is important. Thus there is little danger of trouble, and the different type style makes confusion less likely.

Heat Content of a Substance (7-1.1)

An operational definition of ΔH is developed. The definition of ΔH is straightforward, but the sign convention is *arbitrary*. That is, the difference *could* be

(heat content of reactants)
− (heat content of products)

but the difference as defined in the book is well established. This is its only claim to being "right."

There are two methods used for expressing ΔH. They are explained below, but first some comments on attitude. The method of expression is of only minor importance compared to the concept of heat content. For this reason, do not make a big issue of the conventions. Just use them naturally, possibly with occasional mention of the rationale given.

An *exothermic* reaction is written

$$A + B = C + 20\text{ kcal}$$

or

$$A + B = C \qquad \Delta H = -20\text{ kcal} \qquad (3)$$

The *endothermic* reaction is written

$$D + E + 30\text{ kcal} = F$$

or

$$D + E = F \qquad \Delta H = +30\text{ kcal} \qquad (4)$$

In the first form the position of the energy term shows the type of reaction; in the second, the sign is used to indicate type. Both forms are found in published literature and are used by professional chemists.

The student usually has little trouble with the heat term when it is written as a "reactant" or "product," as in the first form, but difficulty arises when ΔH is written separately. Here is a rationale that may help. Tell the student to imagine he is "inside the reaction system." Then if he (and the reaction) receive heat, ΔH is positive (gain), and the reaction is called *endo*thermic—heat goes in. If he loses heat, ΔH is negative (loss), and the reaction is *exo*thermic—heat goes out.

Expt. 13, THE HEAT OF REACTION, fits here. See p. 220 for guide.

Additivity of Reaction Heats (7-1.2)

Experiment 13 is designed to illustrate the additivity of reaction heats as well as to give the student some firsthand experience at calorimetry. The student is expected to do the experiment before the law is discussed.

The student's experience with Expt. 13 serves as a starting point. However, avoid a long discussion of sources of error and the various heat effects from solutions of different concentrations. The line of attack here is from the student's personal experience, through the vast amount of similar tests (made with much higher accuracy) to the unifying concept—the *law of additivity of reaction heats.* Use other examples.

The use of the law can be driven home by a discussion such as the following. The heat of many reactions is not easy to measure. There must be a definite reaction going on which does not change as it proceeds. The reaction must also proceed at a suitable rate (not too fast or too slow). However, application of the additivity feature of reaction heats allows us to calculate values for reactions that do not fill the requirements given. For example, carbon cannot be burned in oxygen to produce only carbon monoxide (some CO_2 is found also), hence the heat of reaction for $C(s) + \frac{1}{2}O_2(g) = CO(g)$ cannot be measured directly. By using the additive principle and two other equations, we can easily compute the desired ΔH.

$$\begin{array}{llll}
C(s) & +\ O_2(g) & \rightleftharpoons CO_2(g) & +\ 94.0\ \text{kcal} \\
CO(g) & +\ \frac{1}{2}O_2(g) & \rightleftharpoons CO_2(g) & +\ 67.6\ \text{kcal} \\
\hline
C(s) & +\ \frac{1}{2}O_2(g) & \rightleftharpoons CO(g) & +\ 26.4\ \text{kcal}
\end{array}$$

The Measurement of Reaction Heat (7-1.3)

Some details of more complex calorimeters are discussed. There is largely mechanical detail here. You might comment on the qualitative nature of the heat "measurement" (just by feel) in Expt. 12; the somewhat better equipment used in Expt. 5; and the improved technique used in Expt. 13. These comments can be used to lead into a discussion of more elaborate calorimeters. But since these are designed for specific reactions, they will, of course, vary considerably. You may wish to ask the class to suggest the different features that might be required in a calorimeter designed to measure heats of reaction involving:

(a) solutions only;
(b) high pressure gases;
(c) very reactive chemicals (HNO_3, $F_2(l)$, HF, etc.);
(d) small amounts of chemicals.

Predicting the Heat of a Reaction (7-1.4)

This section is the useful culmination of the preceding parts of this chapter. You will notice that, although the heat of formation is employed, we do not introduce the term. It is not needed, and just adds another concept plus a "standard state" (25°C, 1 atm) different from that used for gases.

Use other examples to show the usefulness of this predictive power. Some examples are given in the *Background Discussion* (p. 227).

THE LAW OF CONSERVATION OF ENERGY (7-2)

The next four sections are designed to lead the student toward an understanding of kinetic and potential energies as two distinct types, each of which may appear in several forms. The Law of Conservation of Energy is developed as a regularity which expresses all the results now known.

Conservation of Energy in a Billiard Ball Collision (7-2.1)

In this section we consider an ideal case. The spheres are taken to be perfectly elastic; and the surface on which they roll, frictionless. Actual conditions fall short of such perfection in varying degrees, and $W_1 \neq$ (K.E.), because some of the work produces heat. A similar inequality would hold if the balls were not elastic. Try rolling two putty balls together. You will see that kinetic energy is not conserved. Some of it goes into deforming (and heating) the balls.

Do not get into a discussion of the nonideal features of our model. If some question about friction arises, admit it exists, but stress our interest in the ideal case. Remind the student that, since we will be concerned with the motion of atoms or molecules moving in space, the topic of friction is of less importance to us than to a physicist or mechanical engineer. Particles of a gas, in particular, have essentially no interaction in many cases.

Some students (or physics teachers) may object to our calling work a form of energy, since physicists often define energy as the capacity to do work. We are adhering to the thermodynamic definition of energy conservation, which states that energy change is the sum of two forms of energy—heat and work. Qualitatively stated, the first law of thermodynamics is "energy is conserved"; quantitatively stated, it is $\Delta E = q - w$. The quantitative statement makes it plain that energy is the (algebraic) sum of heat and work.

Conservation of Energy in a Stretched Rubber Band (7-2.2)

This section goes one step beyond the billiard ball case (which involved work and kinetic energy). It involves potential energy and serves to introduce the type of reasoning needed for the chemical energy case. Here we introduce potential energy by the method now familiar to the student Our "model" of energy conservation from the previous section is not adequate for some cases, thus we modify the model as dictated by experiment. There are two points of importance here. One is that the energy conservation law is just another expression of experimental results. It has changed in the past, and will probably do so again (the student sees this thought in Sec. 7-2.4). The second point is to make sure the idea of stored energy is understood, since we will use it in a chemical context in the next section.

Conservation of Energy in a Chemical Reaction (7-2.3)

Now the groundwork of the previous sections can be used. Emphasize the parallelism between the mechanical (Textbook Figure 7-4) and chemical (Textbook Figure 7-7) cases. You can do this in part by using the equation

$$W_1 = (\text{P.E.})_2 = (\text{K.E.})_3$$

and the equation (not in Textbook)

$$W_1 = (H)_2 = Q_3 = (\Delta H)_3$$

These relations, together with Textbook Figures 7-6 and 7-7, make two comparisons: one between mechanical kinetic energy (K.E.) and heat of reaction (ΔH) and another between potential or stored energy (P.E.) and heat content (H). This last term (H) is the "chemical energy" sometimes referred to. Heat content is the energy stored in a molecule or in a particular atomic arrangement. A change in heat content (ΔH) expresses the heat effect caused by the rearrangement of atoms during a reaction.

The Basis for the Law of Conservation of Energy (7-2.4)

Most students will already have heard the statement "energy is conserved," often given in a very authoritarian way. The intent here is to make the law clear and to emphasize its importance. Yet it is no different from other expressions of regularity. We wish to place it in the proper perspective; it is an important generalization, but was derived in the same way as all other such expressions. It has been modified before, and probably will be again.

THE ENERGY STORED IN A MOLECULE (7-3)

The Energy of a Molecule (7-3.1)

The student has already met the idea of storing energy when a liquid boils (see p. 150). You may wish to remind him of this. All steam-operated devices depend on the recovery of the stored energy when the gas condenses (or cools).

This section gives a microscopic description of how energy is stored—in various motions of the atoms. It also takes up other ways to hold energy. The *Background Discussion* has some comments on how the descriptions were deduced.

The films suggested earlier can be shown to illuminate this section. Note the comments given (p. 225). The best practice is to view the films ahead of time and decide how to use them with your class.

Films, VIBRATION OF MOLECULES and
MOLECULAR MOTIONS,
fit here. See p. 225 for summaries.

Energy Changes on Warming (7-3.2)

The Textbook shows the student the magnitude of the energies involved in various types of changes by describing the conditions which prevail as a substance is heated—beginning with phase changes, continuing on to chemical changes involving the formation and/or breaking of bonds as we continue heating to higher temperatures, and finally the disruption of the nucleus itself at energies roughly 10^9 times those of ordinary chemical reactions.

Students can be directed at this point to consider the relative strengths of the kinds of forces involved in holding molecules, atoms, and nuclear particles together. This topic is discussed in some detail in later chapters.

THE ENERGY STORED IN A NUCLEUS (7-4)

Exact Mass Relationships (7-4.1; reduced type)

Man-made nuclear reactions are, relatively, quite new and, of course, have received a great deal of publicity. As a result you may find the student's knowledge and interest in this field to be considerable. In this course, as in most chemistry courses, nuclear reactions form only a small part. This is a natural consequence of the difficulty of carrying out such changes and of the unsettled state of theoretical treatments.

Thus, it is probably best to avoid any discussion of the mechanics of doing nuclear experiments. The equipment for bombardment, fusion, and so on are quite complex and fit more naturally into a physics course than a chemistry course.

EXPERIMENT 12 A STUDY OF REACTIONS

PURPOSE. To teach the student to recognize reactions and to give a backlog of observed reactions for class discussion.

PRELAB DISCUSSION. Tell the student that there are two purposes to this experiment: to look for evidence of chemical changes and to gain experience with a set of reactions that will be used later. All students have observed some chemical reactions, either at home or in other science classes, but it is convenient to have a set of reactions which have been seen under similar conditions by each student.

Do not assign or discuss the equations at this time. These reactions involve principles of oxidation-reduction, acid-base equilibria, reaction rates, and solubility, which are important topics in the next few chapters. The student is to observe now; the details will come later.

TIMING. Experiment 12 should be done between Chapters 6 and 7.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

ring stand, ring, wire gauze and burner
6 or more 13 × 100 mm test tubes
  (2 must be hard glass)
2 additional hard glass test tubes
  (see lab hint 2)
thermometer, $-10°C$ to $110°C$
wood splint
stoppers (cork #3 or rubber #00)

Solid reagents (in small bottles; see lab hint 3)

1 ml ($\frac{2}{3}$ g) ammonium chloride
$\frac{1}{2}$ ml ($\frac{1}{2}$ g) lead dioxide, powdered
$\frac{1}{4}$ ml ($\frac{1}{4}$ g) sodium sulfite (or sodium bisulfite)
$\frac{1}{4}$ ml ($\frac{2}{3}$ g) lead nitrate, powdered
1 ml ($\frac{2}{3}$ g) sodium acetate
3 pellets ($\frac{1}{3}$ g) sodium hydroxide pellets
5 small chips calcium carbonate (marble chips)

Solutions (see lab hint 3)

1 ml 18 M sulfuric acid (see lab hint 4)
5 ml 6 M acetic acid
  (340 ml conc. reagent/liter)
5 ml 1 M acetic acid
  (57 ml conc. reagent/liter)
8 ml 6 M hydrochloric acid
  (513 ml conc. reagent/liter)
5 ml 1 M hydrochloric acid
  (85.5 ml conc. reagent/liter)
5 ml 0.1 M hydrochloric acid
  (100 ml 1 M HCl/liter)
5 ml 0.1 M ferrous sulfate
  (28 g $FeSO_4 \cdot 7H_2O$/liter plus a few drops of H_2SO_4, freshly prepared)
$\frac{1}{2}$ ml 0.1 M manganous sulfate
  (17 g $MnSO_4 \cdot H_2O$/liter)
2 ml 0.1 M potassium bromide
  (12 g KBr/liter)
2 ml 0.1 M potassium chromate
  (19 g K_2CrO_4/liter)
1 ml 0.1 M potassium permanganate
  (16 g $KMnO_4$/liter)
4 ml 0.1 M sodium chloride
  (6 g NaCl/liter)
20 ml 0.1 M sodium oxalate
  (13 g $Na_2C_2O_4$/liter)
2 ml 0.2 M silver nitrate
  (34 g $AgNO_3$/liter)
phenolphthalein (1 g/100 ml 50% ethanol)

Teacher's Demonstration

$\frac{1}{2}$ ml ($\frac{1}{2}$ g) ammonium dichromate (Do not inhale fumes—lung irritant.)

TIME REQUIRED. Plan on using $1\frac{1}{2}$–2 class periods. Convenient stopping places occur after any of the procedures. All are quite independent of each other. To save time, heat the water for Part III while Parts I and II are being done. You may demonstrate Part IV to save additional time.

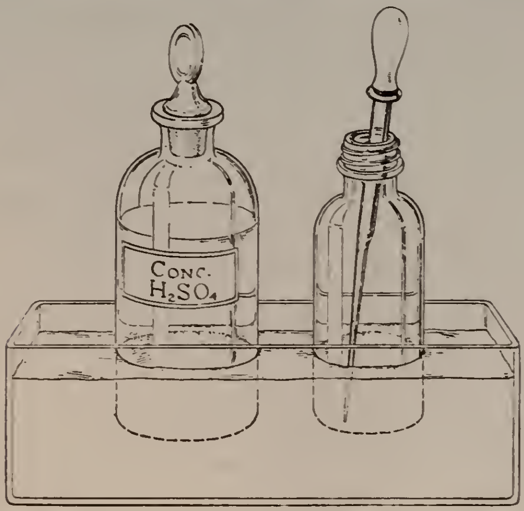
PRECAUTIONS. Caution students about adding concentrated sulfuric acid to water. Explain that water should not be added to the concentrated acid, since this will give a violent release of heat and steam which causes the concentrated acid to spatter all around; serious skin burns and damage to clothing can result.

If concentrated acids are spilled, wash them off with plenty of water, and then neutralize with bicarbonate of soda ($NaHCO_3$) solution. If spilled on the person, use large amounts of water, and neutralize any remaining acid with bicarbonate of soda solution. *Do not under any circumstances* use either a strong base or concentrated $NH_3(aq)$ to neutralize acid in contact with skin or clothing. Have labeled neutralizing solutions on the desks, and point them out. See lab hint 3. The salt $Pb(NO_3)_2$ occasionally spatters when heated strongly. Tell students not to point their test tubes at anyone, and to wear safety glasses.

LABORATORY HINTS

1. It will be time saving for each student to calibrate a test tube by marking 1, 2, 3, 4, and 5 ml lines as indicated in Laboratory Manual Figure 12-1. The tubes can be marked with grease pencil or marking pen, or the marking can be done on attached strips of masking tape
2. The test tubes used in Part II f and in Part IV a will be stained and difficult for the students to clean. It is therefore suggested that the same test tubes be used for all your classes and then saved for next year.
3. As many sets of reagents should be made available as possible in order not to waste time. Since the order is not important, different students may begin on different parts, except that in Part I solutions are prepared for Part II.

   For reagents specified in terms of drops, provide dropper bottles. Others may be kept in regular reagent bottles.
4. Dispensing concentrated sulfuric acid presents several problems: in ordinary dropper bottles, the acid sometimes gets on the rubber of the dropper; in reagent bottles, it tends to drip off the lip, and unless this is rinsed after the stopper is replaced, acid runs down the side of the bottle. You may solve this by using a set consisting of a reagent bottle (125 ml or smaller) with glass stopper and a small bottle in which is stored a medicine dropper with a long glass tube. Place these in a wood block in which holes have been drilled or in a plastic container with plaster of Paris poured to make compartments for the bottles as in the diagram below.



The student lifts the glass stopper in the usual way, dips the dropper into the reagent bottle, dispenses the required number of drops of acid, empties the dropper, and replaces it in the small bottle and the stopper in the reagent bottle. The same medicine dropper is used by all students, and since there is no rinsing, the acid does not become diluted, and contamination is minimized. It is, of course, important to explain that this is contrary to the usual instruction never to put any object into a reagent bottle and never to return unused portions to the bottle. But it gives you a chance to make a very special case of a situation that is potentially dangerous both to the student's person and to his clothing.

EXPECTED RESULTS. Do not discuss the reactions. The following is for your information only.

PART I

What the student observes is the sum of two processes. In the concentrated H_2SO_4 and in the crystal lattice of NH_4Cl, $NaCH_3COO$, and $NaOH$, the particles attract each other, and considerable energy is required to break these bonds. A solvent such as water combines with the ions and releases energy. The heat of hydration of some substances (for example, NaCl) just about offsets the heat of separation of the ions, and there is very little heat effect. For sulfuric acid and NaOH the heat of hydration more than offsets the energy required to separate the ions, and heat is evolved.

With NH_4Cl and $NaCH_3COO$ more energy is required to break up the crystal lattice than is produced from the hydration of the ions, and heat is absorbed. When one mole of NH_4Cl is dissolved in 200 moles of water, ΔH is $+3.9$ kcal. The student may not observe this, however, because of the poor heat conductivity of the glass test tube. Direct him to check the temperature change with a thermometer. A similar amount of energy is absorbed when $NaCH_3COO$ dissolves.

PART II

(a) and (b) Phenolphthalein changes from colorless to pink between pH 8 and 9, hence it is colorless in the H_2SO_4 solution and pink in the sodium hydroxide solution.

(c) The odor of SO_2 will be noted.

$$SO_3^{-2}(aq) + 2H^+(aq) \longrightarrow H_2SO_3(H_2O + SO_2)$$

The student may also note the odor of the HCl, although he may not recognize either. Encourage him to relate them to other, more familiar odors.

(d) The pink color of the MnO_4^- disappears, and the yellow typical of Fe^{+3} appears.

	$E°$
$5[Fe^{+2}(aq) \rightleftharpoons Fe^{+3}(aq) + e^-]$	-0.77 volt
$Mn^{+2}(aq) + 4H_2O(l) \rightleftharpoons MnO_4^-(aq) + 8H^+(aq) + 5e^-$	-1.55 volts
$5Fe^{+2}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightleftharpoons 5Fe^{+3}(aq) + Mn^{+2}(aq) + 4H_2O(l)$	0.78 volt

(e) No change in properties is noted. The resulting solution is a mixture of hydrated ions.

(f) $PbO_2(s) \longrightarrow PbO(s) + \frac{1}{2}O_2(g)$

The PbO_2 decomposes at 290°C, and the PbO melts at 888°C. The test tube is generally heated enough to fuse some of the PbO with the glass. The student may have some difficulty in getting a glowing splint to burst into flame, but having seen the film GASES AND HOW THEY COMBINE for Chapter 2, he will probably succeed after a few trials.

PART III

(a) The tube to which Mn^{+2} is added shows a reaction—evidenced by bleaching of the MnO_4^-—much sooner than the one without Mn^{+2}. The reaction at 50°C is more rapid than that at room temperature. In fact it is very slow at room temperature without Mn^{+2} and may not even be evident to the student.

$$
\begin{array}{rr}
 & E^\circ \\
\hline
2[\mathrm{Mn^{+2}}(aq) + 4\mathrm{H_2O}(l) \rightleftharpoons \mathrm{MnO_4^-}(aq) + 8\mathrm{H^+}(aq) + 5e^-] & -1.55 \text{ volts} \\
5[\mathrm{C_2O_4^{-2}}(aq) \rightleftharpoons 2\mathrm{CO_2}(g) + 2e^-] & 0.49 \text{ volt} \\
\hline
2\mathrm{MnO_4^-}(aq) + 16\mathrm{H^+}(aq) + 5\mathrm{C_2O_4^{-2}}(aq) \rightleftharpoons 2\mathrm{Mn^{+2}}(aq) + 8\mathrm{H_2O}(l) + 10\mathrm{CO_2}(g) & 2.04 \text{ volts}
\end{array}
$$

At these concentrations CO_2 gas will not be noticed. (If the water is very alkaline, there may be a brown precipitate of MnO_2 rather than colorless Mn^{+2}.)

(b) The evolution of gas (CO_2) is clearly more rapid with 6 *M* HCl than with any of the other acids. The 6 *M* acetic acid will react like the 0.1 *M* HCl, and the 1 *M* acetic acid will show very little bubbling.

PART IV

(a) Reddish-brown NO_2 is formed with moderate heating. This ceases when the source of heat is removed and, if the initial heating has not decomposed all the material, may be started again by reheating;

$$\mathrm{Pb(NO_3)_2}(s) \longrightarrow 2\mathrm{NO_2}(g) + \mathrm{PbO}(s) + \tfrac{1}{2}\mathrm{O_2}(g)$$

The student may note the similarity of the residue to that formed by heating PbO_2.

(b)
$$\mathrm{Cl^-}(aq) + \mathrm{Ag^+}(aq) \longrightarrow \mathrm{AgCl}(s) \text{ (white)}$$
$$\mathrm{CrO_4^{-2}}(aq) + 2\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Ag_2CrO_4}(s) \text{ (deep red)}$$

When NaCl and K_2CrO_4 are mixed, the addition of Ag^+ first forms a white precipitate which, because of the yellow CrO_4^{-2} solution, appears creamy yellow. After about ten drops ($\frac{1}{2}$ ml) have been added, the deep red characteristic of Ag_2CrO_4 develops and masks the white AgCl.

The K_{sp} for AgCl(*s*) is 1.7×10^{-10} and for Ag_2CrO_4 is 1.9×10^{-12} at 25°C. For both precipitates to be present the concentrations of Ag^+ must be the same and both K_{sp} values satisfied;

$$[\mathrm{Ag^+}][\mathrm{Cl^-}] = 10^{-10} \quad \text{and} \quad [\mathrm{Ag^+}]^2[\mathrm{Cl^-}]^2 = 10^{-20}$$

Solving $[Ag^+]^2[CrO_4^{-2}] = 10^{-12}$ for $[Ag^+]^2$ and substituting gives

$$\frac{[\mathrm{Cl^-}]^2}{[\mathrm{CrO_4^{-2}}]} = 10^{-8}$$

If the concentration of CrO_4^{-2} is 0.04 *M*, as it will be when diluted to 2.5 ml in this procedure, then

$$[\mathrm{Cl^-}]^2 = 0.04 \times 10^{-8} = 4 \times 10^{-10}$$

and

$$[\mathrm{Cl^-}] \cong 2 \times 10^{-5} \text{ mole/liter}$$

As long as the $[Cl^-]$ exceeds 2×10^{-5} mole/liter, the $[Ag^+]$ will not be great enough for $[Ag^+]^2[CrO_4^{-2}] = 10^{-12}$, and Ag_2CrO_4 will not precipitate.

TEACHER'S DEMONSTRATION

$$\mathrm{(NH_4)_2Cr_2O_7}(s) \longrightarrow \mathrm{N_2}(g) + \mathrm{Cr_2O_3}(s) + 4\mathrm{H_2O}(g)$$

(Do not inhale fumes—lung irritant.)

ANSWERS TO QUESTIONS

1. In which of the experiments was there no evidence of a chemical reaction?

   Answer: In Parts II b (phenolphthalein and sulfuric acid), II e (sodium chloride and potassium bromide solutions), and possibly in III b (the 1 *M* acetic acid). The heat effects often noted in Parts I a–d result from the reactions forming aquated ions which are different species from the undissociated compounds.

2. Which chemical reactions produced a new phase?

   Answer: Gases were produced in Parts II c and f, III b, IV a and in the demonstration. Precipitates were found in IV b.

3. Which reactions in this experiment were exothermic? Which were endothermic?

   Answer: Evolutions of heat were noted in Parts I a and I b, in the demonstration, and possibly in II a and III b. Endothermic reactions were seen in Parts I c, I d, II f, and IV a.

4. In which reactions did an increase in temperature affect the rate?

   Answer: An increase in temperature increased the rate in Part III a. The effect may also be noted for Parts II f, III b, IV a, and the demonstration.

5. In which reactions did an increase in concentration affect the rate?

   Answer: This was clearly evident in Part III b.

6. In Part III a what effect on the rate of reaction did adding the $MnSO_4$ solution have?

   Answer: The rate was increased when $MnSO_4$ solution was added.

7. What evidence did you observe to indicate that in some of the reactions part of the reactants was not used up?

   Answer: The most clear-cut example was Part IV a, in which more NO_2 was released after a second heating, indicating that the reactant was surely not used up in the first trial. In Part IV b, a precipitate continued to form until an excess of $AgNO_3$ solution was added, indicating that, until then, the reactant had not been used up. In Part III b, $CaCO_3$ was left after the bubbling ceased. In the mixtures for which there is no evidence of reaction, the "reactants" might be considered unused.

A QUESTION TO WONDER ABOUT

Account for the results obtained when solutions of hydrochloric acid and of acetic acid—of the same concentration—reacted with $CaCO_3(s)$.

Answer: The student can think about this until Chapter 11.

POSTLAB DISCUSSION. Summarize the kinds of changes that have been observed—energy changes, color changes, production of substances with different properties. You may wish to emphasize the importance of using several different senses in noting changes in temperature, odor, and appearance. The presence of factors affecting the rate of a reaction may be briefly mentioned, but Chapter 8 is the place for full treatment.

EXPERIMENT 13 THE HEAT OF REACTION

PURPOSE. To obtain experimental evidence for reaction heats while letting the student discover the Law of Additivity for such heats.

PRELAB DISCUSSION. The students have already used a simple calorimeter (the can in Expt. 5). Remind them of this, and point out the differences to be met in this experiment. These include weighing the flask in order that the heat absorbed by the flask may be included and having the reaction cause the heat change in the water, rather than using hot water for a heat source.

Make clear that the reactants should be mixed quickly to minimize the reaction time. This will avoid heat loss to the surroundings. Tell the student to read the thermometers as precisely as possible.

Since the equations are given in the introduction, it should be clear to the student that one mole of HCl reacts with one mole of NaOH and that the amounts are equivalent when he uses 100 ml of 0.5 M solution of each. With this as background, the student should understand the reason for weighing as close to two grams of NaOH as may be done conveniently. Emphasize, however, that this need not be 2.00 grams; the student should not waste time trying to get this exact amount. See also lab hint 2.

TIMING. This experiment should be done before any assignment is made in Chapter 7, since the topic is discussed early in the chapter.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

250 ml flask (as a reaction vessel)
(see lab hint 3)
250 ml beaker for holding second solution
thermometer (−10°C to 110°C)
200 ml distilled water
Solid NaOH (4 g) (see lab hint 2)
100 ml 0.5 M NaOH (20 g/liter)

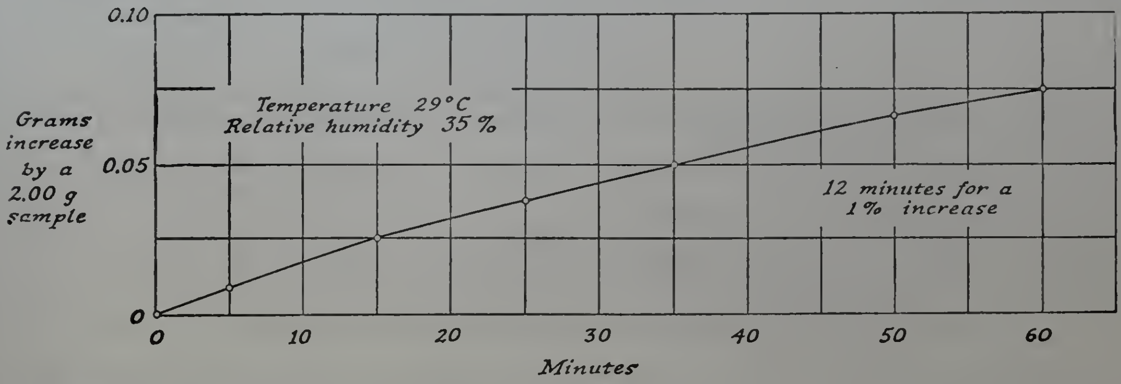
100 ml 0.5 M HCl
(42.8 ml conc./liter)
200 ml 0.25 M HCl
(21.4 ml conc./liter)
} See lab hint 1
100 ml graduates or volumetric flasks
for measuring quantities of distilled
water, NaOH, and HCl
balance (±0.01 g)

TIME REQUIRED. One 45–50 minute period is adequate—more than adequate if students organize the experiment ahead of time. There are convenient stopping places after each of the three reactions, but it is best to do all of the experiment on the same day, since room and water temperatures might differ from day to day.

PRECAUTIONS. Do not touch the $\text{NaOH}(s)$; if some spills, be sure that it is picked up with a paper towel and disposed of either in a waste jar or by dissolving it in the sink. If any is handled, wash hands thoroughly with plenty of water and, if slipperiness persists, with a little very dilute weak acid (0.5 M acetic acid).

LABORATORY HINTS

1. Solutions must be made up at least one day before in order that they will all be at the same (room) temperature.
2. The moisture picked up by the NaOH when exposed to air gives one the impression that the weight will be difficult to obtain accurately, but observation in a typical laboratory situation gives the following graph (values obtained from weighing two different 10 gram samples).



Weight gained by NaOH *exposed to laboratory atmosphere.*

Apparently the amount of water is more noticeable than measurable! It is important, however, to tell the student approximately how many pellets to use and also to have the NaOH in small jars by each balance in order that the jars may be closed promptly. One possibility is to have the proper number of pellets counted out into crucibles stored in a desiccator prior to the experiment. Each student takes a crucible, pours out the pellets onto a weighed piece of smooth, nonabsorbent paper, and weighs them as directed to the nearest 0.01 gram. It has been suggested that flakes would dissolve more rapidly than pellets, but these do not seem as convenient in other ways. (For instance, they are more apt to pack solidly when the stock supply becomes a little moist.) The student will probably need between 10 and 20 pellets.

3. The flask does not need to be dry except for the initial weighing. It is not too easy to dry the inside of the flask with a paper towel, but if heat is used to dry the flask, the student must wait for the flask to cool thoroughly; and this takes as long as it does to push a paper towel around in the flask. Wrapping the towel around a dry test tube brush helps.
4. The calculations may raise the question whether one should use only the weight of water multiplied by the temperature change to get the number of calories or whether one should use the combined weight of water, NaOH, and HCl. The increase in weight is only about 2%, and some of this is counterbalanced by the fact that the specific heat of the solution is slightly (although very slightly) less than that of the pure water. Actually an error of 2% (especially since it is in each of the calculations) is so small as to be insignificant compared to the precision of other measurements.

CALCULATIONS. Point out the section in Appendix 5 on the addition of algebraic equations. Remind students of the meaning of Δ (see Expt. 5). Also discuss the "transition" from $+x$ calories to ΔH.

1. This experiment brings out some rather difficult decisions about precision. The temperature changes caused by the three reactions are based on two readings and are only 2.0 to 3.0 degrees. With the thermometer read to the nearest 0.2°C—one can hardly do better than this—the degree of uncertainty is about 20%. It is suggested that this be discussed with the students to avoid misunderstanding but that in the intermediate calculations more significant figures be retained. However, there is a tendency for students to use a ridiculous number of figures in the calculations. In the following data sheet (an actual sample experiment) a reasonable compromise is suggested.

	Reaction 1	*Reaction 2*	*Reaction 3*
(a) change in temp (Δt)	2.4°C	6.0°C	3.2°C
(b) heat absorbed by solution ($\Delta t \times 200$ g $\times$ 1 cal/g)	480 cal	1200 cal	640 cal
(c) heat absorbed by flask $\cdot$($\Delta t \times$ wt of flask $\times$ 0.2 cal/g)	60 cal	150 cal	80 cal
(d) total heat absorbed	540 cal	1350 cal	720 cal
(e) the number of moles of NaOH used in each reaction	0.052	0.048	0.050
(f) the total amount of heat involved per mole of NaOH	1.04×10^4	2.81×10^4	1.44×10^4

2. As heats of reaction we find

$$\begin{aligned} \Delta H_1 &= -1.0 \times 10^4 \text{ cal/mole} \\ \Delta H_2 &= -2.8 \times 10^4 \text{ cal/mole} \\ \Delta H_3 &= -1.4 \times 10^4 \text{ cal/mole} \end{aligned}$$

3. Comparing ΔH_2 with $\Delta H_1 + \Delta H_3$, we find a difference of 0.4×10^4, which, divided by 2.8×10^4, gives a percentage difference of 14% and is within the degree of uncertainty expected.

We can apply precision criteria earlier, at step (d), to give:

	Reaction 1	*Reaction 2*	*Reaction 3*
Total heat absorbed	500 cal	1400 cal	700 cal
The moles of NaOH in each reaction would be 0.05. We would get the heat/mole of NaOH to be (cal/mole)	1.0×10^4	2.8×10^4	1.4×10^4

Since there are so many individual measurements to interpret in this experiment, it is wise not to get too involved in the problem of precision but to stress that the final answers are not known any closer than one part in ten.

As an explanation for the comparison noted, the student should refer to the equations given in the introduction and find out that both of the processes measured in reactions *1* and *3* are included in reaction *2*.

An examination of student results from past trials reveals that the errors are not consistent—that is, sometimes the sum is higher than ΔH_2, and sometimes lower. We might expect the sum to be slightly lower (as we found in the sample experiment), since the two reactions take a longer total time, and thus any loss to the room is greater than for the single reaction *2*. In the data analyzed, this relationship was not found.

QUESTIONS

1. Write the net ionic equations for *Reactions 2* and *3*.

Answer: (*2*) $NaOH(s) + H^+(aq) \longrightarrow H_2O + Na^+(aq) + x_2$ cal
(*3*) $OH^-(aq) + H^+(aq) \longrightarrow H_2O + x_3$ cal

2. In *Reaction 1*, ΔH_1 represents the heat of solution of $NaOH(s)$. Look at the net ionic equations for *Reactions 2* and *3* and make a statement concerning the significance of ΔH_2 and ΔH_3.

Answer: ΔH_3 represents the heat of reaction for $H^+(aq)$ and $OH^-(aq)$ (the heat of formation of H_2O from the ions). ΔH_2 represents the sum of ΔH_1 and ΔH_3—the heat of solution of $NaOH(s)$ plus the heat of reaction of $H^+(aq)$ and $OH^-(aq)$.

3. Suppose you had used 4 g of NaOH*(s)* in *Reaction 1.*
   (a) What would be the number of calories evolved?
   (b) What effect would this have on your calculations for ΔH_1, the heat evolved per mole?

Answer: (a) The total amount of heat (the number of calories) would be expected to be twice what was observed.

(b) Twice the amount of heat would be divided by twice the number of moles of NaOH, and the value for ΔH_1 should come out the same. The degree of precision would be greater, however, since the least precise measurement is the temperature change, and Δt would be greater if more reactant were used.

POSTLAB DISCUSSION. Experiment 13 leads so directly into the material in Chapter 7 that you should combine discussion of the experiment and the Textbook assignment. Tabulate the class results to emphasize the regularities observed. Individual students may get some unsatisfactory measurements, but the accumulation of data is sure to be convincing.

Supplementary Material

Articles

1. Heat, in general: The entire September 1954 issue of *Scientific American* is devoted to heat, its measurement and application. Pages 58–60 deal with the kinetic theory of heat. Pages 84–132 deal with thermochemistry.
2. Calorimeters are discussed in more detail by:
   D. F. Mowery, Jr., "A portable mixture calorimeter of high absolute accuracy," *Journal of Chemical Education*, 34, 244–245 (1957).
   R. G. Charles, "A calorimeter for determining specific heats of liquids," *Journal of Chemical Education*, 31, 577–579 (1954).
3. M. Gell-Mann and E. P. Rosenbaum, "Elementary particles," *Scientific American*, pp. 72–88, July 1957 (Offprint No. 213).*
4. The fission and fusion processes involved in the evolution of the universe are treated by:
   W. A. Fowler, "The origin of the elements," *Scientific American*, pp. 82–91, September 1956 (Offprint No. 210).*
   G. Gamow, "The evolutionary universe," *Scientific American*, pp. 136–54, September 1956 (Offprint No. 211).*
   F. Hoyle, "The steady-state universe," *Scientific American*. pp. 157–166, September 1956 (Offprint No. 218).*

Books

R. R. Wilson and R. Littauer, *Accelerators*, Doubleday (Anchor Book), Garden City (1960).

This book from the PSSC physics series is for the student exceptionally interested in accelerators. It deals with a number of physical concepts not covered in this course. Page 61 contains a diagram and instructions for making a Van de Graaff generator from very simple, dime store parts.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

VIBRATION OF MOLECULES

A CHEM Study film
Running Time: 12 minutes

This film illustrates several vibration types in some simple molecules. It also contains material beyond our course. The first half might be shown for stimulation of interest.

MOLECULAR MOTIONS

A CHEM Study film
Running Time: 13 minutes

Experiments, models, and animation introduce and interpret translational, rotational, and vibrational molecular motions during both changes of phase and in molecular changes involving the absorption and emission of energy. Correlations between possible molecular motions and bulk chemical and physical properties show the applications of these concepts to directly observable quantities. Professor J. A. Campbell, of Harvey Mudd College, collaborated in the preparation.

Note: Both films cover molecular vibrations. Preview them to decide how you wish to use them.

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* Available from W. H. Freeman and Co., San Francisco. Order by number.

Background Discussion

A big question for chemists is: What is the driving force of a chemical reaction; i.e., why do reactions go? The exact answer for this question is often rather difficult to give for a specific reaction and is somewhat involved for reactions in general. The answer must be related to changes in energy which accompany reactions, since all chemical reactions do show energy changes. Indeed, most reactions with which the student will be familiar liberate heat. In Chapter 7 you will be concerned with methods for measuring and calculating the energy balance in chemical reactions. This brings us to a somewhat more limited (but important) question: Why do chemists care about the heat of reaction? One reason is that the practical value of many reactions is related to energy liberation. Another is that energy change is one of the two factors (change in randomness is the other) which determine reactions. In later chapters we shall study how chemists relate the energy balance and changes of randomness to the question of why reactions go.

The following pages discuss these topics:

Conservation of Energy
Additivity of Reaction Heats
Microscopic Description of Heat Content
Calorimetry
Energy of Nuclear Transformation
Some Conventions in Expressing Reaction Heats

CONSERVATION OF ENERGY

Our treatment of the energy conservation law may be new. This important law is so well known and has such usefulness that it is often given as a dictum. Such authoritarianism is unwarranted, however, because this law evolved in the same manner as all other scientific generalizations.

Consider the totality of energy existing at some ancient time before the concept of energy was devised. All the occurrences we now describe by the law were then taking place, but there was no stated law of energy conservation. Nor was there a gas law or any other description of natural phenomena. Eventually the measuring sciences were developed, and kinetic energy was invented, at first as a mechanical idea. The next step was to divide energy into types: heat, motion of bodies, and so on. Potential energy was invented to account for stored energy. Once there were types for interconversion a conservation law was possible. The total quantity of energy could be broken up into man-made categories.

But these categories are neither unique nor complete. For instance, the type of energy we now call molecular vibration is a fairly recent invention. Nuclear energy is another such example. As each new kind of energy was needed to explain physical phenomena, it was fitted into the conservation pattern. Only rather recently, Einstein's relation between mass and energy has added another extension to this continuing development. Other kinds of energy will undoubtedly be proposed as the structure of the nucleus is revealed more fully.

ADDITIVITY OF REACTION HEATS

Since heats of reaction can be measured directly, the student might question the usefulness of a system for computing them. You should emphasize that some reactions either proceed too slowly to be studied in the calorimeter or do not react in accordance with a single stoichiometry. Here are two problems which illustrate these points.

Acetylene reacts to form benzene in accordance with the equation

$$3C_2H_2(g) = C_6H_6(l) \tag{5}$$

Even when catalyzed the reaction proceeds too slowly for its heat to be measured conveniently. The heat contents of benzene and acetylene are 13.1 and 54.3 kcal/mole, respectively. Thus the heat of reaction of acetylene to form benzene is $\Delta H = 13.1 \text{ kcal} - 3 \times 54.3 \text{ kcal} = -149.8$ kcal/mole C_6H_6.

When nitrogen reacts with oxygen the main product is NO_2 but not NO. How can we find the heat of the reaction forming NO? The gas NO reacts readily with O_2 in accordance with the equation

$$NO(g) + \tfrac{1}{2}O_2(g) = NO_2(g) \qquad \Delta H = -13.5 \text{ kcal/mole NO} \quad (6)$$

which can be combined with

$$\tfrac{1}{2}N_2(g) + O_2(g) = NO_2(g) \qquad \Delta H = 8.1 \text{ kcal/mole } NO_2 \quad (7)$$

to give

$$\Delta H(\text{NO}) = 8.1 \text{ kcal} + 13.5 \text{ kcal} = 21.6 \text{ kcal/mole NO} \quad (8)$$

Other examples of problems of this type are given in references 1 and 2, p. 230.

Another advantage of the calculation method is that in practice it is not easy to measure ΔH, even when the reaction is appropriate. See *Calorimetry.*

MICROSCOPIC DESCRIPTION OF HEAT CONTENT

In Section 7-3.1, the student is given an account of how heat is stored in various motions of the atoms, in positions of the molecules relative to each other, and in the nuclear structure of the atom. These ideas come from experiments we cannot place before the student yet. They will come up later—mostly in Chapters 14 and 15. Briefly they are as follows.

Infrared and microwave spectra yield information explained on the basis of molecular vibration and rotation (Chapter 14). Ultraviolet (UV) and visible spectra result from changes in electron arrangements. Such results are a cornerstone of our description of atomic structure and will be studied in Chapter 15.

Thermochemistry—the experimental aspect of the subject of Chapter 7—gives data about chemical bond energy. We are now beginning to obtain information on energy levels in the nucleus from the various accelerators.

CALORIMETRY

Measuring the heat of a chemical reaction with high accuracy can prove to be a rather difficult experimental feat. Remember that the objective is to measure all the heat evolved in the reaction. The evolved heat does several things: it increases the temperature of (a) the products of the reaction (and even the reactants themselves, if the reaction is slow); (b) the water in the calorimeter; and (c) the calorimeter parts—stirrer, container, thermometer, etc. In addition, some heat is lost to or gained from the surroundings. In simple calorimetry, as performed in Expt. 13, some of these heat effects are lumped together, and others are neglected, which, in part, accounts for the error associated with the experiment.

In dilute solution calorimetry one hopes that the effects of the specific heats of the reagents on the heat capacity of water will cancel each other. The heat capacity of the calorimeter parts is difficult to measure or compute precisely when they are attached to the calorimeter. It is common practice to perform a reaction whose heat effect is known and to assume the difference between the heat obtained and the known heat of reaction to be the heat absorbed by the calorimeter and its parts. This absorbed heat is called the water equivalent of the calorimeter.

In precise calorimetry the chemist must consider the heat lost to or gained from the surroundings. This heat may be calculated from a plot of the experimental rate at which the calorimeter exchanges heat with the surroundings, both at the beginning and at the end of the reaction. Such data can be used to extrapolate to exact initial and final reaction temperatures. When the highest precision is required, the above method of correcting for heat loss is not used. The reaction is performed under *adiabatic* conditions; i.e., under conditions such that no heat is lost to or gained from the surroundings. Adiabatic conditions are commonly achieved by placing the calorimeter in an evacuated vessel within a metallic shield that can be heated electrically. Electrical energy is supplied to the shield at a rate that will maintain a temperature equal to that of the calorimeter, which thus does not gain or lose heat.

Mention is made that heats of reaction measured at constant pressure (ΔH_p) differ from such heats measured at constant volume (ΔH_v). This difference arises because a gas expanding against the pressure of the atmosphere does work and loses energy. Thus ΔH_p is always more positive than ΔH_v. For an exothermic reaction, ΔH_p is a smaller negative number. A gas sample which is compressed by the atmosphere has work done on it and gains energy. Heats given in the Textbook are for reactions measured at constant pressure. For reactions occurring in the solid and liquid phases, the effect of pressure is usually insignificant because the volume change, ΔV, is quite small. For reactions occurring in the gas phase, the difference may be appreciable. Some students will wish more details on how to relate the expansion and contraction of the reaction system to the accompanying energy changes. One way to do this is to show the dimensions of $P\Delta V$.

The work done by the system can be defined by the equation

$$w = P\Delta V \qquad (9)$$

Since pressure is defined as force per unit area, F/L^2, and volume as length cubed, L^3, equation (*19*) may be written

$$w = \frac{F}{L^2} \times L^3 = F \times L \qquad (10)$$

Equation (*10*) is a common definition of work and energy. A more comprehensive treatment of this topic is given on pp. 540–542 of reference 1.

ENERGY OF NUCLEAR TRANSFORMATION

The student will be quite aware of the tremendous amount of energy available from nuclear reactions, as he knows about the atomic bomb and nuclear reactors. Nevertheless, his feeling about the origin of this energy will probably be closer to awe and mystery than to a satisfactory understanding. You may be able to generate a better feeling for the naturalness of this great energy production by discussing one or two naturally radioactive processes—radium decay, for example. Radium and its disintegration products emit energy continually in the form of alpha, beta, and gamma rays. Most of the energy of these rays is dissipated in the form of heat. One gram of radium emits about 132 calories of heat per hour. It can be computed that during its lifetime 1.0 g of radium would emit about 2,400,000,000 calories of heat. In comparison, the burning of 1.0 g of carbon to CO_2 gives 7867 calories. That nuclear reaction energies are many orders of magnitude greater than chemical reactions becomes evident when we realize that the energy available from 1.0 g of radium is about equal to that which can be obtained by burning half a ton of coal.

The student knows that energy can be obtained from both nuclear fusion and nuclear fission. Some students may wish to know more about how to tell which process will be exoergic (energy releasing). You may let him discover this for himself by writing equations in which charge is conserved but mass changes occur. Isotopic masses should be used. A complete list of isotopic masses is given in reference 3, and a partial list is given in references 1 and 2. Two sample equations for illustrative purposes are

$$^{235}_{92}\mathrm{U} + ^{1}_{0}n \longrightarrow ^{95}_{42}\mathrm{Mo} + ^{139}_{57}\mathrm{La} + 2\,^{1}_{0}n + 7\,_{-1}^{0}\beta \qquad (11)$$

$$\begin{aligned}\Delta m &= 94.945 + 138.955 + 2.018 - 235.124 - 1.009\\ &= -0.215\end{aligned}$$

$$^{4}_{2}\mathrm{He} + ^{1}_{0}n \longrightarrow ^{3}_{1}\mathrm{H} + ^{2}_{1}\mathrm{H} \qquad (12)$$

$$\begin{aligned}\Delta m &= 3.00000 + 2.01473 - 4.00386 - 1.00898\\ &= 0.00189\end{aligned}$$

We interpret the mass defect for the first reaction as indicating that it can serve as a source of considerable energy; i.e., energy can be obtained by nuclear fission. The increase of mass in the second reaction indicates that it can proceed only when energy is supplied. We may obtain energy by using the reverse reaction, nuclear fusion. The quantity of energy can be computed from the Einstein equation $E = mc^2$. You should emphasize that some of the energy is expended in the form of kinetic energy of released neutrons. You should understand that Einstein's equation does not give any clue as to why the energy is so large, nor why a particular reaction gives out energy. Often the mass defects are learned by measuring energy changes. In any event, the mass defects and the energy changes are both symptomatic of nuclear stability, which cannot be explained or predicted.

When mass is expressed in grams, and the velocity of light, c, in cm/sec, energy will be obtained in terms of ergs. To express this energy in kcal, use the conversion formula,

$$\text{kcal} = \text{ergs} \times \frac{1\ \text{joule}}{10^7\ \text{ergs}} \times \frac{1\ \text{cal}}{4.184\ \text{joules}} \times \frac{1\ \text{kcal}}{1000\ \text{cal}} \qquad (13)$$

Energy changes of nuclear reactions are commonly expressed in million electron volts (Mev). Such units may be converted to ergs by using the factor

$$1\ \text{ev} = 1.602 \times 10^{-12}\ \text{erg}$$

or

$$1\ \text{Mev} = 1.602 \times 10^{-6}\ \text{erg}$$

We have expressed the energy of nuclear reactions in kilocalories in order to compare them with the heats of more typical chemical changes. This is a simple change of scale from the Mev system mentioned above. There is no "correct" unit for either type of reaction. The choice of units for any experimental measurement is entirely a matter of convenience.

SOME CONVENTIONS IN EXPRESSING REACTION HEATS

For heats of reaction to be meaningful they must be referred to a specific state of the substance. This means that, in addition to mentioning temperature and pressure, the polymorphic modification of the element must be given; for example, diamond or graphite, white phosphorus or red phosphorus. At this point you have an excellent opportunity to discuss the energy accompanying phase transitions in which there is a change in atomic arrangement but no phase change. Some of the more familiar transitions are expressed by these equations:

C(diamond) = C(graphite) $\Delta H = -0.450$ kcal
S(rhombic) = S(monoclinic) $\Delta H = -0.08$ kcal
Sb(black) = Sb(gray) $\Delta H = -2.4$ kcal

REFERENCES FOR ADDITIONAL READING

1. L. A. Hiller, Jr. and R. H. Herber, *Principles of Chemistry*, McGraw-Hill, New York (1960), Chapters 13 and 16.
2. M. D. Taylor, *First Principles of Chemistry*, Van Nostrand, Princeton (1960), Chapters 9 and 11.
3. *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland. Always use a modern handbook. Any edition from the past five years is satisfactory.

Answers to Exercises and Problems

Ex. 7-1. Suppose reactants are mixed in a calorimeter at 25°C and the reaction heat causes the temperature of the products and calorimeter to rise to 35°C. The resultant determination of ΔH applies to what temperature? Explain why it is desirable to keep the final temperature close to the initial temperature in a calorimetric measurement.

Answer

In this example, ΔH applies to a temperature range, 25–35° or 30°C ± 5°. The smaller the temperature rise, the more nearly ΔH represents the reaction heat at a particular temperature.

Ex. 7-2. Predict the heat of the reaction

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

from two reactions listed in Table 7-II. Compare your result with ΔH_{2b} given in Section 7-1.2.

Answer

$$CO(g) \longrightarrow C(s) + \tfrac{1}{2}O_2(g) \qquad \Delta H = +26.4 \text{ kcal/mole CO}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.0$$

$$\text{Net: } CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -67.6 \text{ kcal/mole CO}$$

This is an important type of problem. The student should understand clearly why ΔH for the first reaction is +26.4 kcal, whereas it is −26.4 in Table 7-II and that carbon cancels when the two reactions are added.

Ex. 7-3. Convince yourself that reaction (9) and also $\Delta H_9 = -67.6$ kcal can be obtained by carrying out the indicated summation:

From $\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)$

$\Delta H = +8.1$ kcal

Subtract $\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \longrightarrow NH_3(g)$

Subtract $\Delta H = -11.0$ kcal

And now

add $\tfrac{3}{2}$ times $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$

Add $\tfrac{3}{2}$ times $\Delta H = -57.8$ kcal

Answer

$$-\tfrac{1}{2}N_2 - \tfrac{3}{2}H_2 + \tfrac{1}{2}N_2 + O_2 + \tfrac{3}{2}H_2 + \tfrac{3}{4}O_2 \longrightarrow NH_3 + NO_2 + \tfrac{3}{2}H_2O$$

$$NH_3(g) + \tfrac{7}{4}O_2(g) \longrightarrow NO_2(g) + \tfrac{3}{2}H_2O(g)$$

$$\Delta H = -(-11.0) + (+8.1) + (\tfrac{3}{2})(-57.8) = 19.1 - 86.7 = -67.6 \text{ kcal}$$

Ex. 7-4. Show that the ratio of the molar heat of formation of gaseous water from the elements (a chemical reaction) to the molar heat of the fusion of water (a phase change) is of the order of 50.

Answer

The molar heat of formation is 68.3 kcal (p. 112).

The molar heat of fusion is 1.44 kcal (p. 69). The ratio is 57.8/1.44 = 40.1.

Ex. 7-5. According to the model of Chapter 6, how many nucleons would be present in a uranium nucleus of mass number 235? How many protons are pictured as being present? How many neutrons?

Answer

There are 235 nucleons present; 92 protons and 143 neutrons.

Pr. 1. Given:

$$3C(s) + 2Fe_2O_3(s) + 110.8 \text{ kcal} \longrightarrow 4Fe(s) + 3CO_2(g)$$

Rewrite the equation using one mole of carbon and use the ΔH notation.

Answer

$$C(s) + \tfrac{2}{3}Fe_2O_3(s) \longrightarrow \tfrac{4}{3}Fe(s) + CO_2(g) \qquad \Delta H = 36.93 \text{ kcal}$$

Pr. 2. Given:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(l) \longrightarrow HBr(g) \qquad \Delta H = -8.60 \text{ kcal/mole HBr}$$

Rewrite the equation for one mole of hydrogen gas and include the heat effect as a term in the equation.

Answer

$$H_2(g) + Br_2(l) \longrightarrow 2HBr(g) + 17.2 \text{ kcal}$$

This problem reviews two important points: the methods of showing heat effect; and the quantitative connection between the mass terms (equation) and the energy term (ΔH). Note that the energy term is doubled when the mass terms are doubled. Energy is an extensive property; when more material changes, more energy is used or given up. (Density, on the other hand, is an intensive property—

a property which is independent of amount of material.)

Pr. 3. Which of the following reactions are endothermic?

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H = -57.8$ kcal

(b) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H = +21.6$ kcal

(c) $\frac{1}{2}N_2(g) + O_2(g) + 8.1 \text{ kcal} \longrightarrow NO_2(g)$

(d) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) + 11.0 \text{ kcal}$

(e) $NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \quad \Delta H = +11.0$ kcal

Answer: (b), (c), (e).

Pr. 4. What is the minimum energy required to synthesize one mole of nitric oxide, NO, from the elements?

Answer

One must add 21.6 kcal to ½ mole of $N_2(g)$ and ½ mole of $O_2(g)$ in order to make one mole of NO.

Pr. 5. How much energy is liberated when 0.100 mole of H_2 (at 25°C and 1 atmosphere) is combined with enough $O_2(g)$ to make liquid water at 25°C and 1 atmosphere?

Answer

From Table 7-II (Textbook):

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -68.3 \text{ kcal/mole } H_2O(l)$$

Since one mole of H_2O is formed from one mole of H_2, 0.100 mole of H_2 will form 0.100 mole of $H_2O(l)$ and liberate $(0.100) \times (68.3) = 6.83$ kcal (or, $\Delta H = -6.83$ kcal/0.100 mole of H_2O).

Pr. 6. How much energy is consumed in the decomposition of 5.0 grams of $H_2O(l)$ at 25°C and 1 atmosphere into its gaseous elements at 25°C and 1 atmosphere?

Answer

$$H_2O(l) + 68.3 \text{ kcal} \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

One mole of $H_2O(l)$ absorbs 68.3 kcal during decomposition to elements.

The amount of energy used to decompose 5.0 grams is

$$\frac{5.0 \text{ g}}{18 \text{ g/mole}} \times 68.3 \frac{\text{kcal}}{\text{mole}} = 19 \text{ kcal}$$

Pr. 7. Using Table 7-II, calculate the heat of burning ethane in oxygen to give CO_2 and water vapor.

Ans. $\Delta H = -341$ kcal/mole C_2H_6.

Answer

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g) \qquad \text{(overall reaction)}$$

$$C_2H_6(g) \longrightarrow 2C(s) + 3H_2(g) \qquad \Delta H = +20.2 \text{ kcal}$$

$$2C(s) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = 2(-94.0) = -188.0 \text{ kcal}$$

$$3H_2 + \tfrac{3}{2}O_2(g) \longrightarrow 3H_2O(g) \qquad \Delta H = 3(-57.8) = -173 \text{ kcal}$$

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g) \qquad \Delta H = +20.2 - 188.0 - 173$$

$$\Delta H = -341 \text{ kcal/mole } C_2H_6$$

This value is called the heat of combustion of ethane.

Pr. 8. Given:

$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94.50$ kcal

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94.05$ kcal

Find ΔH for the manufacture of diamond from graphite.

$$C(\text{graphite}) \longrightarrow C(\text{diamond})$$

Is heat absorbed or evolved as graphite is converted to diamond?

Answer

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.05 \text{ kcal}$$

$$CO_2(g) \longrightarrow O_2(g) + C(\text{diamond}) \qquad \Delta H = +94.50 \text{ kcal}$$

Net: $C(\text{graphite}) \longrightarrow C(\text{diamond}) \qquad \Delta H = +0.45$ kcal

Since ΔH is positive, heat is absorbed. Notice how small it is, however, compared to combustion reaction heats. The low value of ΔH shows that it was not a high energy requirement that delayed the production of artificial diamonds.

Pr. 9. To change the temperature of a particular calorimeter and the water it contains by one degree requires 1550 calories. The complete combustion of 1.40 grams of ethylene gas, $C_2H_4(g)$, in the calorimeter causes a temperature rise of 10.7 degrees. Find the heat of combustion per mole of ethylene.

Answer

The heat released by 1.40 g of ethylene is

$$10.7\text{C}^\circ \times \frac{1550 \text{ cal}}{\text{C}^\circ} = \text{cal}$$

This heat was released by 1.40/28.0 mole of ethylene. Thus the heat released per mole is

$$\begin{aligned}\frac{10.7(1550)\ \text{cal}}{1.40/28.0\ \text{mole}} &= 332{,}000\ \text{cal/mole}\\ &= 332\ \text{kcal/mole}\end{aligned}$$

The burning liberates heat, and since less heat content is left in the products than was in the reactants, ΔH is negative.

$$\Delta H = -332\ \text{kcal/mole}\ C_2H_4(g)$$

Pr. 10. The "thermite reaction" is spectacular and highly exothermic. It involves the reaction between Fe_2O_3, ferric oxide, and metallic aluminum. The reaction produces white-hot, molten iron in a few seconds. Given:

$$\begin{aligned}&2Al + \tfrac{3}{2}O_2 \longrightarrow Al_2O_3 &\quad \Delta H_1 &= -400\ \text{kcal/mole}\\ &2Fe + \tfrac{3}{2}O_2 \longrightarrow Fe_2O_3 &\quad \Delta H_2 &= -200\ \text{kcal/mole}\end{aligned}$$

Determine the amount of heat liberated in the reaction of 1 mole of Fe_2O_3 with Al.

Ans. $\Delta H = -200$ kcal/mole Fe_2O_3.

Answer

$$\begin{aligned}&2Al + \tfrac{3}{2}O_2 \longrightarrow Al_2O_3\\ &\qquad \Delta H_1 = -400\ \text{kcal/mole}\ Al_2O_3\\ &Fe_2O_3 \longrightarrow 2Fe + \tfrac{3}{2}O_2\\ &\qquad \Delta H_2 = +200\ \text{kcal/mole}\ Fe_2O_3\\ \hline &2Al + Fe_2O_3 \longrightarrow 2Fe + Al_2O_3\\ &\qquad \Delta H_3 = \Delta H_1 + \Delta H_2 = (-400) + 200\\ &\qquad \Delta H_3 = -200\ \text{kcal/mole}\ Fe_2O_3\end{aligned}$$

Pr. 11. How much energy is released in the manufacture of 1.00 kilogram of iron by the "thermite reaction" mentioned in Problem 10?

Answer

$$\begin{aligned}\Delta H &= -200\ \text{kcal/mole}\ Fe_2O_3\\ &= -200\ \text{kcal/2 moles Fe}\\ &= -100\ \text{kcal/mole Fe}\end{aligned}$$

$$\begin{aligned}1.00\ \text{kg Fe} &= 1.00 \times 10^3\ \text{g Fe} = \frac{1.00 \times 10^3\ \text{g}}{55.8\ \text{g/mole}}\\ &= 17.9\ \text{moles}\end{aligned}$$

$$\Delta H = \left(-100\,\frac{\text{kcal}}{\text{mole Fe}}\right)\left(17.9\,\frac{\text{moles Fe}}{\text{kg Fe}}\right)$$

$$\Delta H = -1790\ \text{kcal/kg Fe}$$

Pr. 12. How many grams of water could be heated from 0°C to 100°C by the heat liberated per mole of aluminum oxide formed in Problem 10?

Answer

One hundred calories are necessary to raise 1.00 g of water from 0°C to 100°C. The heat liberated per mole of Al_2O_3 formed is 200 kcal $= 200 \times 10^3$ cal. The amount of water that could be heated from 0°C to 100°C is

$$\frac{200 \times 10^3\ \text{cal}}{100\ \text{cal/gram}} = 2.00 \times 10^3\ \text{g} = 2.00\ \text{kg}$$

Pr. 13. Which would be the better fuel on the basis of the heat released per mole burned, nitric oxide, NO, or ammonia, NH_3? Assume the products are $NO_2(g)$ and $H_2O(g)$.

Answer

The burning of $NO(g)$ can be shown by the equation

$$NO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

To find ΔH for this reaction, it is necessary to break the reaction down into steps for which ΔH is known.

$$\begin{aligned}&NO(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g)\\ &\qquad \Delta H = -21.6\ \text{kcal}\\ &\tfrac{1}{2}N_2(g) + O_2(g) \rightleftharpoons NO_2(g)\\ &\qquad \Delta H = +8.1\ \text{kcal}\\ \hline &NO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons NO_2(g)\\ &\qquad \Delta H = -13.5\ \text{kcal/mole NO}\end{aligned}$$

The burning of $NH_3(g)$ can be shown by the following equation:

$$NH_3(g) + \tfrac{7}{4}O_2(g) \rightleftharpoons NO_2(g) + \tfrac{3}{2}H_2O(g)$$

This can be broken down into the following steps for which ΔH is known.

$$\begin{aligned}&NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)\\ &\qquad \Delta H = +11.0\ \text{kcal}\\ &\tfrac{1}{2}N_2(g) + O_2(g) \rightleftharpoons NO_2(g)\\ &\qquad \Delta H = +8.1\ \text{kcal}\\ &\tfrac{3}{2}H_2(g) + \tfrac{3}{4}O_2(g) \rightleftharpoons \tfrac{3}{2}H_2O(g)\\ &\qquad \Delta H = \tfrac{3}{2}(-57.8)\ \text{kcal}\\ \hline &NH_3(g) + \tfrac{7}{4}O_2(g) \rightleftharpoons NO_2(g) + \tfrac{3}{2}H_2O(g)\\ &\qquad \Delta H = -86.7 + 19.1\\ &\qquad\quad\ = -67.6\ \text{kcal/mole}\ NH_3(g)\end{aligned}$$

If the products of combustion of $NH_3(g)$ are assumed to be $NO(g)$ and $H_2O(g)$, the value of ΔH is -54.1 kcal/mole $NH_3(g)$. The overall conclusion is the same: $NH_3(g)$ is the better fuel on the basis of energy per mole of fuel burned.

Pr. 14. What is the minimum energy required to synthesize sulfur dioxide from sulfuric acid?

$$H_2SO_4(l) \longrightarrow SO_2(g) + H_2O(g) + \tfrac{1}{2}O_2(g)$$

Ans. $\Delta H = +65$ kcal/mole $SO_2(g)$.

Answer

kcal for reaction as written

$$H_2SO_4(l) \longrightarrow H_2(g) + \tfrac{1}{8}S_8(s) + 2O_2(g) \qquad \Delta H = +194$$

$$\tfrac{1}{8}S_8(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -71.0$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -57.8$$

$$H_2SO_4(l) \longrightarrow SO_2(g) + H_2O(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = +65$$

To one mole of $H_2SO_4(l)$ there must be added 65 kcal to make one mole of $SO_2(g)$.

Pr. 15. Why is the Law of Conservation of Energy considered to be valid?

Answer

Because it "explains"—accurately correlates—a large amount of experimental data.

Pr. 16. What do you think would happen in scientific circles if a clearcut, well-verified exception was found to the Law of Conservation of Energy as stated in the text?

Answer

Either the law would be modified to fit the exception (plus all previous data) or it would be discarded and a new generalization sought. The same would be true for any other law.

Pr. 17. Is energy conserved when a ball of mud is dropped from your hand to the ground? Explain your answer.

Answer

Yes, energy is conserved. The potential energy the mud had in your hand is converted into kinetic energy as the glob falls. When it hits the ground, the particles of mud are moved relative to each other. This movement requires energy and results in heating. Thus the kinetic energy is converted to heat.

Pr. 18. What becomes of the energy supplied to water molecules as they are heated in a closed container from 25°C to 35°C?

Answer

The molecules move about more rapidly and rotate more quickly. The vibrations of the atoms within a particular molecule also increase.

Pr. 19. Outline the events and associated energy changes that occur on the molecular level when steam at 150°C and 1 atmosphere pressure loses energy continually until it finally becomes ice at −10°C.

Answer

(1) As the steam is cooled to 100°C the molecules slow down, hence their kinetic energy decreases. Moreover, the molecules rotate and vibrate less violently.

(2) As the steam condenses to liquid water at 100°C, the molecules come much closer together, thus the potential energy decreases.

(3) During cooling to 0°C (still liquid water) there is a decrease in kinetic energy, rotational energy, and vibrational energy.

(4) The liquid water at 0°C freezes to ice at 0°C. The molecules lose their randomness of motion. Their positions become fixed, such that their principal motion is one of vibration about a point. This is accompanied by a decrease of potential energy.

(5) Finally, cooling the ice to −10°C decreases the kinetic energy of the system. The molecules vibrate less rapidly about their lattice positions.

Pr. 20. The heat of combustion of methane, CH_4, is −210 kcal/mole:

$$CH_4(g) + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H = -210 \text{ kcal}$$

Discuss why this fuel is better than water gas if the comparison is based on one mole of carbon atoms.

Answer

For one mole of carbon atoms, methane releases much more heat (210 kcal/mole compared to 125.4). Even if we add enough hydrogen to the water gas to give the same number of atoms of C and H as in CH_4, the total heat effect is −183.2 kcal, still less than 210.

The sophisticated student may realize that this comes partly from the different combination of atoms. The water gas is already partly "burned" in the sense that the carbon has reacted with half its total possible oxygen.

Pr. 21. In a nuclear reaction of the type called "nuclear fusion," two nuclei come together to form a larger nucleus. For example, deuterium nuclei, ${}^{2}_{1}H$, and tritium nuclei, ${}^{3}_{1}H$, can "fuse" to form helium nuclei, ${}^{4}_{2}He$, and a neutron.

$${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n \qquad \Delta H = -4.05 \times 10^{8} \text{ kcal}$$

How many grams of hydrogen would have to be burned (to gaseous water) to liberate the same amount of heat as liberated by fusion of one mole of ${}^{2}_{1}H$ nuclei? Express the answer in tons (1 ton = 9.07×10^{5} g).

Answer

One mole of H_2 burned to $H_2O(g)$ liberates 57.8 kcal.

$\frac{4.05 \times 10^{8}}{57.8}$ moles of H_2 burned to $H_2O(g)$ liberate 4.05×10^{8} kcal.

7.01×10^{6} moles of H_2 burned to $H_2O(g)$ liberate 4.05×10^{8} kcal.

$(7.01 \times 10^{6}) \times (2.02 \text{ g/mole})$
$= 1.42 \times 10^{7}$ g of H_2 liberate 4.05×10^{8} kcal.

$\frac{1.42 \times 10^{7} \text{ g}}{9.07 \times 10^{5} \text{ g/ton}} = 15.7$ tons of H_2 liberate 4.05×10^{8} kcal, the heat liberated by 2.00 grams of deuterium fusing with tritium.

Pr. 22. Which of the following reactions is most likely to have a heat effect of −505 kcal? Which would be -1.7×10^{6} kcal? Which would be +7.2 kcal?

(a) $UF_6(l) \longrightarrow UF_6(g) \qquad \Delta H = ?$

(b) $U(s) + 3F_2(g) \longrightarrow UF_6(g) \qquad \Delta H = ?$

(c) ${}^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \qquad \Delta H = ?$

Answer

(a) +7.2 kcal
(b) −505 kcal
(c) -1.7×10^{6} kcal

Pr. 23. Fission of uranium gives a variety of fission products, including praseodymium, Pr. If the process by which praseodymium is formed gives ${}^{147}_{59}Pr$ and three neutrons, what is the other nuclear product?

$${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{147}_{59}Pr + \underline{\qquad} + 3\,{}^{1}_{0}n$$

Answer

The subscript indicates the number of protons. We begin with 92 (in the uranium nucleus), and 59 are accounted for in the praseodymium nucleus. The remaining protons (92 − 59 = 33) are in the other product. Element 33 is arsenic, ${}_{33}As$.

The superscript indicates the total number of nucleons. We begin with 235 + 1 = 236. Of these, praseodymium accounts for 147, and the three neutrons account for 3 more. The remaining nucleons are in the arsenic nucleus.

$$236 - 147 - 3 = 86$$

The product is the arsenic isotope, ${}^{86}_{33}As$.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1–3 relate to the following information.

Hydrogen gas and oxygen gas react according to the following equations:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 115.6\text{ kcal}$$
$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l) + 136.6\text{ kcal}$$

1. How much more energy is stored in one mole of hydrogen molecules and $\frac{1}{2}$ mole of oxygen molecules than is stored in one mole of gaseous water molecules?

   Answer: 57.8 kcal.

2. What is the ΔH for the formation of liquid water from hydrogen gas and oxygen gas?

   Answer: $\Delta H = -68.3$ kcal/mole of H_2O.

3. Use the information given in the two equations to find the energy required to evaporate one mole of water, $H_2O(l)$.

   Answer: 10.5 kcal.

Questions 4–6 relate to the following information.

The two balanced equations (I) and (II) are for reactions in which gaseous carbon dioxide is produced from the combustion of (I) solid carbon and (II) gaseous carbon monoxide.

$$C(s) + O_2(g) \rightleftharpoons CO_2(g) + 94.0\text{ kcal} \qquad \text{(I)}$$
$$CO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO_2(g) + 67.6\text{ kcal} \qquad \text{(II)}$$

4. On the basis of the information given in equation (II), and assuming no change in temperature or pressure, one can correctly conclude that

   (1) The rate of reaction is rapid.
   (2) The total number of moles of products is the same as the total number of moles of reactants.
   (3) The reaction is exothermic.
   (4) The weights of the products are greater than those of the reactants.
   (5) There will be an increase in the volume of the reactants and products taken together as the reaction proceeds.

   Answer: 3.

5. When 112 grams of carbon monoxide are consumed according to equation (II), which of the following occurs (atomic weights: C = 12.0; O = 16.0)?

   (1) 1.0 mole of carbon dioxide is produced.
   (2) 67.6 kcal of heat are generated.
   (3) 2.0 moles of oxygen are consumed.
   (4) 0.25 mole of carbon dioxide is produced.
   (5) 0.50 mole of oxygen is consumed.

   Answer: 3.

6. On the basis of calculations using equations (I) and (II), find how much heat in kcal per mole of carbon would be produced in the following reaction.

   $$C(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO(g) + \underline{\qquad}\text{ kcal/mole carbon}$$

   (1) 20.6,
   (2) 26.4,
   (3) 41.2,
   (4) 161.6,
   (5) None of the above.

   Answer: 2.

7. Complete the following reactions, which indicate the method of producing americium.

   (1) $^{238}_{92}U + {}^{4}_{2}He \longrightarrow {}^{241}_{94}Pu + \underline{\qquad}$
   (2) $^{241}_{94}Pu \longrightarrow {}^{241}_{95}Am + \underline{\qquad}$

   Answer: (1) $^{1}_{0}n$.
   (2) $^{\ 0}_{-1}e$.

8. It has been determined by calorimetric measurement that the complete fission of 500 grams of uranium yields about 10^{13} calories. The heat of combustion for 500 grams of coal is about 5×10^6 calories. Compare the amount of energy obtained

when one kilogram of coal burns to that obtained when one kilogram of uranium undergoes fission.

Answer

$$\frac{\text{energy fusion}}{\text{energy burning}} = \frac{1 \times 10^{13}\ \text{cal/500 g}}{5 \times 10^{6}\ \text{cal/500 g}}$$

$$= 2 \times 10^{6}$$

9. When concentrated sulfuric acid is added to water, heat is liberated. The heat of dilution is about 18 kcal/mole of H_2SO_4 diluted with a large volume of water. Using the law of additivity of heat, predict how much heat would be released if 9.8 grams of H_2SO_4 were added to sufficient water such that all the heat of dilution would be released.

Answer

$$\frac{18\ \text{kcal}}{\text{mole}} \times \frac{1\ \text{mole}}{98\ \text{g}} \times 9.8\ \text{g}\ H_2SO_4 = 1.8\ \text{kcal}$$

10. Given the two equations

$$H_2(g) + O_2(g) \rightleftharpoons H_2O_2(l) + 44.84\ \text{kcal}$$

and

$$H_2O_2(l) \rightleftharpoons H_2O(l) + \tfrac{1}{2}O_2(g) + 23.48\ \text{kcal}$$

determine ΔH for

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(l)$$

Answer: Add the two equations to obtain

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(l) + 68.32\ \text{kcal}$$
$$\Delta H = -68.32\ \text{kcal}$$

11. Given the three equations

$$Ca(s) + 2H_2O(l) \rightleftharpoons Ca^{+2}(aq) + 2OH^-(aq) + H_2(g) + 103\ \text{kcal}$$
$$CaO(s) + H_2O(l) \rightleftharpoons Ca^{+2}(aq) + 2OH^-(aq) + 19.5\ \text{kcal}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(l) + 68.3\ \text{kcal}$$

Determine ΔH for

$Ca(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons CaO(s) +$ ______ kcal

Answer

$$\begin{array}{l}
Ca(s) + 2H_2O(l) \rightleftharpoons \\
\quad Ca^{+2}(aq) + 2OH^-(aq) + H_2(g) + 103\ \text{kcal} \\
-[CaO(s) + H_2O(l) \rightleftharpoons \\
\quad Ca^{+2}(aq) + 2OH^-(aq) + 19.5\ \text{kcal}] \\
\hline
Ca(s) - CaO(s) + H_2O \rightleftharpoons H_2(g) + 83.5\ \text{kcal} \\
\quad + [H_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(l) + 68.3\ \text{kcal}] \\
\hline
Ca(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons CaO(s) + 151.8\ \text{kcal} \\
\Delta H = -151.8\ \text{kcal}
\end{array}$$

CHAPTER

8

THE RATES OF CHEMICAL REACTIONS

Intent and Approach

Students will start this chapter with some idea that reactions proceed at different rates. However, you can expect they will have no idea of how to explain this or how to tie it to energy effects or the kinetic theory of gases.

This chapter will provide the explanation of reaction rate via the activated complex theory. This theory, combined with the kinetic theory of molecular motion, permits understanding how variation of concentration or temperature and adding a catalyst can change reaction rate. The heat of reaction is also integrated with the diagram used to show the activated complex. In addition to tying in some previous theories, the concepts introduced here will be used in the next chapter, on equilibrium.

Students are introduced to some of the principles of chemical kinetics (rate of reaction) by means of Expt. 14, the "iodine clock" reactions. The experiment permits the student to observe directly the effects of temperature and concentration on the rate of one set of chemical reactions.

It is important to remind the student that this is one of the frontiers in chemistry; that our understanding of reaction mechanisms is at best very limited; and that this is one of the exciting and important areas open to the able and interested chemistry student. In particular, the specific activated complex is known for only a very few reactions, and the exact mechanism is not available for many cases.

Outline

1. General comments; how rates are specified (Textbook, pp. 124–125).
2. Factors affecting rates of chemical reactions are described (8-1.1 and Expt. 14).
3. How the nature of reactants influences the rate (8-1.1).
4. Collision theory is developed as a model for understanding the effect concentration has on reaction rate (8-1.2). The quantitative effect is handled separately (8-1.4).
5. Reaction mechanism is explained and illustrated (8-1.3).
6. The collision theory, the temperature effect on reaction rate, the distribution of kinetic energies, and the threshold energy for reaction are discussed (8-1.5).
7. Activation energy and the activated complex are introduced (8-2.1) along with the potential energy diagram to describe a reaction.
8. Heat of reaction is related to the potential energy diagram (8-2.2).
9. The action of catalysts is related to the activated complexes and potential energy diagram (8-2.3). A more thoroughly discussed example is provided in reduced type (8-2.4).

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
Expt. 14	1	Expt. 14					“Clock” Reaction
S 8-1/8-1.2 (pp. 125–127)	2	Film, AN INTRODUCTION TO REACTION KINETICS	1	1–4	5, 6, 8	7	Some Factors Affecting Rate
S 8-1.3/8-1.4 (pp. 127–129)	3	Discussion	2	9–11			Reaction Mechanism
S 8-1.5 (pp. 129–132)	4	Discussion			13	12	Effect of Temperature, Energy Distribution
S 8-2/8-2.2 (pp. 132–135)	5	Film, CATALYSIS		14, 20	15–19	21	Activation Energy
S 8-2.3 (pp. 135–137)	6	Problems			22		Catalysis
Expt. 14 a (optional)	7	Expt. 14a					A Catalyzed Reaction
	8	Film, CATALYSIS Review, Quiz					

New Concepts

1. Collision theory explains the change of reaction rates by temperature and concentration.
2. Most reactions proceed by a series of reactions involving only two-particle collisions. The series is called the mechanism of the overall reaction.
3. Activation energy.
4. Distribution of kinetic energy values.
5. Catalysts influence the rate by providing a new, more favorable path for the reaction.

Development

INTRODUCTION

Experiment 14 is used to introduce the student to both the qualitative and quantitative aspects of the factors which affect rates of chemical reactions. The basic factors to be considered include the nature of the reactants, the temperature, and the concentration.

The student is probably aware that some reactions go rapidly and others more slowly, but any quantitative measure of this, or any explanation for it, will probably be new to him. The units of reaction rate are similar to the units of rate of travel—amount/time compared to miles/time. The units used for "amount" and "time" are chosen for convenience only.

Expt. 14, A STUDY OF REACTION RATES, fits here. See p. 247 for guide.

FACTORS AFFECTING REACTION RATES (8-1)

The Nature of the Reactants (8-1.1)

It may seem axiomatic that the nature of the reactant should have some influence on the rate and type of reaction. This section gives a rule of thumb for deciding on a rate. There is a buried point here that the student is not ready for as such—that is, to lay the basis for an explanation of the generally slow rates with which organic substances react. The whole of organic chemistry would be different if organic reactions were quite rapid. Consider the number of compounds that will combine with oxygen but, at room temperature, do so at a rate so low that for practical purposes there is no reaction. These reactions are of the type that require bond breakage. As is true of any general statement, the rules given here and the above remarks apply to the majority of chemical changes, but not to every one.

Effect of Concentration: Collision Theory (8-1.2)

Collision theory is introduced as a model for describing chemical reactions and explaining reaction rates. Reactions occur as a result of collision between two particles; hence it is reasonable that any change which increases the reactant concentrations gives more collisions per unit time and will increase reaction rate; for example, by increasing the pressure on a gas, by increasing the state of subdivision of reactants, and so on. Do not make a flat statement that a rise in concentration will give a faster rate. This rule does not always apply to the overall equations which are usually written. If we dealt with the complete reaction mechanism, then the rate of each would be affected by concentration. It is best to use the concentration effect as a reasonable extension of collision theory, which turns out to be true many times and is understandable in terms of the reaction mechanism.

Film, AN INTRODUCTION TO
REACTION KINETICS,
fits here. See p. 255 for summary.

Reaction Mechanism (8-1.3)

Consider a very *complex* reaction involving the breaking, forming, and rearranging of numerous bonds. Such a reaction could not easily proceed at a favorable rate when you consider the necessity for collisions of numerous particles. Thus most complex reactions occur in a series of simple steps usually involving two-particle collisions. This series of reaction steps is called the mechanism of the reaction. Each step of the mechanism is governed by the same principles affecting rates of reaction that have been outlined earlier and each has its own potential energy curve involving its specific activation energy and its own activated complex. Note that the slowest reaction in the mechanism series becomes the "rate determining step" for the entire reaction. Stress that the two following statements are good, general rules to remember. The reaction mechanism usually involves simple steps. The overall equation does not give the mechanism. The qualification in the first statement allows for slow reactions which could proceed at a low rate by complex steps. If a reaction is fast under normal conditions, it is safe to assume that the reaction involves simple steps. This statement does *not* say that all reactions have only simple steps.

As a corollary to the statements above, the kinetic behavior of a reaction is not (necessarily) given by the overall equation. Thus the study of kinetics has theoretical importance for understanding reactions, as well as practical value in revealing their speed.

The second example in the Textbook [equation (*10*), p. 128] uses two chemicals whose names are not given because they are "beyond" the student now. One of these, HOBr, is hypobromous acid; the student will learn this in Chapter 19 as an example of an oxyacid. The other, HOOBr, peroxyhypobromous acid, is a peroxyacid—a type we will not discuss.

The names of these compounds can be given along with the remark that remembering them is not important at this stage. Notice, however, that this example was carefully selected to illustrate a mechanism involving only species showing *normal* bonding rules. If you give other examples, try to avoid confronting the students with peculiar bonding situations (such as HO_2 and CH_2).

The Quantitative Effect of Concentration (8-1.4) (reduced type)

This section goes into a little more detail about the collision theory.

Effect of Temperature: Collision Theory (8-1.5)

In this section the experimental evidence for the distribution of kinetic energies of molecules is shown. The principles of the experiment, not the details of the apparatus, are important. The result given in Textbook *Figure 8-3 is vital.* Equally crucial is the change of this distribution with temperature (Figure 8-4 in the Textbook). Make sure the student understands this curve.

In explaining Figure 8-4 be careful to note that point *E does not* mark the lower limit of molecules that can react. It shows the threshold energy and the number of molecules having more than enough energy to achieve the activated complex. The molecules with energy greater than *E* are most likely to react, but any particular molecule can react if it collides with a sufficiently energetic partner.

The energy value at *E* is often associated by implication with $\Delta H^{\ddagger}$—activation energy. If this is true, then all the molecules "above *E*" can react with a stationary molecule because the first molecule has enough energy alone. However, two somewhat less energetic molecules may together have enough energy to react. It is probably best to treat *E* as a *qualitative* line. It shows there is some value above which a molecule is most likely to react. Do not fail to put over the important idea that, when E is out on the "tail" of the distribution, a small change in temperature makes a large change in the number of molecules above E.

The number of collisions a single molecule of methane makes in one second is derived from the kinetic theory by means of the "mean free path." Standard physical chemistry texts show this derivation, and some mathematically inclined student may enjoy working on it further.

THE ROLE OF ENERGY IN REACTION RATES (8-2)

Activation Energy (8-2.1)

The mountain pass analogy is an easy introduction to the potential energy diagram (Figure 8-5 in the Textbook). The latter is an important figure used to great advantage in describing the relationship between activation energy and rates of reaction. The activation energy is the minimum energy the colliding particles must acquire in order to bring about a chemical reaction. This is represented as an "energy barrier" which must be successfully overcome in order for a reaction to proceed. Each reacting pair of particles must go over this barrier.

The transitory state of the reacting particles that reach the top of the barrier is called the *activated complex*. Here the reactants (1) possess their highest potential energy and (2) may separate into original reactants or proceed to the products of the reaction. Use this model: a car at the top of the pass can roll down either side of the mountain. The activation energy may be thought of as the difference between the potential energy of the particle in the activated complex state and the potential energy possessed by the original, separate reactant molecules. Relatively little is known about the complex itself. It is some transitory combination of the reacting atoms (molecules) in a state of high potential energy. Do not be drawn into a discussion of it.

The activation energy is not hard to determine, at least in theory. The Arrhenius equation relates reaction rate, k, to temperature, °K, in this way:

$$2.303 \log k = -\Delta H^{\ddagger}/RT$$

When k is measured at several temperatures, then a plot of $\log k$ versus $1/T$ usually gives a straight line of slope $-\Delta H^{\ddagger}/2.3R$.

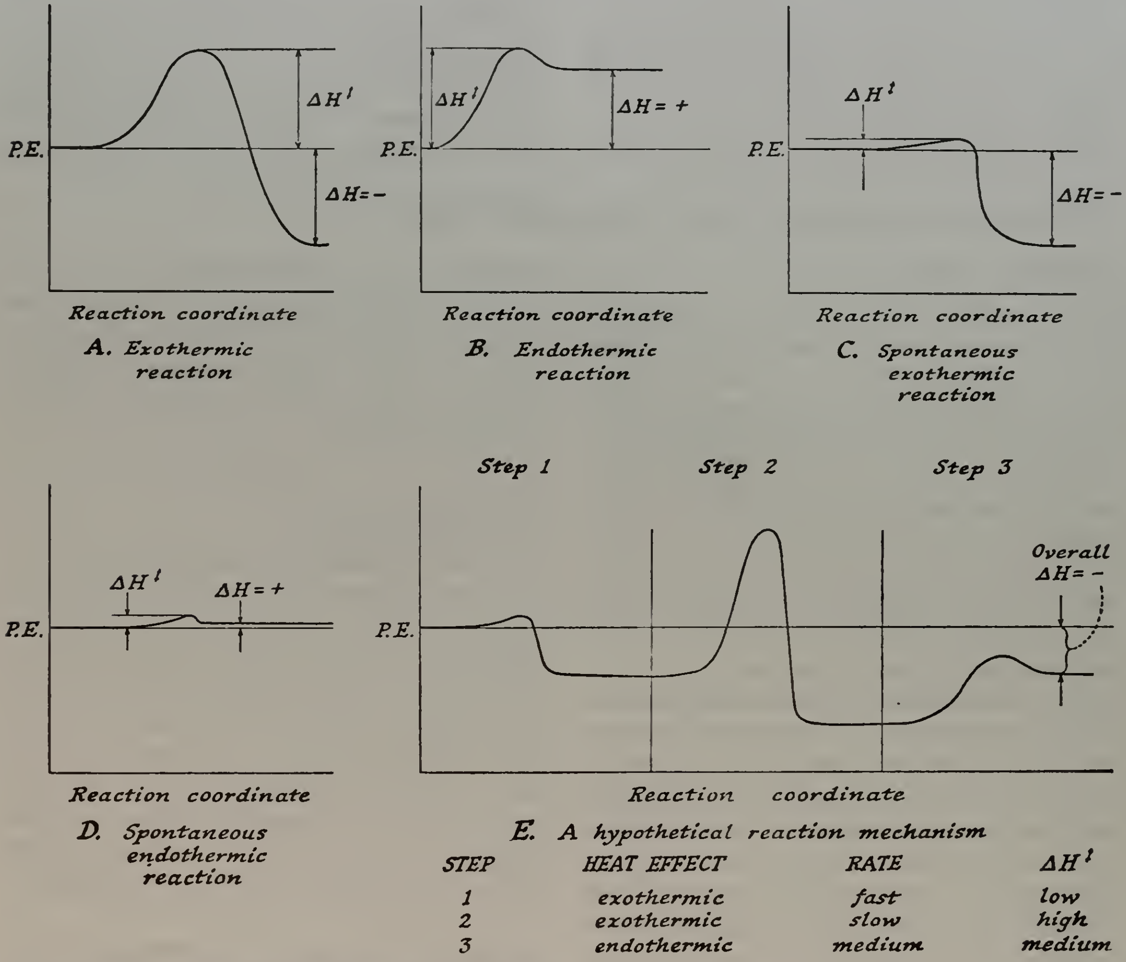
The film AN INTRODUCTION TO REACTION KINETICS is very helpful for showing the activated complex and energy of activation. The first half is the most useful. The second half jumps from topic to topic rather rapidly and gets into catalysis—a subject better illustrated with the CHEM Study film CATALYSIS. See p. 255 for details of both films.

Heat of Reaction (8-2.2)

Use the potential energy diagram at this point to discuss endothermic versus exothermic reactions. Suggest the possible appearance of curves representing reactions which occur spontaneously. If the products of the reaction have a lower potential energy than the reactants, energy must have been released, and hence the reaction is exothermic (ΔH is negative). If the products of the reaction have a higher potential energy than the reactants, energy must have been absorbed, and the reaction is endothermic (ΔH is positive).

Figure 8-1 contains some sample potential energy diagrams that illustrate several types of reactions. Parts (A) and (B) are straightforward. Parts (C) and (D) are for the special cases in which $\Delta H^{\ddagger}$ is so small that the reaction is spontaneous; that is, so many molecules (at a given temperature) have enough energy that most collisions are fruitful. Part (D) is useful to explain why there are few spontaneous endothermic reactions. The special relation shown by the diagram does not often occur.

Part (E) of the figure may be used at your discretion to illustrate a *hypothetical* diagram for an entire reaction mechanism. The three steps are analyzed in the caption and show one possible cause for a slow reaction (note the large $\Delta H^{\ddagger}$ of the second step). This diagram, plus the section on reaction mechanism, should convince the student that there is much to learn



A. Exothermic reaction

B. Endothermic reaction

C. Spontaneous exothermic reaction

D. Spontaneous endothermic reaction

E. A hypothetical reaction mechanism

STEP	HEAT EFFECT	RATE	$\Delta H^{\ddagger}$
1	exothermic	fast	low
2	exothermic	slow	high
3	endothermic	medium	medium

Fig. 8-1. **Some hypothetical potential energy diagrams.**

about a reaction *and* that the overall equation, though quite useful, does not describe all aspects of the chemical change.

The discussion of the mathematical relationship between activation energies for the forward and reverse reactions, which occurs in reduced type at the end of this section, can be used to further fix these concepts in the minds of the more able and interested students.

Action of Catalysts (8-2.3)

There may be several possible reaction mechanisms for a chemical reaction, but one will always be the most favorable because it has the lowest activation energy. A catalyst provides a new path which is even more favorable because it has a still lower activation energy or produces a more favorable geometry, rendering more collisions effective. It is well to emphasize the fundamental property of catalysts at this point; they are substances which increase the rate but which are not permanently consumed by the reaction.

The mountain pass analogy is extended to illustrate catalysis. The catalyst does not lower the activation energy of the uncatalyzed activation complex; it makes a *new activated complex* possible, and in this manner achieves the lower activation energy. This aspect is *not* shown by the mountain pass model, and so will need some stress in class.

The formic acid example (Textbook Figures 8-9 to 8-11) illustrates the point fully. In many catalysts of practical importance, the new complex is some interaction with special sites on a solid surface of metal or oxide (usually SiO_2, Al_2O_3, or SiO_2-Al_2O_3 mixtures). In principle these examples are similar to that given for formic acid,—but they are complicated and not well understood.

Film, CATALYSIS,
fits here. See p. 255 for summary.

In the formic acid example, we mention the hydrogen ion, H^+. You will see that when we discuss acids (Chapter 11) we use H_3O^+. The point is that we do not want to give the justifications for the hydrated form here in the chapter on rates. Make no special point about *either* representation now; let the argument develop in Chapter 11. In the film, the proton will be shown as a part of a sulfuric acid molecule, H_2SO_4. This is appropriate because the film shows the reaction in pure formic acid, where undissociated sulfuric acid molecules are present.

Occasionally the term "negative catalyst" is heard. This is a poor phrase for the following reasons. It implies the existence of a substance (not consumed in the reaction) which slows down a reaction. This, in turn, would mean an activated complex of *higher* activation energy than the uncatalyzed reaction. But molecules do not pick their "mountain pass" for scenery; they choose the lowest energy route. Thus the regular reaction would occur along with a few high energy cases that might proceed over the higher energy barrier. The net effect of the higher pass could *only* be to speed up the reaction.

There are substances which can cause a reaction to go more slowly. But the change in rate is caused by the substance reacting (*and being consumed*) while removing a needed reactant or catalyst. The lowered concentration of the reactant, or loss of catalyst, leads to a lower rate. For example, sodium hydroxide will reduce the rate of formic acid decomposition by consuming the catalyst, H^+.

A more dramatic example is the commercial reaction in which large hydrocarbon molecules are broken ("cracked") and hydrogen is added. The process uses a platinum catalyst in the form of very small pieces (a few hundred Å in diameter), which provide a large surface area. Sulfur reacts with the surface and, in effect, removes it. For all practical purposes, the reaction stops after the addition of a minute amount of sulfur, which is called a "poison" for the catalyst.

Expt. 14a, A STUDY OF REACTION RATES II (Optional),
fits here. See p. 252 for guide.

EXPERIMENT 14 A STUDY OF REACTION RATES

PURPOSE. To show quantitatively the influence of temperature and concentration on the time required for a reaction to occur.

PRELAB DISCUSSION. Avoid any "clues" about how temperature and concentration affect rate. (The student will, of course, have had some experience with these influences in Expt. 12.) Suggest that the observations in that earlier experiment were qualitative and that, now, quantitative data will be collected.

The mechanism of the indicator reaction is not clearly understood and need not be discussed. It is advisable to discuss the use of the starch-iodine reaction as an indicator to show that the HSO_3^- has been used up. That is, I^- reacts with IO_3^- to form I_2. Before this I_2 reacts with starch, however, it is consumed as indicated in the following reaction

$$I_2(\text{dissolved}) + HSO_3^-(aq) + H_2O(l) \rightleftharpoons 2I^-(aq) + SO_4^{-2}(aq) + 3H^+(aq)$$

When the HSO_3^- has been consumed, then I_2 accumulates and reacts sufficiently with starch to give the blue color. Stress the need for uniformity in mixing. (See lab hint 3.)

TIMING. Use this experiment as an introduction to Chapter 8. It may be given concurrently with the first assignment.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

2 test tubes (18 × 150 mm)
400 ml beaker
graduate (10 or 25 ml)
1 or 2 thermometers, −10°C to 110°C
clock with sweep second hand (1 per class)
burner, ring stand, ring, and wire gauze or electric plate for heating water
about 500 g ice for cooling water (about an average ice tray full)
optional: pipets (see Part I, lab hint 5)

SOLUTIONS. (Quantities are based on a class of fifteen pairs. Note that different individuals will be assigned different parts of the experiment.)

600 ml solution *A* (4.3 grams KIO_3/liter) (see lab hint 2 for extra dilution to be made)
1 liter solution *B* (0.2 gram $Na_2S_2O_5$, 4 grams soluble starch, and 5 ml 1 *M* H_2SO_4/liter) (see lab hints 1 and 2); $Na_2S_2O_5$ hydrolyzes to $NaHSO_3$ in ionic solution.
distilled water at room temperature

TIME REQUIRED. A 45–50 minute period is sufficient for each pair to do one experiment in each section and have time for organization. Many students will have time for optional parts. Could be done in two days with a break between Parts I and II.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. Make a paste of the starch in a small amount of water, add this slowly to 900 ml of boiling water, boil for a few minutes, cool, add other chemicals, and make up to 1 liter.

   If the solutions are made up more than 24 hours before use, dissolve only the first two substances listed for solution *B*. The sulfuric acid is added just before use. Unless this order is followed, the concentration of the HSO_3^- will become too low to give a suitable reaction rate.

Each group will need 30 ml of solution *B* for the minimum number of trials. A liter will allow for additional experiments or repetitions.

2. You should check the solutions just before the experiment and be prepared to make some adjustment in order to obtain appropriate reaction rates. For Part I adjust the concentration of the solutions such that at room temperature between 10 and 15 seconds are required when solution *A* is used without dilution. If your solutions require too much time, add $Na_2S_2O_5$ or a little more acid to solution *B*. If the reverse is true, dilute solution *A*. The solutions should react in about ten seconds in order to obtain a reasonable rate for the various dilutions. For Part II dilute solution *A* to about half concentration to give a room-temperature reaction time of 20–25 seconds. For a more concentrated solution, the reactions at higher temperatures will be too rapid. Each pair will need between 16 and 25 ml of solution *A* for the minimum number of trials (10 ml for the first portion of Part I; an average of 5 ml for the second; and 5 ml diluted to 10 ml for Part II). To allow for additional experiments or repetitions, prepare 600 ml.
3. Pouring the solutions back and forth offers several advantages: it gives standard mixing to help different students achieve comparable results; and it gives thorough, rapid mixing. The mixing should take only 5 or 6 seconds.

PART I

4. Have the entire class use one of the concentrations first, to help them understand the experiment. This aids in the discussion of precision.
5. If pipets are available, their use may be introduced at this time with increased accuracy in diluting. The water used in making the dilutions should be at room temperature to avoid introducing another variable.
6. There is no point in carrying dilutions down to any more than one part of solution *A* to four parts of water because the reaction time becomes extremely variable.

PART II

7. If two thermometers are available, the temperatures of the two solutions (*A* and *B*) should be taken rather than the temperature of the water bath. More uniform results are obtained when the solutions are kept overnight at a temperature close to that which the student is going to use. By omitting the sulfuric acid, part of solution *A* and part of *B* may be put in a refrigerator, part in an oven slightly above room temperature, and part left at room temperature. Students may then take solutions from the supply whose temperature is closest to that which they are assigned to observe.
8. As regards the assignment of temperature, under no condition should a temperature above 40°C be used for comparative purposes, because the concentration of the HSO_3^- is decreased so much that misleading results are obtained. The reaction is very slow at 0° and is difficult to observe. In order to get an indication of the uncertainty for the various points, it is wise to have several students assigned to each temperature studied. Temperatures of 5°, 15°, 25°, and 35°C give enough data for plotting and allow several duplicate determinations for each temperature. Above 50°C the iodine-starch complex is unstable.

CALCULATIONS AND QUESTIONS FOR PART I

1. The concentration of KIO_3 in solution *A* is 0.02 *M*. Calculate the number of moles of potassium iodate in each milliliter of solution *A*.

Answer: If KIO_3 is 0.02 *M*, there will be 0.02 mole in one liter of solution or 0.02×10^{-3} mole in each milliliter.

2. Calculate the initial molar concentration of KIO_3 in each of the mixtures of *A* plus *B* prepared in Part I.

Answer: The number of moles of KIO_3 per liter will be 0.009, 0.008, 0.007, etc., depending upon the dilution made.

3. Why is it important to keep the total volume at 10 ml during the dilutions of solution *A*?

Answer: If the volume were not kept at 10 ml, the concentration would be much more difficult to calculate, and the concentration of solution *B* would also be varied.

4. Plot the graph of the concentration-time data with time on the vertical axis (ordinate) and the concentration of the KIO_3 on the horizontal axis (abscissa). Use the data of other members of the class also.

Answer: The data from which the graph shown in Figure 8-2 was plotted were in very close agreement at most of the points:

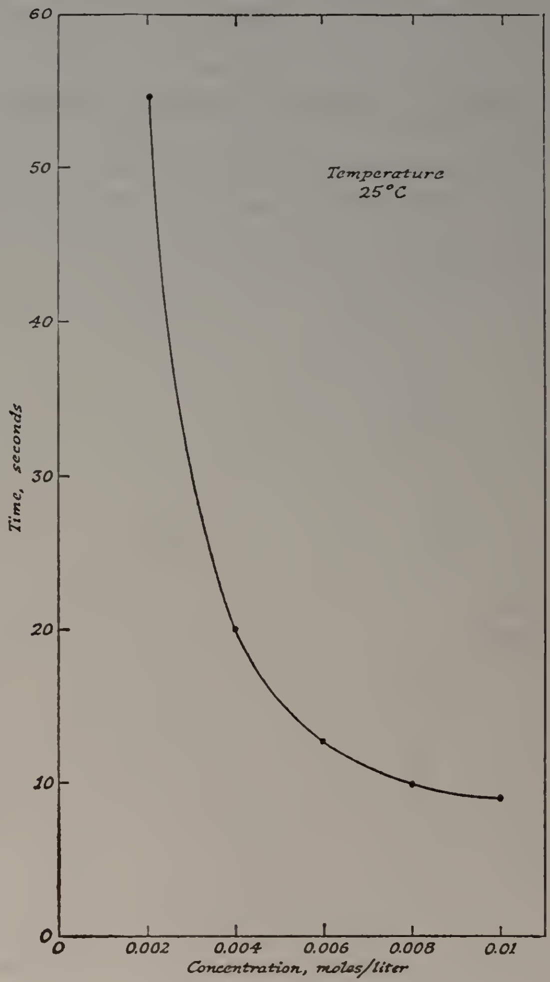


Fig. 8-2

Reaction time versus KIO_3 concentration.

Concentration-time Data

	Number of Reports	*Range of Time* (seconds)	*Average* (seconds)
Initial conc., no dilution (0.01 *M*)	9	2	9
$\frac{4}{5}$ initial conc. (0.008 *M*)	9	2	10
$\frac{3}{5}$ initial conc. (0.006 *M*)	11	3	12
$\frac{2}{5}$ initial conc. (0.004 *M*)	10	3	20
$\frac{1}{5}$ initial conc. (0.002 *M*)	10	29	54

The reaction is complicated and is influenced by H^+ concentration.

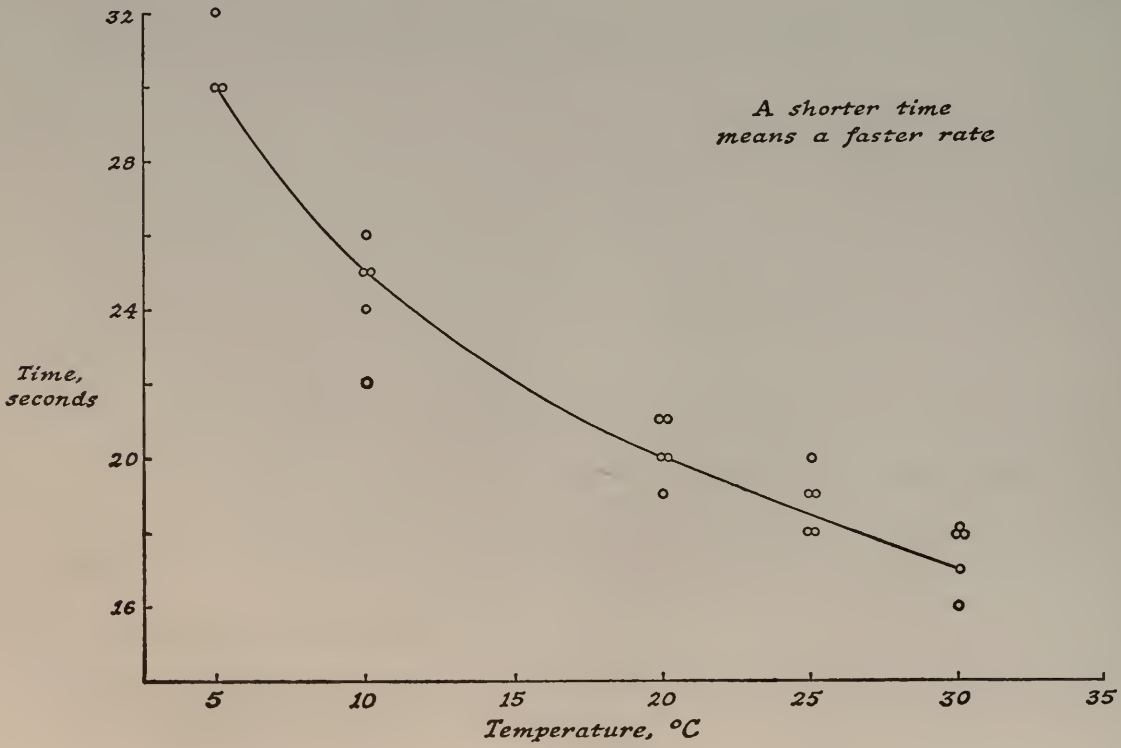
5. What generalizations can you make concerning the effect of varying the concentration on the time of the reaction?

Answer: From the usual data the student will certainly answer that increasing (decreasing) the concentrations decreases (increases) the time, or vice versa.

6. How is the time of the reaction related to the rate of the reaction?

Answer: A shorter time means a faster rate.

Fig. 8-3. **Reaction time versus reaction temperature.**



CALCULATIONS AND QUESTIONS FOR PART II

1. Plot a graph of the temperature-time data, with temperature on the horizontal axis (abscissa) and time on the vertical axis (ordinate).

   Answer: Figure 8-3 shows a graph, obtained by one class of students, in which each individual result is plotted. Note that in some tests either the recorded temperature was not correct or some other factor varied. Such data offer an opportunity for discussing precision.

2. What general relationships can you derive from the above graph?

   Answer: In general, an increase in temperature decreases the time for the reaction. Suggest that better students plot various functions of time versus temperature in search of a linear relation. For the data shown here, the inverse of time ($1/t$) versus temperature yields a reasonably straight line.

3. Make a prediction of the time of the reaction at 0°C and at 50°C assuming that the other variables in the experiment are kept constant.

   Answer: The predictions for 0°C and for 50°C are best reported as ranges. Using the data from the graph above one might say 35–40 seconds for 0°C and 14–16 seconds for 50°C.

POSTLAB DISCUSSION. Plot data from as many individuals as possible in order that your students may see the range. Point out the increasing certainty obtained from more measurements. Since there are a number of factors influencing this reaction which are not being investigated, and since the concentration in solution *B* does vary with standing, results taken on different days or from different "mixes" should not be compared quantitatively. The important point to make is that the rate of this overall reaction is increased by increasing temperature and by increasing concentration. Point out also the value in discovering a straight-line function so as to make extrapolation more certain, but be sure students understand the limitations.

EXPERIMENT 14a (OPTIONAL) A STUDY OF REACTION RATES II

PURPOSE. To provide an additional study of factors affecting rates of reaction.

PRELAB DISCUSSION. Little or no discussion is necessary if students have already done Expt. 14. If this experiment is being used in place of Expt. 14, see the prelab and postlab discussion for that experiment.

Emphasize the need for uniformity in mixing. (See lab hint 4.)

TIMING. Consider this an optional experiment to be done at the end of the chapter, after catalysts are discussed (Sec. 8-2.3).

EQUIPMENT NEEDED (PER PAIR OF STUDENTS)

2 250 ml Erlenmeyer flasks
pinch clamp
13 × 100 mm test tube
a piece of $\frac{3}{16}$ in. or $\frac{1}{4}$ in. ID rubber tubing (about 50 cm long)
a piece of $\frac{3}{16}$ in. or $\frac{1}{4}$ in. ID rubber tubing (about 4 cm long)
glass bends 6 mm tubing (about 20 cm overall length) (see diagram)
1 hole stopper (#6)
2 hole stopper (#6)
thermometer (−10 to 110°C)
ring stand and clamp
50 ml or 100 ml graduate
clock or watch with sweep second hand
30 ml sodium hypochlorite (commercial bleach, 5% solution)
6 ml 0.17 *M* cobaltous nitrate (49.5 g $Co(NO_3)_2 \cdot 6H_2O$/liter)

TIME REQUIRED. This experiment will require one full 45–50 minute laboratory period.

PRECAUTIONS. Observe the usual lab precautions. If any of the NaOCl is spilled, wash it up immediately with water.

LABORATORY HINTS

1. It is recommended that each pair of students do Part I; they should then do as many of the other assigned parts as time will permit. The teacher should assign all of the parts in order that data will be obtained for each of the experimental variables.
2. Be sure to use a fresh bottle of sodium hypochlorite bleach (obtained in the grocery store as Purex, Clorox, etc.)
3. Note that Part I, step (e) says the reaction flask is to be tipped, *not* inverted. The test tube must be "caught" by the end of the glass bend in such a way that it is not free to move (see figure in Manual). The solution in the test tube will flow out, but the hypochlorite solution will not enter the test tube. Do not tip it a second time.
4. After mixing, swirl the flask constantly and uniformly. This will give a uniform mixture and will free the surface of the catalyst, with the result that the rate of O_2 evolution will be constant. It was found that the fast swirling gives consistent data.

EXPECTED RESULTS. Figure 8-4 indicates the kind of results that can be expected from the experiment. Improper mixing and failure to swirl can give erratic results.

1. Room temp with 5% NaOCl.
2. Room temp plus 10°C, 5% NaOCl.
3. Room temp minus 10°C, 5% NaOCl.

4. Room temp with two-fold dilution.
5. Room temp with 5% NaOCl and mixed catalyst [$Co(NO_3)_2$ and $Fe(NO_3)_3$].

ANSWERS TO QUESTIONS

1. Make as quantitative a statement as possible concerning the relation between the temperature and the rate of the reaction.

   Answer: At room temperature the rate was about 10 ml/minute, whereas at room temperature plus 10°C the rate increased to about 35 ml/minute.

2. If you had carried out the decomposition at 60°C, what would you predict the appearance of the curve to be?

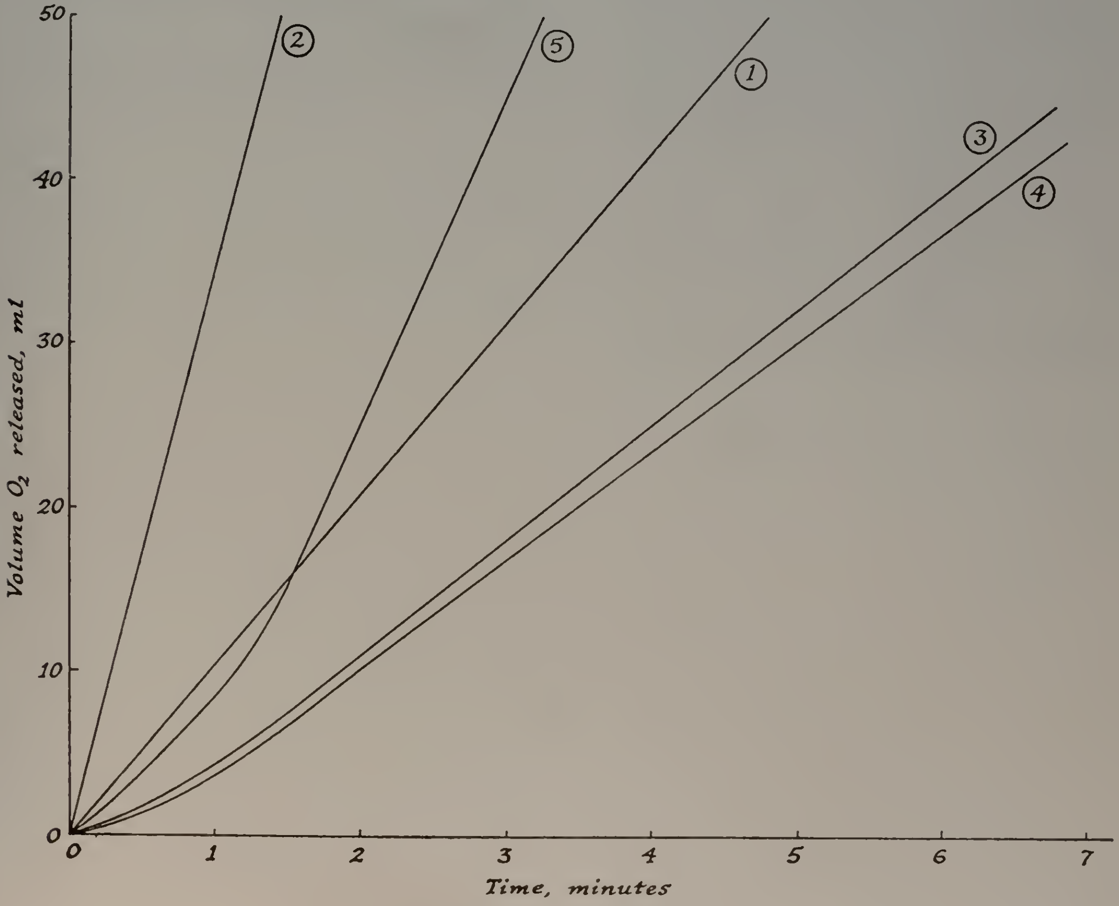
   Answer: The curve would be steeper than for room temperature plus 10°C.

3. Compare the observed rates for diluted and nondiluted NaOCl solutions.

   Answer: A two-fold dilution reduced the rate from about 10 ml/minute to about 6 ml/minute.

4. Predict where the rate curve would be if the concentration of sodium hypochlorite in the bleaching solution were 10% instead of the 5% actually present.

Fig. 8-4. **Effect of several factors on reaction rate.**



Answer: The rate curve for 10% NaOCl would probably lie between the rate curve for room temperature and the rate curve for room temperature plus 10°C. It would probably increase the rate to about 20 ml/minute. That is, doubling the concentration would about double the rate, according to the data evaluated.

5. (*Optional*) Do other solid oxides serve as catalyst? What was the effect that you noted for a mixture of oxides?

Answer: The only other catalyst tried was an oxide of iron, produced by adding $Fe(NO_3)_3$ to the NaOCl. This oxide was not a good catalyst. Only about 1 ml of oxygen was released. It can be seen from the chart, however, that a combination of $Co(NO_3)_2$ and $Fe(NO_3)_3$ was more effective as a catalyst than was either when used alone.

Supplementary Material

Articles

1. L. P. Lessing, "High speed chemistry," *Scientific American*, pp. 29–35, May 1953. How scientists study transitional compounds formed in the course of very fast reactions and how these reactions are put to practical use.
2. J. D. Roberts, "Organic chemical reactions," *Scientific American*, pp. 117–126, November 1957 (Offprint No. 85).* An informative article describing the mechanism of reaction for several well-known organic reactions.

Books

J. A. Campbell, *Why Do Chemical Reactions Occur?* Prentice-Hall, Englewood Cliffs (1965). Additional information about driving forces, rates and mechanisms for teachers and able students.

E. L. King, *How Chemical Reactions Occur*, Benjamin, New York (1963). Additional information about reaction rates and mechanisms for teachers and advanced students.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

1. AN INTRODUCTION TO REACTION KINETICS

A CHEM Study film
Running Time: 13 minutes

This film was prepared in collaboration with Dr. Henry Eyring. It treats the reactions of Cl_2 and I_2 with H_2; touching on mechanism, activation energy, collision geometry, reversibility and equilibrium (10 minutes). The last few minutes deal more sketchily with catalysis and the effect of temperature and pressure. The film is good enough to show twice: the first time as an introduction; the second time, after Chapter 8 has been covered. If only one showing is planned, schedule it late in the chapter.

2. CATALYSIS

A CHEM Study film
Running Time: 17 minutes

This film, prepared in collaboration with Dr. R. E. Powell, treats five examples of catalysis. The second, formic acid decomposition, is particularly well related to the text (pp. 137–139). The other four reactions and the points they illustrate are:

$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$	(catalyst not consumed)
$Cr^{+3} \longrightarrow Cr^{+6}$	(catalyst forms intermediate)
$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$	(dissociation on catalyst surface)
a biological reaction	(an enzyme as a catalyst)

Good use is made of potential energy diagrams.

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* Available from W. H. Freeman and Co., San Francisco. Order by number.

Background Discussion

In Chapter 7 you discussed how to find the energy balance of a chemical reaction—both how to measure it and how to compute it. You also pointed out some possible ways in which energy can be stored in a molecule. In Chapter 8 you will be concerned with the rates of chemical reactions. You may wonder why this great emphasis on reaction rates, especially since this subject has been of little concern in the high school chemistry course. If you have doubts about the wisdom of such an approach, consider the ultimate goal of the chemists—i.e., the prediction of the conditions that induce chemical reaction. The chemist is concerned with three basic questions: Can reaction occur? How long will it take? How far will the reaction proceed?

In Chapter 7 the point was made that many reactions occur with the evolution of heat. For some of these (the reaction of NO with O_2), all that is required is to bring the reactants together; for others (the reaction of H_2 with O_2), the reactants must be heated or ignited by a spark. What is responsible for the great difference in the rate of these two exothermic reactions? This problem will be explored in some detail in this chapter. It can be pointed out now, however, that many reactions, even exothermic ones, require an input of energy to start them. This "starting" energy is released when the reaction is completed. Endothermic reactions require more energy than is actually consumed when the reaction occurs. Since the energy required to initiate reaction is not absorbed in the reaction, it is called *activation energy*. Reaction rates and activation energy form the subject matter of this chapter.

The emphasis we place on activation energy and reaction rates does not result from our great knowledge of these properties at the present time—indeed, much of our knowledge of reaction rates is still obtained by purely empirical methods—but rather from the recognition that one of the most important unsolved problems in chemistry is the accurate prediction of reaction rates. By presenting chemistry from this point of view you are involving the beginning student in the really significant problems of modern chemistry.

The following topics are discussed:

Reaction Rates: Ways to Measure
Reaction Rates: Order of Reaction and Reaction Rate Constants
Activation Energy
The Distribution Curve
Factors Affecting Reaction Rates
Reaction Mechanism
Catalysis

REACTION RATES: WAYS TO MEASURE

Reaction rates are determined by measuring the rate at which some property of the reaction changes. Among the properties which have been studied are color, volume of the system, pressure, index of refraction, rotation of polarized light, weight of precipitate produced, and *p*H. The examples in Table 8-I illustrate how some of these properties are applied. The reactions are for illustration only; not to be studied in detail.

REACTION RATES: ORDER OF REACTION AND REACTION CONSTANT

An examination of the graph plotted in Expt. 14 shows that the rate of that overall reaction depends on the concentration of the reactants. The student may inquire about the concentration at which the rate should be measured and about how reaction rate can be tied to a particular reaction. This will give you an opportunity to use some quantitative equations. Suppose the reaction of interest is given by the equation

$$N_2O_5 \rightleftarrows 2NO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

A quantitative definition of the rate of this reaction is

$$\frac{-\Delta[N_2O_5]}{\Delta t} \qquad (2)$$

which is read: the change in concentration of dinitrogen pentoxide with change in time. The minus sign shows that N_2O_5 is a reactant and is used up as time goes on. The brackets indi-

Table 8-1. **Illustrative Examples of Properties Used to Follow Reaction Rates**

Property Changing	*Sample Reaction*
color	$N_2O_4(g) \rightleftharpoons 2NO_2(g)$
volume	$N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2}O_2(g)$
pressure	$H_2O_2(l) \rightleftharpoons H_2O(l) + \frac{1}{2}O_2(g)$
rotation of polarized light	$\underset{\text{SUCROSE}}{C_{12}H_{22}O_{11}} + H_2O \rightleftharpoons \underset{\text{GLUCOSE}}{C_6H_{12}O_6} + \underset{\text{FRUCTOSE}}{C_6H_{12}O_6}$
absorption of light	$\underset{\substack{\text{EUROPIUM(II)}\\ (\textit{colorless})}}{Eu^{+2}(aq)} + H^+(aq) \rightleftharpoons \underset{\substack{\text{EUROPIUM(III)}\\ (\textit{pink-red})}}{Eu^{+3}(aq)} + \frac{1}{2}H_2(g)$
weight	$Ag^+(aq) + NO_3^-(aq) + \underset{\substack{\text{METHYL}\\ \text{IODIDE}}}{CH_3I(aq)} \rightleftharpoons AgI(s) + \underset{\substack{\text{METHYL}\\ \text{NITRATE}}}{CH_3NO_3(l)}$
*p*H	$\underset{\text{ETHYL ETHER}}{(C_2H_5)_2O(l)} + HI(aq) \rightleftharpoons \underset{\text{ETHYL IODIDE}}{C_2H_5I(l)} + \underset{\text{ETHANOL}}{C_2H_5OH(l)}$

cate concentration, usually expressed in atmospheres for gases. Since the value of the ratio in expression (*2*) will depend on the time over which it is measured, it is customary to define the reaction rate for an extremely short interval of time and write it as

$$\frac{-d[N_2O_5]}{dt} \tag{3}$$

Since experiment shows that the rate of this reaction is directly proportional to $[N_2O_5]$, we can write

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5] \tag{4}$$

where k is a constant that is characteristic of the reaction under study. It is called the *reaction rate constant*, and defines the fraction of N_2O_5 that reacts per unit of time. In a first-order reaction the *fraction* which reacts per second is independent of the particular concentration of N_2O_5. Equation (*4*) contains only first degree terms; it is said to define a *first-order reaction.*

The rate of the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{5}$$

is expressed by the equation

$$\frac{-d[NO_2]}{dt} = k[NO_2]^2 \tag{6}$$

The rate of this reaction depends on the square of the concentration of the reactant, and since this rate equation is of the second degree, the reaction is defined as second-order.

Reaction rate constants are computed from the kind of data obtained in Expt. 14; i.e., concentration-time data. To do this it is convenient to change the form of equations (*4*) and (*6*) by integrating. Equation (*4*) yields

$$\ln [N_2O_5] = -kt + \ln [N_2O_5]_0 \tag{7}$$

where $[N_2O_5]_0$ is the initial concentration of N_2O_5 at t = zero. The abbreviation ln means natural logarithm (as opposed to the base 10 logarithm). Observe that equation (*7*) is of the form $y = mx + b$, the plot of which is a straight line. Sample plots of some rate data for a first-order reaction are shown in Figure 8-5. In Figure 8-5A, the data are plotted as they were in Expt. 14. In Figure 8-5B, the logarithm (base 10) of the concentration is plotted against time. The slope of the line is equal to $-k$, hence k can be computed readily.

In a similar manner equation (*6*) can be integrated to give

$$\frac{1}{[NO_2]} = -kt + \frac{1}{[NO_2]_0} \tag{8}$$

which also is of the form $y = mx + b$. A plot of $1/[NO_2]$ against time will produce a straight line with a slope equal to $-k$, giving the rate constant of a second-order reaction. It should be possible to use the techniques discussed above

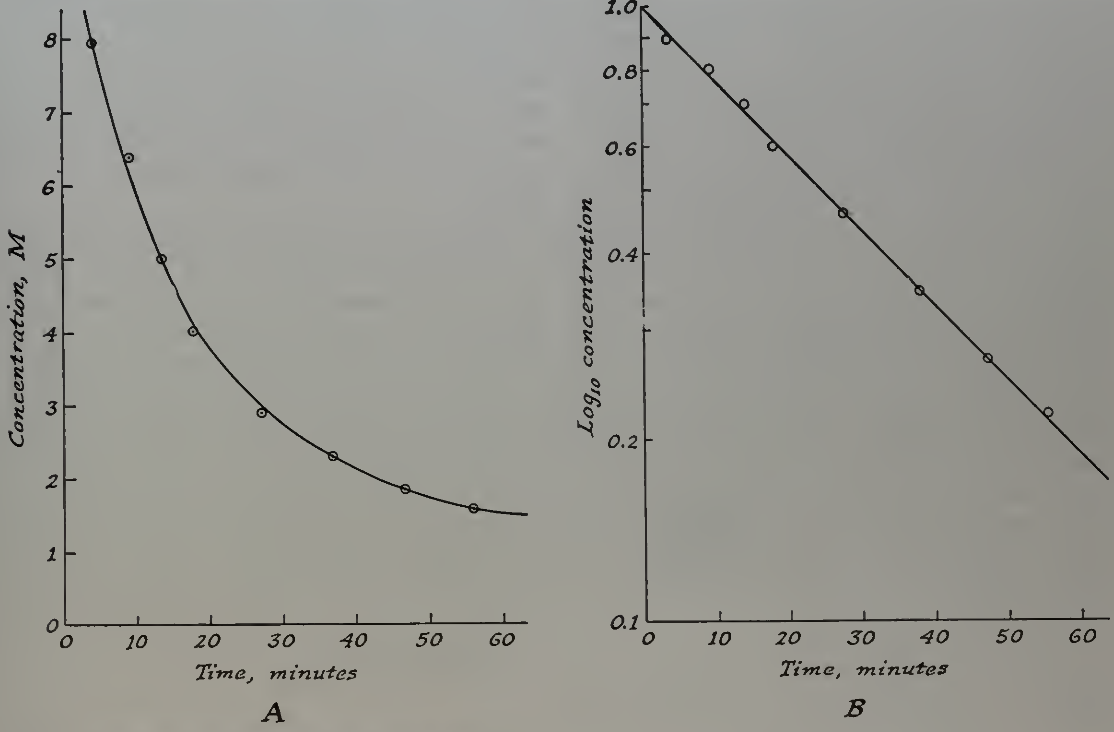


Fig. 8-5. **Two ways to plot the same rate data.**

to show the more inquisitive students how rate constants are obtained.

The product of the exponents of the concentration terms in a rate equation may not be an integer, but fractional or zero. In these cases the order of the reaction is said to be fractional or zero. There is nothing special about a fractional-order reaction.

Fractional orders arise from successive reactions. Here is a general case:

$$A_2 = 2A \text{ (fast)} \qquad K = \frac{[A]^2}{[A_2]}$$

$$A + X = B \text{ (slow)}$$

$$\frac{-d[X]}{dt} = k[A][X]$$

But, from the first reaction,

$$[A] = \sqrt{K[A_2]}$$

hence

$$\frac{-d[X]}{dt} = k\sqrt{K}[A_2]^{1/2}[X]$$

A specific example is diborane,

$$B_2H_6 \rightleftharpoons 2BH_3$$
$$BH_3 + X \rightleftharpoons \text{products}$$

The various *k*'s for the different orders of reaction have different units. They are shown below.

Order	*k*	*Units* *(conc. in moles/liter)*
0	k_0	moles/liter/sec
1	k_1	sec^{-1}
2	k_2	liter mole^{-1} second^{-1}
.	.	.
.	.	.
.	.	.
n	k_n	liter^{n-1} mole^{1-n} second^{-1}

ACTIVATION ENERGY

We commented about activation energy in the section on philosophy. You should discuss this in some detail in your lectures. Many students will want to know more about it, such as: How is it measured? Can it be calculated? What does it mean? Activation energies can be calculated for some very simple reaction such as $H^* + H—H \rightleftharpoons H—H^* + H$ (the asterisk is used here merely to label one of the hydrogen atoms). Such calculations involve the use of quantum mechanics, which is beyond our level of mastery at this time. On the other hand, an understanding of how activation energies are measured can be grasped by your more alert students. In Expt. 14 the student studied the way in which the rate of a reaction varied with temperature. Such data could be used to compute specific reaction rates at various temperatures. It has been shown experimentally that the variation of the specific reaction rate with temperature is given by the equation

$$\frac{d(\ln k)}{dT} = \frac{\Delta H^{\ddagger}}{RT^2} \qquad (9)$$

where $\ln = 2.303 \log_{10}$, $\Delta H^{\ddagger}$ = activation energy, T = absolute temperature, and R = the gas constant (1.99 cal mole^{-1} deg^{-1}). Integration of equation (9) yields

$$\log_{10} k = \frac{-\Delta H^{\ddagger}}{2.3R}\left(\frac{1}{T}\right) + B \qquad (10)$$

where B is a constant. Here again, when $\log_{10} k$ is plotted against $1/T$, a straight line is obtained that has the slope

$$-\frac{\Delta H^{\ddagger}}{2.3R}$$

The activation energy can then be evaluated from the slope of this line. Activation energies have been evaluated in this way for a number of reactions, and have values ranging from 1 to 100 kcal/mole. High activation energies are associated with slow reaction rates.

Rewriting equation (*10*) to express the difference in reaction rates at the temperatures T_1 and T_2 yields

$$2.3 \log_{10} \frac{k_1}{k_2} = -\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (11)$$

You have probably heard the expression that "a 10°C rise in temperature will about double the rate of reaction." Let us investigate this statement. We can find from equation (*11*) that for this statement to be true at room temperature, $\Delta H^{\ddagger}$ must be about 15 kcal/mole. The derivation of equation (*11*) includes the assumption that $\Delta H^{\ddagger}$ is constant with temperature change.

Immediately we see two difficulties with this rule of thumb. First, the rule can't fit except over a small range near room temperature. For instance, the change in rate from 325°C to 335°C for such a reaction would be only 20%. At −125°C a rise of 10°C would make a *28 fold increase in rate!* Second, not all (or even most) reactions oblige by having $\Delta H^{\ddagger} = 15$ kcal/mole.

You can still make use of the expression by saying that sometimes it is true and that this illustrates how big the temperature effect can be. Only the better students need be told that, for the reasons given above, the effect can be either greater or less.

These results are more supporting evidence that molecules with energy in excess of a certain minimum energy are most likely to react. Reference to Figure 8-4 in the Textbook shows that a small increase in temperature does not greatly increase the average kinetic energy of the molecules. If reaction occurred mainly among molecules with average kinetic energy, such a small increase of temperature could not produce a marked effect on reaction rate. The marked change of rate of some reactions with a rise in temperature is just what would be expected if molecules with energy greater than E of Figure 8-4 are reacting; for it is the number of these high energy molecules which increases so rapidly with temperature.

THE DISTRIBUTION CURVE

Distribution curves are usually plotted with number (or fraction) of molecules having a specified energy as the ordinate and with energy as the abscissa. The area under such a curve is the total number of molecules. You can illustrate this by plotting students of a given height versus height. Such a curve for a class might look like

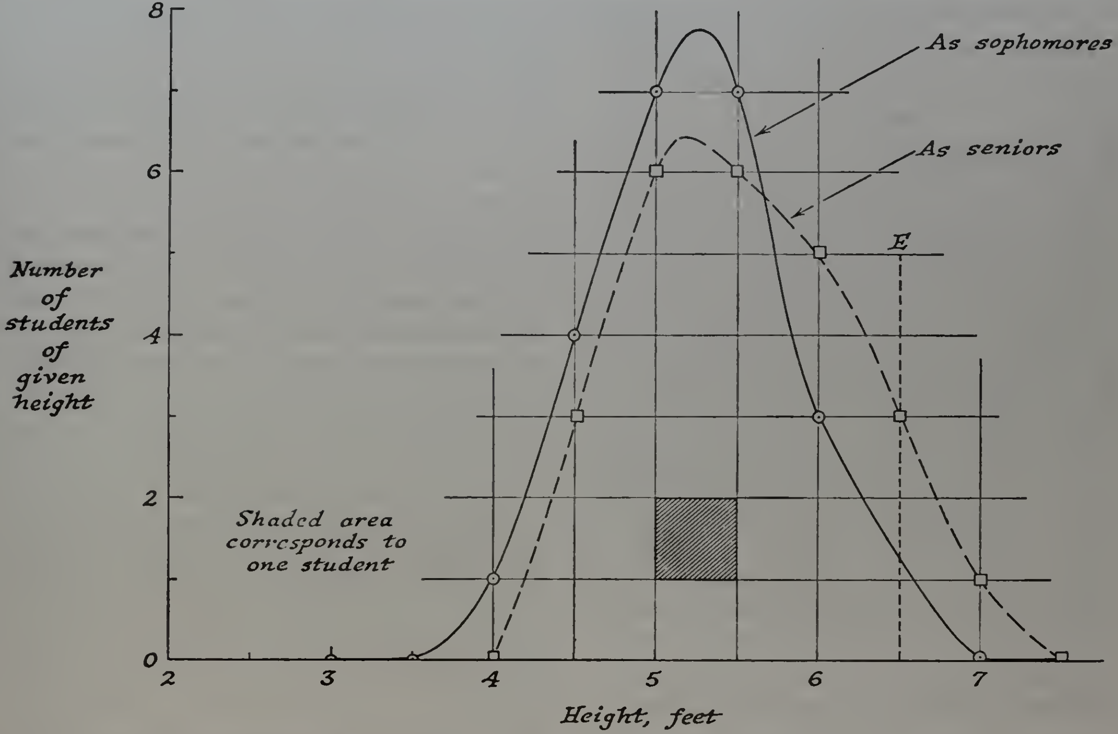


Fig. 8-6. **Hypothetical distribution** *of heights in a chemistry class.*

the solid line in Figure 8-6 (a hypothetical curve for a class of 24 sophomores).

The small, shaded square shows the meaning of area. If the entire area is counted in terms of this unit, one finds about 24 students in the distribution, which is in agreement with the known class size. When this distribution changes shape (suddenly several students have a spurt of growth and move to a new height group) it should be clear that the area does *not* change. The same reasoning applies to the molecular case and is the basis for equating number of molecules with area under the curve. Since there are billions of molecules, the curve is much more clearly defined than that in our hypothetical case.

You can use the same height distribution to show the effect of "temperature" on the tail of the curve. In our model, we allow two years to pass and then remeasure the class (dashed line for seniors). Notice how the number beyond *E* has increased very much relative to what it was. Here *E* marks the point of rapid rate of reaction by the basketball coach.

Support for the view that only a certain fraction of the molecules of a system possess sufficient energy to make reaction probable when they collide is obtained from a computation of the number of collisions in a molecular system. An equation (developed from kinetic molecular theory) for computing the number of collisions between like molecules is

$$Z = \frac{1}{2}\sqrt{2}\pi n^2 d^2 \sqrt{\frac{8kT}{\pi m}} = 2n^2 d^2 \sqrt{\frac{\pi kT}{m}} \qquad (12)$$

where n is the number of molecules per cubic centimeter, d is the molecular diameter, and $\sqrt{8kT/\pi m}$ is the average speed of a molecule of mass m. Solution of equation (*12*) shows that HI molecules at 280°C and a concentration of

1 mole/liter collide about 6 × 10^{31} times per second per cubic centimeter. However, reacting in accordance with the equation

$$2HI \rightleftharpoons H_2 + I_2 \quad (13)$$

H_2 is produced at a rate of only about 2 × 10^{14} molecules per second per cubic centimeter, which means that only three in about 10^{17} collisions are effective in producing reaction. Apparently, molecules must acquire a certain critical energy before they can react. This energy is that which the reactants must acquire to mount the potential energy hill shown in Figure 8-6 of the Textbook.

The large proportion of ineffective collisions is *not* brought out in the film AN INTRODUCTION TO REACTION KINETICS for this reason: it would be impractical to draw 10^{17} collisions to show just three fruitful ones. You can prevent a wrong impression of the relative frequency of reaction by commenting on this mechanical limitation.

FACTORS AFFECTING REACTION RATES

We have assumed that molecules will not react unless they possess the necessary activation energy. The student may inquire whether all such molecules react when they collide. To answer this question you need to know the number of molecules that possess the necessary activation energy. An approximation of this number can be obtained from the exponential form of equation (*9*), which is

$$k = Ae^{-\Delta H^{\ddagger}/RT} \quad (14)$$

This equation was defined first by Arrhenius. The factor $e^{-\Delta H^{\ddagger}/RT}$ defines the fraction of molecules which possess the necessary energy to react. In terms of the simple collision theory presented in the Textbook (Secs. 8-1.2–8-1.5) the reaction rate, k, ought to equal the product of the total number of molecular collisions and the fraction, $e^{-\Delta H^{\ddagger}/RT}$, of these collisions that possess the required activation energy, $\Delta H^{\ddagger}$. If this statement were true, A in equation (*14*) would merely be the number of molecular collisions. This simple model applies satisfactorily for a few gaseous reactions. For the decomposition of HI, which occurs in accordance with the equation (*13*), we can calculate k to be 2.10 × 10^{-3} liter mole^{-1} sec^{-1} at 700°K. The experimental value is 1.57 × 10^{-3}. For most chemical reactions, however, the rate calculated on the basis of the model presented in Secs. 8-1.2–8-1.5 is much larger than the experimental rate.

The simple model presented in the Textbook assumes hard elastic spheres which can collide with free transfer of kinetic energy. If a molecule is struck by another molecule having the proper energy, a reaction should occur, and reaction rates computed on the basis of this simple model should agree with measured reaction rates. The failure of agreement must mean that our simple model is not completely correct.

That such a simple model does not reproduce the behavior of more complicated molecules really is not surprising, for molecules involved in such reactions may contain a number of bonds, only one of which is broken in a particular reaction. For reaction to take place, the collision must occur such that most of the energy is imparted to the bond to be broken; i.e., the molecules must collide with the proper orientation. The requirement that molecules collide at a certain spatial orientation for maximum chance of reaction is called *collision geometry.* It has been suggested that equation (*14*) be written

$$k = pZe^{-\Delta H^{\ddagger}/RT} \quad (15)$$

where p, the steric factor, measures the geometrical requirement and Z, the frequency factor, measures the collision number. See p. 295 for further discussion of Arrhenius' equation.

The spatial orientation most conducive for chemical reaction may represent an orientation which has a high potential energy for the approach of the reactant molecules. Owing both to ionic charges and to those resulting from permanent and induced dipoles, molecules tend to approach each other in certain preferred orientations. Further, two molecules may collide with sufficient energy to react and yet not do so because vibrational energy is quantized and because the energy cannot be transferred in the proper size quantum (see Chapter 15). *The molec-*

ular species formed when molecules collide with sufficient energy to react is called an activated complex. Even the formation of such a complex does not insure reaction, for the complex has some probability of decomposing to reform the reactants rather than the products. The answer to the student's question, then, is that molecules with sufficient activation energy definitely may collide without reacting. One conclusion from the foregoing discussion is that in all reactions, endothermic as well as exothermic, the activated complex always decomposes with the liberation of energy.

REACTION MECHANISMS

The beginning student is apt to assume that chemical equations define the mechanism by which a reaction proceeds; i.e., the number of molecules of reactants written in the equation must collide simultaneously in order to form the products. Although this is true of some reactions, it is not true for most. For example, in the decomposition of HI, equation (*13*), two molecules of HI collide and produce H_2 and I_2. In the reaction of Fe^{+2} and MnO_4^{-1}, five Fe^{+2} and eight H^+ do not collide with each other simultaneously. Indeed, as pointed out in the text, even a three-body collision is rare. Complex reactions are believed to occur in a series of simple steps. The mechanism of a reaction is derived from a study of reaction rates. Some examples will be given to illustrate how this is done.

We have assumed that molecules must collide to react. For the decomposition of HI this means that two molecules must collide to form H_2 and I_2. Thus the rate of this reaction would be expected to be given by the equation

$$\frac{-d[\mathrm{HI}]}{dt} = k[\mathrm{HI}]^2 \qquad (16)$$

Experimentally the rate of this reaction does fit this second-order rate equation. Such a reaction is said to be bimolecular; i.e., the actual mechanism involves the collision of two molecules.

According to collision theory, all reactions should be at least bimolecular, since at least two molecules must collide for any reaction to occur. However, the decomposition of N_2O_5, equation (*1*), and a number of other reactions are known to follow the first-order rate law (equation *4*). How can the order of such reactions be explained in terms of collision theory? It is quite probable that even a first-order chemical reaction is bimolecular and does not involve simply the decomposition of a molecule, although there are many reactions whose rates are defined quite well by the first-order rate law. The decomposition of ozone is such a reaction. A possible mechanism for this reaction is given by the series of equations

$$O_3 + O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_3^* + O_3 \quad \text{(fast)} \qquad (17)$$

$$O_3^* \overset{k_3}{\rightleftharpoons} O_2 + O \quad \text{(slow)} \qquad (18)$$

$$O + O_3 \rightleftharpoons 2O_2 \qquad (19)$$

The rate of formation of oxygen is controlled by the decomposition of activated ozone, O_3^*, shown in reaction (*18*) and can be written

$$\frac{d[\mathrm{O_2}]}{dt} = k_3[\mathrm{O_3^*}] \qquad (20)$$

Note that $d[O_2]/dt$ is positive because O_2 is a product and is being *formed* as time goes on. Reaction (*17*) is reversible, and at equilibrium under relatively high pressures the concentration of the activated molecules remains fairly constant:

$$\frac{[\mathrm{O_3^*}]}{[\mathrm{O_3}]} = \frac{k_1}{k_2} = K_e \qquad (21)$$

Therefore the rate of decomposition of ozone appears to be first-order even though it involves some bimolecular collisions.

Trimolecular reactions are possible but rather rare. This is true because three-body collisions are rather infrequent. An example of a trimolecular reaction which follows the third-order rate law is

$$2NO + O_2 \rightleftharpoons 2NO_2 \qquad (22)$$

The rate of this reaction is given by the equation

$$\frac{-d[\mathrm{NO}]}{dt} = k[\mathrm{NO}]^2[\mathrm{O_2}] \qquad (23)$$

CATALYSIS

We have postulated that a catalyst functions by providing a new reaction path with lower activation energy (Textbook Figure 8-8). Some students may want to know more about the mechanism by which a catalyst works. Some possible ways that the faster reaction may be achieved are by (a) promoting the formation of a new activated complex; (b) providing a path by which energy can be transferred in small steps; or (c) promoting the optimum geometry. Two broad classes of catalysts are recognized—heterogeneous catalysts and homogeneous catalysts. Heterogeneous catalysts are usually solids having a very large surface area, either finely divided, such as platinum black, or quite porous, such as activated charcoal.

A heterogeneous catalyst (a two-phase system; often gaseous reactants on a solid catalyst) may be pictured as having a large number of molecules on the surface. Molecules in the body of the material have their binding forces neutralized in all directions. Surface molecules have unusual properties because of their incompletely satisfied bonding possibilities. When a dipolar molecule such as HI strikes such a surface in just the right way, it will adhere. Its vibrations will be altered by the catalyst, and it probably receives sufficient energy to become dissociated. It now becomes more probable that another HI molecule will strike the adsorbed one at just the correct orientation for reaction. Heterogeneous catalysts are indeed quite effective in increasing the rate of decomposition of HI. The activation energy of 44 kcal/mole for the noncatalyzed reaction is reduced to 25 kcal/mole on the surface of platinum and 14 kcal/mole on the surface of gold.

The reaction between H_2 and O_2 is highly exothermic, but a mixture of the two gases may be kept indefinitely without reacting appreciably. Yet when the two gases are brought together on the surface of finely divided platinum, they burst into flame. Apparently the vibration frequency is altered so much that the hydrogen molecules actually dissociate into atoms with the necessary activation energy to react when struck by an oxygen molecule.

REFERENCES FOR ADDITIONAL READING

Because the material of this chapter is not extensively treated in conventional elementary textbooks, you may want some specific references. The following two should prove quite helpful.

1. L. A. Hiller, Jr. and R. H. Herber, *Principles of Chemistry*, McGraw-Hill (1960), Chapter 15.
2. M. D. Taylor, *First Principles of Chemistry*, Van Nostrand (1960), Chapter 9.

Answers to Exercises and Problems

Ex. 8-1. Are any of the following three reactions likely to be extremely rapid at room temperature? Are any likely to be extremely slow at room temperature? Explain.

(a) $Cr^{+2}(aq) + Fe^{+3}(aq) \longrightarrow Cr^{+3}(aq) + Fe^{+2}(aq)$

(b) $3Fe^{+2}(aq) + NO_3^-(aq) + 4H^+(aq) \longrightarrow 3Fe^{+3}(aq) + NO(g) + 2H_2O$

(c) $\underset{\substack{\text{liquid}\\ \text{gasoline}}}{C_8H_{18}} + 12\frac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$

Answer

Reaction (a) may be very rapid. It does not involve bond breaking or a large number of ions. Thus the mechanism may be that shown by the overall equation.

Reaction (c) can be expected to be slow, because it is a complicated reaction requiring that many bonds be broken. In fact the student will probably recall from his experience that gasoline (*at room temperature*) does not combine readily with oxygen, although the reaction is clearly exothermic when it does occur. There are many bonds to break and to form, and the mechanism is likely to be much more complex than is shown by (c).

Ex. 8-2. Imagine five people working together to wash a stack of very greasy dishes. The first two clear the table and hand the dishes to the third person who washes them and hands them on. The last two persons dry and stack them. Which step is likely to be the rate determining step? In the light of your answer, discuss how the rate of the overall process would be affected if a sixth person joined the group (a) as a table clearer; (b) as a second dishwasher; (c) as a dish dryer.

Answer

The dishwashing step is probably rate determining. A sixth worker would then not change the overall rate if he joined the clearers or dryers. As a second dishwasher, he would increase the rate, probably doubling it.

A second dishwasher would possibly cause another step to become rate determining—probably drying. Emphasize that there is always a step that fixes the rate. Eliminating one bottleneck only brings the next most limiting one into play.

Pr. 1. The rate of movement of an automobile can be expressed in the units miles per hour. In what units would you discuss the rate of:

(a) Movement of movie film through a projector;
(b) Rotation of a motor shaft;
(c) Gain of altitude;
(d) Consumption of milk by a family;
(e) Production of automobiles by an auto assembly plant.

Answer

Many answers could be given. Some of them are:

(a) Frames/second; feet of film/second;
(b) Revolutions/minute, rpm;
(c) Feet/second;
(d) Quarts/week;
(e) Hundreds of automobiles/month.

Pr. 2. Pick the member of each pair having the greater reaction rate. Assume similar conditions within each pair.

(a) Iron rusting or copper tarnishing.
(b) Wax burning or paper burning.
(c) Evaporation of gasoline or evaporation of water.

Answer

(a) Iron rusts faster than copper tarnishes. The reactions are assumed to take place in ordinary air.
(b) Paper burns faster than wax.
(c) Gasoline evaporates faster than water.

Pr. 3. Describe two homogeneous and two heterogeneous systems that are not described in the text.

Answer

Homogeneous systems

(1) A solution of sugar in water.
(2) Many alloys: e.g., an alloy of gold and copper; solder; and coin silver. Some alloys are compounds; if the melting point is sharp the alloy is probably a compound.
(3) Air or any mixture of gases.
(4) Some kinds of colored glass.

Heterogeneous systems

(1) Concrete.
(2) A pile of beans containing gravel.

(3) A suspension such as muddy water.
(4) Raisin bread.

Pr. 4. Explain why there is danger of explosion where a large amount of dry, powdered, combustible material is produced.

Answer

The tremendous increase in surface offers many more opportunities for collision between particles of combustible material and oxygen from the air. The rate of reaction goes up with the number of collisions. It is a type of concentration effect.

Pr. 5. Explain (at the molecular level) why an increase in concentration of a reactant may cause an increase in rate of reaction.

Answer

As the concentration of reactant molecules rises, the number of collisions per second involving that reactant rises. If the rate of reaction is at all limited by such collisions, the rate rises.

Pr. 6. Consider two gases A and B in a container at room temperature. What effect will the following changes have on the rate of the reaction between these gases?

(a) The pressure is doubled.
(b) The number of molecules of gas A is doubled.
(c) The temperature is decreased at constant volume.

Answer

(a) Doubling the pressure increases the concentration of both reactants and consequently increases rate.
(b) Doubling the number of molecules of A increases the concentration of A and hence may result in an increase in reaction rate.
(c) Decreasing the temperature results in fewer molecules with sufficient energy to cause a reaction as well as fewer collisions per unit time, owing to a decrease in the kinetic energy of molecules. Both of these factors reduce the reaction rate. The first, however, is far more important than the latter.

Pr. 7. In an important industrial process for producing ammonia (the Haber Process) the overall reaction is

$$N_2(g) + 3H_2 \longrightarrow 2NH_3(g) + 24{,}000 \text{ calories}$$

A yield of approximately 98% can be obtained at 200°C and 1000 atmospheres of pressure. The process makes use of a catalyst which is usually finely divided mixed iron oxides containing small amounts of potassium oxide, K_2O, and aluminum oxide, Al_2O_3.

(a) Is this reaction exothermic or endothermic?
(b) Suggest a reason for the fact that this reaction is generally carried out at a temperature of 500°C and 350 atmospheres in spite of the fact that the yield under these circumstances is only about 30%.
(c) What is the ΔH for the reaction in kcal/mole of $NH_3(g)$?
(d) How many grams of hydrogen must react to form 1.60 moles of ammonia?

Answer

(a) Exothermic.
(b) The higher temperature is used because the reaction rate is faster at 500°C. The 30% NH_3 can be easily separated (by liquefaction) and the unreacted N_2 and H_2 recycled. The lower pressure is used because of the cost of high-pressure equipment.
(c) $\Delta H = -12$ kcal/mole of $NH_3(g)$.
(d) Three moles H_2 give 2 moles NH_3;
$\frac{3}{2}$ moles of H_2 give 1 mole NH_3;
$(1.60)(\frac{3}{2})$ moles H_2 give 1.60 moles NH_3;
$(1.60)(\frac{3}{2})(2.02 \text{ g/mole})$ moles $= 4.85$ g H_2;
4.85 g H_2 give 1.60 moles NH_3.

Pr. 8. Give several ways by which the rate of combustion in a candle flame might be increased. State why the rate would be increased.

Answer

(1) Burn the candle in compressed air. Blow pure O_2 on it. Add to the wax a substance that releases oxygen on heating. All of these are effective because the concentration of one reactant, O_2, is increased.
(2) Increasing the temperature of the flame would have a direct effect of increasing the rate and an indirect effect of making more gaseous material available.
(3) Find a catalyst.
(4) At first glance, one might suggest a supply of more wicks, or a larger wick. This would increase the rate of consumption of candle wax, but would not necessarily increase the rate of the reactions taking place within one particular flame.

Pr. 9. State three methods by which the pressure of a gaseous system can be increased.

Answer

(1) Decrease the volume of the container.
(2) Increase the temperature at constant volume.
(3) Add more molecules.
(4) Initiate a reaction that produces more molecules than are consumed.

Pr. 10. Do you expect the reaction

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$$

to represent the mechanism by which ethylene, C_2H_4, burns? Why?

Answer

No. As written, the reaction involves a four-body collision. This is not likely to occur. The simultaneous breaking of C—C bonds, C—H bonds, and O—O bonds and the forming of C—O bonds and H—O bonds is regarded as unlikely.

Pr. 11. A group of students is preparing a 10-page directory. The pages have been printed and are stacked in 10 piles, page by page. The pages must be: (1) assembled in order, (2) straightened, and (3) stapled in sets. If three students work together, each performing a different operation, which might be the rate-controlling step? What would be the effect on the overall rate if the first step were changed by ten helpers joining the individual assembling the sheets? What if these ten helpers joined the student working on the second step? The third step?

Answer

Step 1 is the rate-controlling step, since at best it would require more time than the other two steps. An increase of 10 helpers on Step 1 would be reflected in a considerable increase in rate. In this particular example a considerable increase in rate for Step 1 might eventually cause one of the other steps (e.g. Step 3) to become the rate-controlling step.

The same ten helpers on Step 2 or Step 3 would not increase the overall rate, since the slow Step 1 is the rate-controlling step.

Pr. 12. Describe the life and death of an ordinary, empty water glass. Utilize the concept "threshold energy."

Answer

Ordinarily a glass experiences many bumps and knocks without being seriously damaged—not enough energy having been supplied to form a fracture in the network of atoms of which the material is made. A particularly sharp blow, however, can shatter the glass. A certain minimum amount of energy—the "threshold energy"—must be supplied before the glass will break.

Pr. 13. An increase in temperature of 10°C rarely doubles the kinetic energy of particles, and hence the number of collisions is not doubled. Yet, this temperature increase may be enough to double the rate of a slow reaction. How can this be explained?

Answer

A 10° rise in temperature is not much (about one-thirtieth of the absolute temperature at room conditions). Yet it has a large effect on many reaction rates. This results from the shape of the energy distribution curve (Textbook Figure 8-1). The extra kinetic energy resulting from the increased temperature increases the number of molecules having high energy. For many reactions, only a relatively few molecules have sufficient energy to be likely to react. The proportion of these is greatly increased by a temperature rise of even 10°C.

Pr. 14. In a collision of particles what is the primary factor that determines whether a reaction will occur?

Answer

The primary factor is whether they collide with sufficient energy to surmount the activation energy barrier and cause a reaction.

Pr. 15. In Figure 8-6, why is kinetic energy decreasing as NO_2 and CO go up the left side of the barrier, and why is kinetic energy increasing as CO_2 and NO go down the right side? Explain in terms of conservation of energy and also in terms of what is occurring to the various particles in relation to each other.

Answer

As the CO_2 and NO ascend the left side of the barrier, the kinetic energy which they must possess in order to achieve this state is gradually changed to the potential energy of the activated complex. In achieving this state, the molecules had to overcome the mutually repulsive forces existing between them; hence the activated complex is highly unstable.

After its formation, the activated complex may then either separate and return to the original reactants or rearrange and separate into the products. In either event, the relatively high potential energy possessed by the activated complex is changed into kinetic energy of the product molecules (or reactants if reaction is not completed).

Pr. 16. Phosphorus, P_4, exposed to air burns spontaneously to give P_4O_{10}; the ΔH of this reaction is -712 kcal/mole P_4.

(a) Draw an energy diagram for the net reaction, explaining the critical parts of the curve.

(b) How much heat is produced when 12.4 grams of phosphorus burn?

Answer: See Figure 8-7.

(a) Since the reaction is spontaneous, the curve must have at most a small energy barrier (small compared to kT). Activation energy is very low. The reaction is rapid and highly exothermic ($\Delta H = -712$ kcal/mole). The figure shows that the products have considerably less potential energy than the original reactants.

(b) $P_4 + 5O_2 \rightleftharpoons P_4O_{10}$

$$\Delta H = -712 \text{ kcal/mole } P_4$$

$$12.4 \text{ g } P_4 = \frac{12.4 \text{ g}}{124 \text{ g/mole}} = 0.100 \text{ mole}$$

$$(0.100 \text{ mole})\left(712 \frac{\text{kcal}}{\text{mole}}\right)$$

$$= 71.2 \text{ kcal heat produced by burning 12.4 grams } P_4$$

Pr. 17. Considering that so little energy is required to convert graphite to diamond (recall Problem 8, Chapter 7), how do you account for the great difficulty found in the industrial process for accomplishing this?

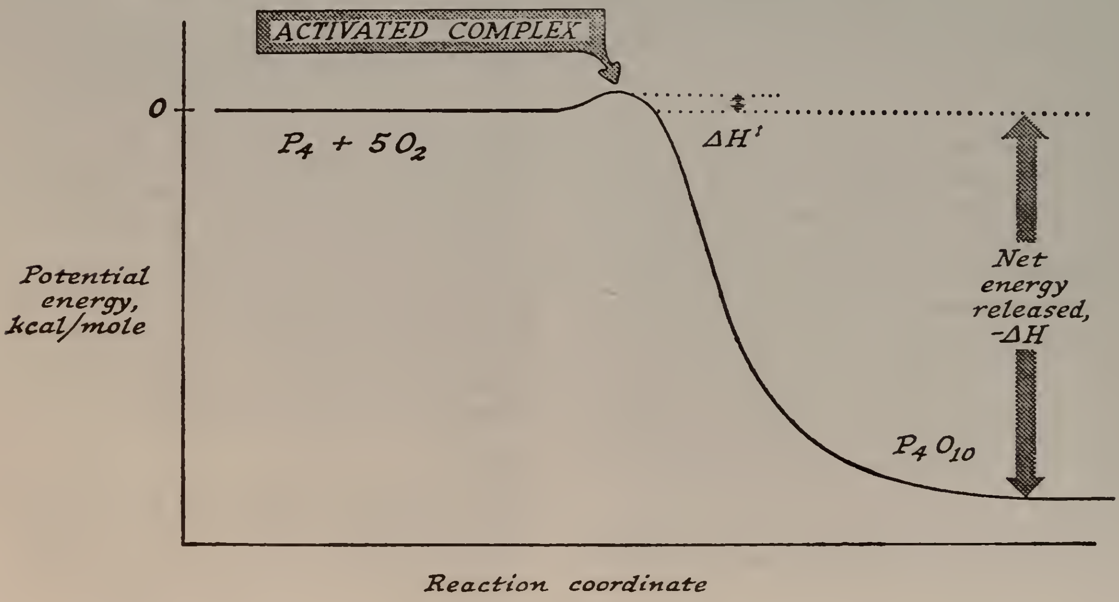
Answer

The activation energy must be very high. This would result in a very low rate of reaction.

You may wish to add these items to illustrate points discussed:

(1) A high temperature is used. This increases the rate of both forward and reverse reactions; it also aids diffusion.

Fig. 8-7. **Potential energy diagram** *for the reaction* $P_4 + 5O_2 \rightleftharpoons P_4O_{10}$



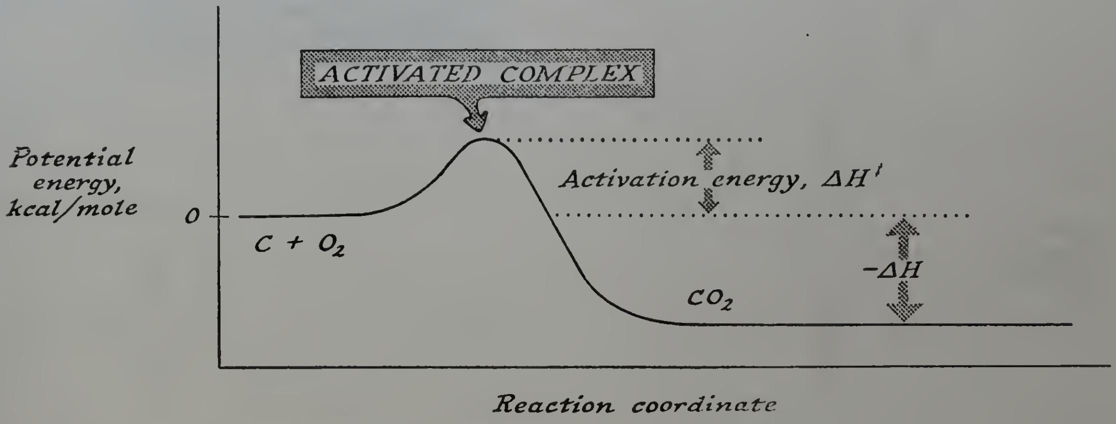


*Fig. 8-8*R. **Potentoial energy diagram** *for the reaction* $C + O_2 \rightleftarrows CO_2$.

(2) A high pressure is used. This favors the formation of the substance occupying the least volume. (This is an example of Le Chatelier's Principle, which the student will study in Chapter 9.) The density of diamond is 3.51 g/cc; of graphite, 2.25 g/cc.

(3) A catalyst is used (a transition metal). This, according to our model, provides a route with a lower energy barrier.

Pr. 18. Why does a burning match light a candle?

Answer

The activation energy of at least one reaction involved in the burning of a match head is very low—so low, in fact, that the energy supplied to the match head by the abrasion during striking is sufficient to get that reaction going. The heat from it causes a series of reactions. Such is not true of the materials in the candle. These reactants have a greater "energy barrier." Rubbing the wick is not a practical way to supply enough activation energy. The energy from another source of heat, the match, is needed.

Pr. 19. Draw an energy diagram for the reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

(a) When the C is in large chunks of coal.

(b) Is the curve changed if very fine carbon powder is used?

Answer

(a) Refer to Figure 8-8.

(b) The curve is unchanged. The reaction will proceed faster, but the activation energy will remain the same, as will ΔH. The energy requirement for fruitful collisions is determined by the nature of the particles involved. It is true that the carbon powder will offer more opportunities for fruitful (as well as unfruitful) collisions, but the energy requirement for a fruitful collision remains unchanged.

Pr. 20. Sketch a potential energy diagram which might represent an endothermic reaction. (Label parts of curve representing activated complex, activation energy, net energy absorbed.)

Answer: See Figure 8-9 (p. 270).

Pr. 21. Why is it difficult to "hardboil" an egg at the top of Pike's Peak? Is it also difficult to cook scrambled eggs there? Explain.

Answer

The egg being hardboiled is heated by water that boils well below 100°C at this altitude. At this temperature not many molecules in the egg have enough energy to produce reactive collisions. The cooking takes a long time. The scrambling process is not so hindered. The frying pan can easily be heated to essentially the same temperature as at sea

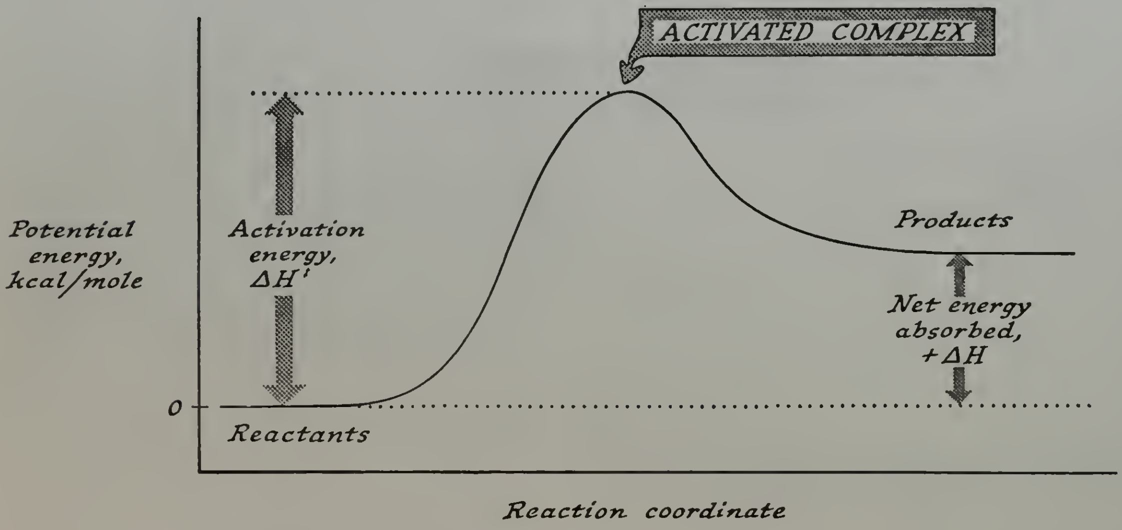


Fig. 8-9. **Potential energy diagram** *for an endothermic reaction.*

level. Any water naturally present readily evaporates, and the egg cooks easily.

Pr. 22. Give two factors that would increase the rate of a reaction, and explain why these do increase the rate?

Answer

(1) Temperature. An increase in temperature increases the number of particles having sufficient energy to produce fruitful collisions. Another factor, but less important than the above, is that the average kinetic energy will be increased. This will result in greater velocities and hence more collisions per unit time.

(2) Concentration. An increase in concentration will give more particles per unit volume and hence more collisions per unit time.

(3) Catalyst. A catalyst that increases a reaction rate does so by providing a new mechanism. If the activation energy of the limiting step of the new mechanism is lower than the activation energy of the limiting step of the uncatalyzed reaction, then the rate is increased very much.

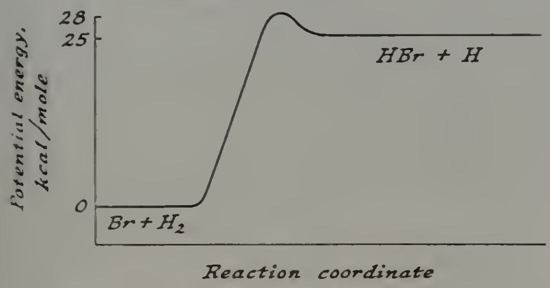
Suggested Quiz Questions

The following questions are designed for an open book quiz. There are too many for a one-period test; make a selection to fit your class.

Figure 8-10 illustrates a potential energy diagram for the reaction represented by the equation

$$Br + H_2 \longrightarrow HBr + H$$

Fig. 8-10. **Potential energy diagram** *for the reaction* $Br + H_2 \rightleftharpoons HBr + H$.



1. What is the heat of reaction, ΔH, in kcal/mole of HBr for the reaction $Br + H_2 \longrightarrow HBr + H$?

   Answer: ΔH = 25 kcal/mole.

2. What is the energy of activation, $\Delta H^{\ddagger}$, for the reaction $Br + H_2 \longrightarrow HBr + H$?

   Answer: $\Delta H^{\ddagger}_{R}$ = 28 kcal/mole.

3. What is the energy of activation, $\Delta H^{\ddagger}$, for the reaction $H + HBr \longrightarrow H_2 + Br$?

   Answer: $\Delta H^{\ddagger}_{L}$ = 3 kcal/mole.

4. What would be the effect on the shape of the curve representing the path of the reaction if a catalyst were added?

   Answer
   The peak of the curve would be lowered approaching the 25 kcal/mole level.

5. Which portion of the curve represents the existence of an activated complex?

   Answer
   The peak at highest potential energy.

6. Is the reaction $Br + H_2 \longrightarrow HBr + H$ endothermic or exothermic?

   Answer: Endothermic.

7. How does an increase in temperature affect the rate of a chemical reaction? Explain in terms of molecular kinetic energy

   Answer
   The rate is increased. A small increase in temperature greatly increases the number of molecules possessing greater than the minimum threshold kinetic energy.

8. Consider a flame which is produced as oxygen gas and butane, C_4H_{10}, burn to produce gaseous carbon dioxide and water. If butane is consumed at the rate of 2.24 liters/minute, (measured at STP), what is the rate of production of carbon dioxide in moles/minute?

   Answer

   2.24 liters/minute = 0.1 mole/minute

   $C_4H_{10} + 6\frac{1}{2}O_2 \rightleftharpoons 4CO_2 + 5H_2O$ + heat

   For each mole of C_4H_{10} consumed, four moles of CO_2 are produced. The rate of production of CO_2 will be 0.4 mole/minute. This assumes a steady state condition.

For Questions 9 and 10 consider the following reactions as they occur at room temperature.

$Ag^+(aq) + I^-(aq) \rightleftharpoons AgI(s)$ (*1*)

$C_{25}H_{52}(s) + 38O_2(g) \longrightarrow 25CO_2(g) + 26H_2O(l)$ (*2*)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ (*3*)

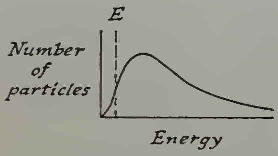
9. Which of the reactions, if any, may be extremely slow at room temperature?

   Answer: (*2*) and (*3*).

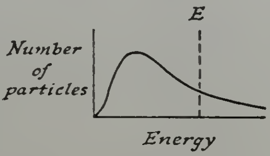
10. Which of the reactions, if any, may be extremely fast at room temperature?

    Answer: (*1*).

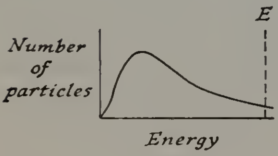
Consider the following identical kinetic energy distribution curves for four different reactions all at the same temperature. Only the threshold energy (E) is different.



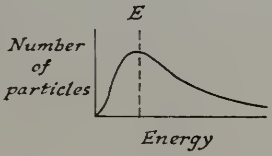
Reaction A



Reaction B



Reaction C



Reaction D

11. Select the fastest and slowest reaction.

Answer: Fastest; reaction A.
Slowest; reaction C.

12. If a catalyst were added to a reacting system, what effect, if any, would this have on the kinetic energy distribution curve and on the threshold energy for the reaction?

Answer
Adding a catalyst to a reacting system does not change the kinetic energy distribution curve, but lowers the threshold energy requirement such that more molecular collisions are successful in producing reactions.

CHAPTER

9

EQUILIBRIUM IN CHEMICAL REACTIONS

Intent and Approach

Two important questions capture the chemist's interest for all chemical reactions: How fast does the reaction proceed? To what extent does the reaction proceed in a given direction? In Chapter 8 we discussed the rate of chemical reactions. In this chapter our primary concern is the extent of a given reaction.

Emphasis should be placed on the dynamic nature of chemical equilibrium and on its relation to the rates of the opposing reactions. Le Chatelier's Principle is worth stressing as a tool for predicting the effect of various changes on the equilibrium of the system.

Here once again you are afforded an excellent opportunity to introduce the student to one of the great frontier areas in chemistry. What are the factors which determine equilibrium? Why does one reaction favor the formation of products and a similar one the formation of reactants? The last section of this chapter proposes a model system for a chemical reaction which indicates that reactions will tend to proceed toward more stable molecular substances; i.e., those with lower energies. Yet many examples can be given to indicate that this is not always the case, thus there must be another factor which determines or fixes the equilibrium state. This can be qualitatively described as the randomness implied by temperature.

Outline

QUALITATIVE ASPECTS

1. Equilibrium is described as constancy of macroscopic properties in a closed system (9-1.1).
2. The dynamic nature of chemical equilibrium is stressed. In chemical reactions, at equilibrium, microscopic processes continue, but in a balance which yields no macroscopic changes (9-1.2).
3. The state of equilibrium, i.e., the relative concentrations of reactants and products, is not discernible from the balanced equation. This information must be obtained from other experimental data (9-1.3).
4. Equilibrium conditions for a given chemical system can be altered by changes in temperature or concentration, but not by catalysts (9-1.4).
5. Neither the equation nor the equilibrium constant gives information on the rate at which a reaction approaches equilibrium (9-1.5).
6. Le Chatelier's Principle (9-1.6) helps predict changes in equilibrium conditions.
7. The Haber process provides an example of an equilibrium reaction for which Le Chatelier's Principle aids in adjusting conditions (9-1.7).

QUANTITATIVE ASPECTS

8. An equilibrium constant is derived from experimental data and generalized to the law of chemical equilibrium (9-2.1, 9-2.2).
9. The significance of the magnitude of *K* and the calculations involving use of equilibrium constants are taken up in Secs. 9-2.2 and 9-2.3 (reduced type).
10. Factors which determine the equilibrium constant for a reaction are discussed (9-2.4).

New Concepts

1. Le Chatelier's Principle.
2. Law of chemical equilibrium—expression for equilibrium constant.
3. Factors that determine equilibrium conditions.
4. Equilibrium in a chemical reaction as a dynamic balance of microscopic changes.

Development

QUALITATIVE ASPECTS OF EQUILIBRIUM (9-1)

Introduction

The concept of chemical equilibrium is introduced by referring to the discussion in Secs. 5-1.1–5-1.3 concerning the equilibrium between various phases. Chemical equilibrium is characterized by a lack of change in macroscopic processes resulting from the balance between the opposing processes still continuing at the molecular level.

Recognizing Equilibrium (9-1.1)

The best practice is to start with the CHEM Study film EQUILIBRIUM. This film uses a good analogy (many commonly thought of are steady state situations) and then uses the solubility of I_2 in alcohol-water as the principal chemical example.

Make sure the student is aware of the subtle but important difference between equilibrium and steady state (Exercise 9-1 and Problems 1 and 2 may help). Think through any analogies you want to use to make sure they are good ones.

Two other points of pedagogy must be mentioned here. The first is that when you describe attaining equilibrium and reach the point where there is "no change in macroscopic processes," stress that this means there is *no observable* change. This will avoid confusion over the semantics involved in stating that there is no change, even though reactions in both directions are still going on. You can help clarify this by distinguishing between the *experimental facts* (lack of observable change) and the *interpretation* (reactions must be continuing). We do not have direct experimental proof of the second statement, since any experiment designed to detect changes will work only on a system which has not reached equilibrium! We believe reactions continue (unobserved) at equilibrium because this proposal is consistent with many kinds of data, the changes which occur in *K*, and our experience with the kinetic theory. The second point is that, in the Textbook and film examples, we have talked about only a few properties for each system—the color of NO_2-N_2O_4 gas, the color of I_2 solution, or the color and pressure of bromine gas. But at equilibrium *all properties become constant.* We used color changes for demonstration, but the reaction $CaCO_3 \longrightarrow CaO + CO_2$ (Textbook Figure 9-2) shows another type. In all reactions, at least in principle, any property could be used. We choose the most convenient for experiment.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
Review Sec. 5-1.1 to 5-1.3 S 9-1/9-1.2 (pp. 142–147)	1	Discussion NO_2-N_2O_4 Demonstration	1	**1**,* 3–6	2		Recognition and Dynamic Aspects of Equilibrium
S 9-1.3/9-1.6 (pp. 147–150)	2	Discussion Film, EQUILIBRIUM	2	8, 10	7, 9, **11**, 12	13–16	Le Chatelier's Principle
Expt. 15	3	Demonstration of $FeSCN^{+2}$ system Introduce Expt. 15					
Expt. 15	4	Finish Expt. 15					
S 9-1.7/9-2.1 (pp. 150–152)	5	Discuss Expt. 15 and S9-1.7/9-2.1	3	19	**17**		Applying Equilibrium Considerations
S 9-2.2 (pp. 152–155) S 9-2.3 opt.	6	Sample Problems Discussion	4, 5		20–22	18, **23**, 24	Law of Chemical Equilibrium
S 9-2.4 (pp. 155–159)	7	Discussion		25	26		Factors determining Equilibrium
Review	8	Problems					

* Boldface indicates problems whose answers are given in the Textbook.

Note: Expt. 16 requires solutions made a few days in advance.

The radioactive measurements in the film EQUILIBRIUM provide an example. The I_2 crystals and solution were at equilibrium (as shown by the color) when the radioactive iodine was added. It is clear that, at that instant, the balance was destroyed. The radioactive I_2 was not distributed in its equilibrium proportions. We then "watched" that distribution change by means of the Geiger counter. However, the point here is that we *observe change in a system not yet at equilibrium*. From this nonequilibrium behavior we make logical inferences about the solubility equilibrium of regular (nonradioactive) iodine.

As a second example, consider the often quoted (and demonstrated) case of a crystal hung in a saturated solution of the same material. The crystal will change shape, especially if it has broken edges. Yet the only reason change occurs is because equilibrium does *not* exist. Small crystals dissolve and large crystals grow *because small crystals dissolve faster*. The same is true of broken crystal faces; they dissolve faster than perfect faces. At equilibrium *NO* macroscopic changes occur.

The Dynamic Nature of Equilibrium (9-1.2)

The NO_2-N_2O_4 bulb demonstration is used as a means of demonstrating the dynamic nature of equilibrium processes. This experiment allows you to demonstrate (by means of easily observable color changes) the fact that in chemical reactions equilibrium involves continuing microscopic processes, but in a balance that results in no further macroscopic changes. The Textbook gives a good description, but the visual experience helps bring it to life.

The State of Equilibrium (9-1.3)

Make the student realize that the equation for the chemical reaction does not give any information about the actual concentrations of the products and reactants at equilibrium. These must be determined experimentally. The "state of equilibrium" for a particular system consists of the proportional concentrations of products and reactants present at equilibrium.

Use the equilibrium data given for the following reaction (at 2273°K and 1 atmosphere) to show that the final equilibrium state is the same regardless of the direction from which you choose to approach it.

$$H_2O(g) \rightleftharpoons H_2(g) + \tfrac{1}{2}O_2(g)$$

This attainment of the same "state of equilibrium" from all directions is an important experimental test of reaching equilibrium.

Altering the State of Equilibrium (9-1.4)

Changes in temperature, concentration, and pressure affect the conditions at equilibrium. Anything which affects the rate of one of the reactions involved in an equilibrium may affect the conditions that prevail at equilibrium.

Catalysts affect the rates of both the forward and the reverse reaction equally, and consequently do not alter the equilibrium state. A section of the *Background Discussion* shows why this is the case.

The reaction

$$Fe^{+3}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{+2}(aq)$$

is to be used in Experiment 15 for the determination of an equilibrium constant. Introduce it now just to demonstrate the concentration effect. Show that adding more Fe^{+3} or SCN^- darkens the solution, indicating more $FeSCN^{+2}$.

Demo. 4, CHEMICAL EQUILIBRIUM,
fits here. See p. 281 for guide.

Expt. 15, CHEMICAL EQUILIBRIUM,
fits here. See p. 284 for guide.

The NO_2-N_2O_4 bulb experiment can be referred to again at this point to demonstrate the effect of temperature. It can be quickly shown that different temperatures give different equilibrium states (color changes).

Attainment of Equilibrium (9-1.5)

There exist many combinations of chemicals, known to the student, that do not appear to be reacting, although the equilibrium state greatly favors the products of these potential reactions.

The most common examples are flammable substances (gasoline, wood, paper), which often exist for years in direct contact with oxygen. The student should understand, however, that once reaction has started, these materials are consumed in favor of products. Until then, equilibrium is not attained, because the rate of reaction is extremely slow (if no one supplies activation energy from a match). Many reactions between solids are quite slow in reaching equilibrium.

Film, EQUILIBRIUM,
fits here. See p. 289 for summary.

Predicting New Equilibrium Concentrations: Le Chatelier's Principle (9-1.6)

Before starting to explain Le Chatelier's Principle, remind the students of the dynamic equilibrium model. Point out that because of the differences in activation energy for the two reactions which are in balance, the number of molecules of reactants and of products will differ.

Now you can ask for discussion of the consequences of various "disturbances" to the system. Let's describe these in terms of *increases* in the factors. Similar (but reverse) arguments will hold for decreases.

Concentration. This type of change initially increases the number of one kind of molecule. Since this molecule is involved in more collisions, the reaction using it becomes faster. This leads to a rise in the concentration of reactants for the reverse reaction, and so on. As a result of this reaction, the concentrations of all species are changed. The same effect is achieved by increasing the partial pressure of one gaseous species.

Pressure. (In a practical sense, this discussion applies to gases only.) The effect is quite like that of a concentration change. Higher pressures give more molecules per cubic centimeter. The reaction involving more gaseous species will be affected more because it is more dependent on concentration—there are more concentration terms in the rate equation. The reaction will produce more of the kind of molecules which act in the reverse way. This leads to a change in the reverse rate, and a new state of equilibrium is attained, in which more of the molecules having more atoms per molecule are favored. If there is no reaction leading to fewer total molecules, then no change in equilibrium results. All these effects are summed up by the statement: a change applied to a system at equilibrium causes the equilibrium to shift so as to partially counterbalance the change.

Temperature. A rise will increase the kinetic energy of all molecules. But the reactant molecules in the reaction that absorbs energy will begin to react somewhat faster. This will raise the concentration of reactants for the reverse reaction and speed it up. A new equilibrium state will be reached in which products from the energy-absorbing reaction are increased.

Application of Equilibrium Principles: The Haber Process (9-1.7)

This example affords the opportunity to predict the effect of various changes on the equilibrium conditions of a well-known commercial process. It serves as an excellent example of the importance of the rate of the reaction. An increase in temperature results in the formation of less product, but unless the temperature is increased, no appreciable reaction will occur. (The rate is too slow for reaction to be economically useful.) An increase in pressure favors increased yield of product. Here the cost of high pressure equipment results in a compromise. Removing the product (NH_3) and recycling the unreacted N_2 and H_2 result in further economy.

QUANTITATIVE ASPECTS (9-2)

The Equilibrium Constant (9-2.1)

Experiment 15 and the data for the $2HI(g) = I_2(g) + H_2(g)$ equilibrium given in this section can be used by the student to find the relationship between the concentrations of reactants and products at equilibrium. The advantage of this approach lies in the opportunity the better student has to discover this relationship rather than having it imposed upon him.

The Law of Chemical Equilibrium (9-2.2)

Use the relationship discovered in Experiment 15 and Sec. 9-2.1 to develop the law of chemical equilibrium. Given the reaction

$$aA + bB \rightleftharpoons eE + fF$$

we then have, at equilibrium,

$$\frac{[E]^e[F]^f}{[A]^a[B]^b} = K = \text{a constant}$$

The use of brackets in this expression stands for concentration of substance, usually expressed in moles/liter. You should use them consistently.

In determining the value of K for a given reaction you omit the concentrations of any solid materials appearing in the reaction, since their concentration is fixed by their density and crystal structure and is constant for the reaction in question. In reactions involving water as one of the reactants or products (and carried out in an aqueous medium), the concentration of the water may be ignored in the equilibrium expression since usually only a tiny fraction of water is reacting. The concentration of water changes hardly at all. See Table 11-I in this Guide. It can be considered a constant in the expression for the equilibrium constant. This approximation is most accurate for dilute solutions. Of course these "omissions" are conventions, and mean that the unvarying term is really still present, but as part of the constant itself.

The student should have a firm feeling that a large K means products are favored—that is, the equilibrium mixture consists largely of products. And of course the converse holds—a small K means reactants are favored.

Use a few, worked-out, simple examples to show that K is much greater than one when the products are in excess and vice versa. First, pick examples in which the balanced equation has no coefficients except one. Then gradually use the others. Choose the concentrations such that K is not near one but, instead, outside the range 0.01–100. For the more complicated reactions it is not easy to see what a value of K in this range means in terms of product concentration relative to reactant concentration; it depends upon the particular reaction.

Students should approach the calculations involving equilibrium constants by carefully noting what information is required and what information is given. The first step in most calculations involves setting up the expression for the equilibrium constant for the reaction being considered. At this point the student should tabulate what he knows about the experimental data connected with the reaction—i.e., the initial and final concentrations of reactants and products.

The more able student should be encouraged to examine the reasoning applied in the example in the Textbook in order to determine when a reasonably good answer can be obtained by approximation without resorting to the use of the quadratic formula. These calculations provide another area in which the teacher can emphasize the importance of carefully analyzing and understanding the problem rather than attempting to routinely substitute values in a formal expression.

The Law of Chemical Equilibrium Derived from Rates of Opposing Reactions (9-2.3) (reduced type)

The Factors Which Determine Equilibrium (9-2.4)

The "golf ball" analogy described in this section is an attempt to give the student some insight into the factors which determine equilibrium. So far we have discussed those factors which can alter the conditions of a given equilibrium. We are now interested in what possible explanations can be advanced to account for the fact that one reaction will favor products whereas another will favor reactants.

The analogy as used here implies that all exothermic reactions proceed with a loss in energy, which is in keeping with our experience for many reactions. It further implies, however, that an exothermic process would not reverse itself. This is not found to be the case. Further, some endothermic or energy-absorbing processes occur spontaneously. Our first model does not offer an explanation for these phenomena.

It is clear that some other factor (entropy) in addition to minimum energy fixes the equilibrium state. Entropy is an expression of the randomness implied by temperature and is discussed in the background sections of this chapter and of Chapter 5. At any given time some of the product molecules in a chemical reaction may possess very high energies indeed, and may react to form the original substances.

You should stress this important fact. Even in a spontaneous, highly exothermic reaction, where most of the product molecules do indeed have relatively low potential energies compared to the reactant molecules, *some* of the product molecules will have sufficiently high random thermal energies to cause the reverse reaction to occur. At higher temperatures the energy difference between reactants and products becomes less and less important because there is so much randomness caused by thermal motion. You may want to call particular attention to the brief discussion, at the end of this chapter, of some of the implications which can be drawn from the above concept.

DEMONSTRATION 4 CHEMICAL EQUILIBRIUM

PURPOSE. To introduce, in a qualitative way, the reaction for which the equilibrium constant is to be determined in Expt. 15. This reaction is also discussed in the Textbook in Sec. 9-1.4.

EQUIPMENT NEEDED. Quantities will depend upon the size of the class and the room. If an overhead projector is conveniently available, smaller quantities may be used and the demonstration projected. Amounts are for one demonstration in a small class.

25 ml 0.002 *M* KSCN (0.19 g KSCN/liter)
0.5 ml 0.2 *M* $Fe(NO_3)_3$
[80 g $Fe(NO_3)_3 \cdot 9H_2O$/liter]
small sample of KNO_3 solution
KSCN crystals

Na_2HPO_4 crystals
100 ml beaker
4 18 × 150 mm test tubes
stirring rod

TIME REQUIRED. This will depend upon the amount of previous discussion and upon the number of "side excursions" during the demonstration. The average time required is probably 15–20 minutes.

PROCEDURE	QUESTIONS AND DISCUSSION
1. Put 25 ml of 0.002 *M* KSCN and 25 ml of water into a small beaker. Have 0.2 *M* $Fe(NO_3)_3$ in a dropper bottle. Give students the names of the reagents.	What ions are present (before mixing)? $K^+(aq)$, $SCN^-(aq)$, $Fe^{+3}(aq)$, $NO_3^-(aq)$
2. Put three or four drops of $Fe(NO_3)_3$ into the beaker, and stir.	What possible explanation is there for the color change? Color changes usually indicate a chemical change, and in this reaction, K^+ might combine with NO_3^- and Fe^{+3} with SCN^-.
3. Have the solution of KNO_3 ready.	Is there evidence that the color is not due to KNO_3? Students may have used $K^+(aq)$ and $NO_3^-(aq)$ in Expt. 11, but show a sample of KNO_3 solution. *Conclusion:* The color is most likely some combination of $Fe^{+3}(aq)$ and $SCN^-(aq)$. Investigation has shown the reaction to be $Fe^{+3}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{+2}(aq)$ (Point out the conservation of charge.) Note that $FeSCN^{+2}(aq)$ is the hydrated thiocyanoiron(III) ion.
4. Divide the solution in the beaker into four test tubes. Use the first as a reference. To the second add some small crystals of KSCN.	What does this addition do to the concentration of $SCN^-(aq)$? The $[SCN^-(aq)]$ increases. (Here is a good opportunity to remind the student that brackets mean "concentration," usually measured in moles/liter.)

What can we conclude from the intensification of color?

More $\text{FeSCN}^{+2}(aq)$ must have formed.

How can this have happened, since no more $\text{Fe}^{+3}(aq)$ was added?

There was some unreacted $\text{Fe}^{+3}(aq)$ present. [In fact, the concentrations of $\text{SCN}^{-}(aq)$ and of $\text{Fe}^{+3}(aq)$ were about equal, with that of $\text{Fe}^{+3}(aq)$ a bit in excess. But do not calculate these concentrations or tell the student the "correct" answer. Just accept the suggested explanation.]

5. To the third tube add three drops of 0.2 *M* $\text{Fe(NO}_3)_3$.

What does this addition do to the concentration of $\text{Fe}^{+3}(aq)$?

The concentration of $\text{Fe}^{+3}(aq)$ increases.

What can we conclude from the intensification of color?

More $\text{FeSCN}^{+2}(aq)$ formed.

How can this have happened, since no more $\text{SCN}^{-}(aq)$ was added?

There must have been some unreacted $\text{SCN}^{-}(aq)$ present. You will probably find that you must supply this answer, since the student will be thinking that $\text{Fe}^{+3}(aq)$ is in excess and that all the $\text{SCN}^{-}(aq)$ reacted. Now point out that approximately equal amounts of the two ions were added. Ask how the color due to $\text{FeSCN}^{+2}(aq)$ could have increased unless some $\text{SCN}^{-}(aq)$ was available. Make a hypothesis. Some of all the species—products and reactants—are present at equilibrium.

6. To the fourth tube add a few small crystals of Na_2HPO_4, one at a time, with shaking between additions.

What could explain the reduction in color?

A reaction with $\text{FeSCN}^{+2}(aq)$, with $\text{Fe}^{+3}(aq)$, or with $\text{SCN}^{-}(aq)$.

What ions have been (are being) added, and, considering their charges, with which of the above might they react?

The $\text{Na}^{+}(aq)$ could react with $\text{SCN}^{-}(aq)$. The $\text{HPO}_4^{-2}(aq)$ could react with $\text{Fe}^{+3}(aq)$ or with $\text{FeSCN}^{+2}(aq)$.

The student does not have the information available but may be told that NaSCN is present as $\text{Na}^{+}(aq)$ and $\text{SCN}^{-}(aq)$. He may then conclude that this would not affect the color. He may also be told that $\text{HPO}_4^{-2}(aq)$ plus $\text{Fe}^{+3}(aq)$ form a colorless ion, $\text{FeHPO}_4^{+}(aq)$. From these statements he may conclude that $\text{FeHPO}_4^{+}(aq)$ accounts for the loss of color, since decreasing the $\text{Fe}^{+3}(aq)$ would decrease the amount of $\text{FeSCN}^{+2}(aq)$ formed.

The general equation may be written and the implications of Le Chatelier's Principle discussed.

$$Fe^{+3}(aq) + SCN^{-}(aq) \rightleftarrows FeSCN^{+2}(aq)$$

Finally, discuss the purpose of Expt. 15 and direct the student to get a data and calculation sheet prepared for the experiment.

The Laboratory Manual has a discussion of the relationship between depth and concentration (on p. 43). This relationship should be demonstrated prior to its use. Using $FeSCN^{+2}$ is not completely satisfactory as dilution shifts the equilibrium enough so that the color and intensity change caused by a twofold dilution is detectable. To avoid this, and to put the student on familiar ground, use tea. Pour drinkable tea into each of two test tubes to about 3 cm depth. Dilute one solution with an equal volume of water, i.e., cut its concentration in half and double its depth. Now wrap the tubes in white paper and have the students look down the length of the tubes at a light source such as an overhead projector. The colors appear to be the same. The amount of color depends directly on both concentration and depth.

$$\text{color} = kc_1d_1$$

If both colors appear to be the same, then

$$kc_1d_1 = kc_2d_2 \quad \text{or} \quad \frac{c_1}{c_2} = \frac{d_2}{d_1}$$

EXPERIMENT 15 CHEMICAL EQUILIBRIUM

PURPOSE. To determine an equilibrium constant experimentally, both as an introduction to the idea of equilibrium constants and to illustrate an important aspect of "searching for regularities."

PRELAB DISCUSSION. Demonstration 4 is the prelab for this experiment. Discuss lab hints 5 and 6.

TIMING. This experiment should be done in Chapter 9, after the qualitative discussion of equilibrium and before discussing equilibrium constants. It must be done before Sec. 9-2.1 is assigned, however, since the calculations are specifically referred to there. Demonstration 4 should precede the experiment.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

25 ml 0.002 *M* KSCN (0.19 g/liter) (lab hint 1)
15 ml acidified 0.2 *M* $Fe(NO_3)_3$ [81 g $Fe(NO_3)_3 \cdot 9H_2O$ plus 40 ml conc. HNO_3 per liter] (lab hint 2)
distilled water
5 test tubes (lab hint 3)
25 ml graduate (it is convenient to have a 10 ml graduate also and/or a 5 ml pipet)
250 ml beaker
diffused light source or white paper (lab hint 4)
centimeter scale
medicine dropper

TIME REQUIRED. You will need one 45–50 minute period. The experiment should be completed in one day, since the colors tend to fade while standing.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. If 5 ml pipets are provided, each student may take 25–30 ml of KSCN from the stock bottle and then place 5 ml portions in his test tubes. If graduates are being used to measure the volume, it is more convenient to have the stock solution in enough squeeze bottles such that no student need wait long.
2. Squeeze bottles are convenient for dispensing the $Fe(NO_3)_3$ solutions. You will probably save time by describing the dilution procedure for $Fe(NO_3)_3$, and will ensure that students understand it. The use of a second graduate will avoid confusion in measuring 5 ml portions of the different dilutions. Tell students to record initial concentration of SCN^- ion.
3. Flat-bottomed vials (often used in biology) are ideal for the color comparison. They eliminate errors due to curvature and unevenness. If these vials are not available, use the smallest diameter test tube you have that will hold 10 ml. A 13 × 100 mm tube will just barely hold this volume, hence mixing is messy.
4. Matching the tubes for color intensity causes some students difficulty. The white paper background needs to be well lighted. If available, diffused light sources are helpful. A light box with a ground glass top may often be borrowed from either the commercial or the art department. You can make a light box by wiring a 150 W bulb in a wooden box topped by a piece of window pane made translucent by rubbing it with 100 mesh grinding compound obtained from your auto shop or garage.
5. If a student is having difficulty, these suggestions may be helpful.
   (a) When the colors seem close, take out a dropper full of the darker solution, and then return some of the solution drop-wise until the tubes match.
   (b) Hold the tubes close together, and blink your eyes between "looks" to help avoid eye fatigue.

(c) Some may find it more convenient to match all the tubes to the lightest one by pouring different amounts out of each of the other four. The ratio is worked out in the same way. Tube 1 is still the standard tube, because it contains the standard concentration.

6. It is very important to suggest that students use exponential notation in recording concentrations and in doing calculations in this experiment. Many will need help in getting started on the calculations, especially in those involving the determination of concentration.

CALCULATIONS. Those students who use exponential notation easily will have no difficulty in finding some constant numerical relationship; the others will need help. See the *Postlab Discussion* for suggestions that may be helpful while the calculations are being carried out.

SAMPLE DATA AND CALCULATION TABLE

Column

A. Initial concentration of Fe^{3}*(aq)* after one to one dilution.

B. Initial concentration of SCN^-*(aq)* after one to one dilution.

C. Ratio $= \dfrac{\text{depth in standard tube}}{\text{depth in nonstandard tube}}$ when the two are matched.

D. Equilibrium concentration of $FeSCN^{+2}$*(aq)* obtained by multiplying ratio (column C) by equilibrium conc. of $FeSCN^{+2}$*(aq)* in Tube 1.

E. Equilibrium concentration of Fe^{+3}*(aq)* obtained by subtracting equilibrium conc. of $FeSCN^{+2}$*(aq)* (column D) from initial conc. of Fe^{+3}*(aq)* (column A).

F. Equilibrium concentration of SCN/*(aq)* obtained by subtracting equilibrium conc. of $FeSCN^{+2}$*(aq)* (column D) from initial conc. of SCN^-*(aq)* (column B).

Tube No.	A *Initial* $[Fe^{+3}]$	B *Initial* $[SCN^-]$	C *Ratio*	D *Equ l.* $[FeSCN^{+2}]$	E *Equil.* $[Fe^{+3}]$	F *Equil.* $[SCN^-]$	*Calculations (as on Laboratory Manual p. 45)* (a)*	(b)	(c)
1	1×10^{-1}	1×10^{-3}	1.0	1.0×10^{-3}	9.9×10^{-2}	0			
2	4×10^{-2}	1×10^{-3}	0.92	9.2×10^{-4}	3.9×10^{-2}	8×10^{-5}	2.9×10^{-9}	0.45	290
3	1.6×10^{-2}	1×10^{-3}	0.81	8.1×10^{-4}	1.5×10^{-2}	1.9×10^{-4}	2.3×10^{-9}	0.064	280
4	6.4×10^{-3}	1×10^{-3}	0.66	6.6×10^{-4}	5.7×10^{-3}	3.4×10^{-4}	1.3×10^{-9}	0.011	340
5	2.6×10^{-3}	1×10^{-3}	0.46	4.6×10^{-4}	2.1×10^{-3}	5.4×10^{-4}	5.2×10^{-10}	0.0025	410
					Approximate ratio (largest/smallest)		5.4	170	1.5

* See p. 288 for an alternate calculation.

QUESTIONS

1. Which of the combinations of concentrations, (a), (b), or (c), gives the most constant numerical value? This form is known as the equilibrium constant expression.

   Answer: The most constant is the combination

$$\frac{[FeSCN^{+2}]}{[Fe^{+3}][SCN^-]}$$

   If the student has tried all other possible combinations, he will, of course, find that the reciprocal of this expression is also "equally" constant.

2. Restate this expression, in words, using the terms reactants and products.

   Answer: The equilibrium concentration of the substances formed, divided by the product of the equilibrium concentrations of the reactants, gives a constant. Or, since he will be reading the text at this time, he may say the *product* of the concentrations of the substances formed as well as the product of the concentrations of the reactants, even though in this situation only one substance is formed.

3. Give a possible explanation as to why such a relationship might exist.

Answer: It is hoped that the student will interpret this question to mean: "Why does dividing the concentration of products by the concentration of reactants give a constant?" Each reaction rate is dependent upon the concentration of *its* reactants; thus at equilibrium, when the rates of the opposing reactions are equal, dividing [products] by [reactants] gives a constant.

POSTLAB DISCUSSION. If the student works out the relationships suggested, he will have had no trouble seeing that one relationship certainly is more constant than the others, even though the matching of colors was not a very precise method. With the data summarized in the sample calculations, the values for

(a) $[Fe^{+3}][FeSCN^{+2}][SCN^-]$

(b) $\dfrac{[Fe^{+3}][FeSCN^{+2}]}{[SCN^-]}$

and

(c) $\dfrac{[FeSCN^{+2}]}{[Fe^{+3}][SCN^-]}$

have been included. There are, of course, other combinations.

Each student's data will show some variation, which may undermine confidence in the equilibrium concept. Here are three ways to combat such a loss of morale.

(1) Make use of the ratios of largest to smallest value calculated for each expression. Usually he will find values such as (a) ~5, (b) ~200, (c) ~1. Clearly, (c) is more nearly constant.
(2) Show Figure 9-1 as a sample of one set of actual data. Remind the student that he made each test only once and thus obtained little indication of central tendency.
(3) Make a plot like Figure 9-1 from your own class data. Use the median values of the different ratios to calculate a set of K's. Use this set as the most meaningful one—it is based on all the data collected.

The species present in the solutions are not necessarily the same at all concentrations, nor is the actual equilibrium constant known. Don't be concerned if there is considerable variation in constants; this is an "order of magnitude" experiment, not a precise determination. Students have reported K's between 100 and 700, although within a single class working under similar conditions, the spread is often smaller.

The assumption that the reaction is 100% in the standard tube is not correct. It may be about

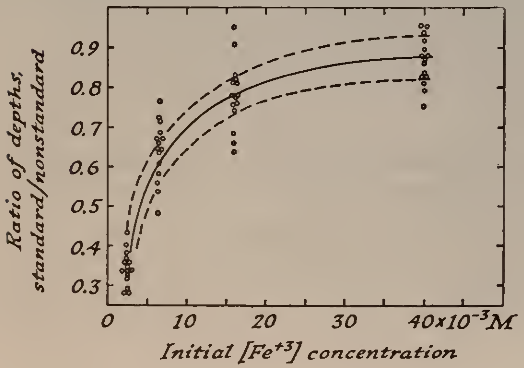


Fig. 9-1

Typical values for equilibrium concentration of $FeSCN^{+2}$ versus initial concentration of Fe^{+3}.

95%. The error thus introduced is greater in the first tube compared (tube 2) than in the succeeding tubes. The most significant measure may thus seem to be tube 5, but errors in dilution become greater for each succeeding tube. We may thus assume that the "best" values may be for tubes 3 and 4.

The more able and interested students seem inclined to follow up this experiment with more precise color comparisons in order to make the determination more reliable.

As an aid in developing the idea that concentration is squared, not doubled, when two of the same species appear in an equation, try the following procedure:

1. In Experiment 15 the student derives a simple K

$$\mathrm{Fe^{+3}}(aq) + \mathrm{SCN^{-}}(aq) \rightleftharpoons \mathrm{FeSCN^{+2}}(aq) \qquad K = \frac{[\mathrm{FeSCN^{-2}}]}{[\mathrm{Fe^{+3}}][\mathrm{SCN^{-}}]}$$

2. Ask what he would expect for some similar reaction, such as

$$\mathrm{H^{+}}(aq) + \mathrm{SO_4^{-2}}(aq) \rightleftharpoons \mathrm{HSO_4^{-}}(aq) \qquad K = \frac{[\mathrm{HSO_4^{-}}]}{[\mathrm{H^{+}}][\mathrm{SO_4^{-2}}]}$$

   Note the similarity to step 1—all species are ionic and appear once.

3. To lead the student away from the idea that only ionic reactions are to be considered, ask about another type, for instance

$$\mathrm{Ba}(g) + \mathrm{S}(g) \rightleftharpoons \mathrm{BaS}(g) \qquad K = \frac{[\mathrm{BaS}]}{[\mathrm{Ba}][\mathrm{S}]}$$

4. At this stage, ask for a general formula of this simple type

$$A + B \rightleftharpoons C \qquad K = \frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}$$

5. Now add a small complication.

$$\mathrm{Na^{+}}(aq) + \mathrm{H^{+}}(aq) + \mathrm{SO_4^{-2}}(aq) \rightleftharpoons \mathrm{NaHSO_4}(\text{in sol'n}) \qquad K = \frac{[\mathrm{NaHSO_4}]}{[\mathrm{Na^{+}}][\mathrm{H^{+}}][\mathrm{SO_4^{-2}}]}$$

   Note the relation to step 2.

6. Now (without fanfare) slip in the 2 factor by asking about

$$\mathrm{H^{+}}(aq) + \mathrm{H^{+}}(aq) + \mathrm{SO_4^{-2}}(aq) \rightleftharpoons \mathrm{H_2SO_4}(\text{in sol'n}) \qquad K = \frac{[\mathrm{H_2SO_4}]}{[\mathrm{H^{+}}][\mathrm{H^{+}}][\mathrm{SO_4^{-2}}]}$$

7. Rewrite step 6 making algebraic simplification

$$2\mathrm{H^{+}}(aq) + \mathrm{SO_4^{-2}}(aq) \rightleftharpoons \mathrm{H_2SO_4}(\text{in sol'n}) \qquad K = \frac{[\mathrm{H_2SO_4}]}{[\mathrm{H^{+}}]^2[\mathrm{SO_4^{-2}}]}$$

8. Generalize

$$2A + B \rightleftharpoons D \qquad K = \frac{[\mathrm{D}]}{[\mathrm{A}]^2[\mathrm{B}]}$$

9. Finally go to a completely general reaction when the class is ready

$$aA + bB \rightleftharpoons qQ + rR \qquad k = \frac{[Q]^q[R]^r}{[A]^a[B]^b}$$

At step 6 if someone asks why you don't use $2\mathrm{H^{+}}$ in the K expression, lead them to admit that this is adding concentrations. Point out that Experiment 15 showed that multiplication is applicable. Work in the idea that they are merely getting confused because two of the reacting species are the same.

ALTERNATE CALCULATION FOR EXPERIMENT 15. By making a slight change in the numerical relationships suggested to the student (p. 45 of Laboratory Manual) you can get the experimental answer for a point that often causes student confusion.

Change. Before the students make the calculations, change the triple product in 5(a) to the following:

$$\frac{[\mathrm{FeSCN}^{+2}]}{[\mathrm{Fe}^{+3}] + [\mathrm{SCN}^{-}]}$$

Advantage. This new wrong answer is slightly easier for the student but mainly it gives him the experimental answer to why you do not add concentration terms. Addition does not give a constant. Often students want to add, particularly when a species appears in the equation with a multiplier of two. Recall this form suggested above to remind them addition is not the proper operation. If you use this modification then one column of the sample data table will be different. Under (a) in the column third from the right, the values would be

Tube No.	(a)
1	
2	2.1×10^{-2}
3	4.1×10^{-2}
4	7.2×10^{-2}
5	7.8×10^{-2}
Approximate ratio (largest/smallest)	4

Supplementary Material

Articles

S. Z. Levin and R. S. Wagner, "The nature of iron(III) thiocyanate in solution," *J. Chem. Education*, 30, 445–450 (1953). This paper (useful for teachers) gives information about the nature of the compound in Expt. 15.

Books

1. B. H. Mahan, *Elementary Chemical Thermodynamics*, Benjamin, New York (1963). Good background reading for teachers.
2. L. K. Nash, *Elements of Chemical Thermodynamics*, Addison-Wesley, Reading, Mass., (1962). Good background reading for teachers.
3. J. A. Campbell, *Why Do Chemical Reactions Occur?*, Prentice-Hall, Englewood Cliffs (1964). Good supplementary reading for teachers and able students.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

EQUILIBRIUM — A CHEM Study film
Running Time: 24 minutes

This film was produced in collaboration with Dr. G. C. Pimentel and fits quite closely with the Textbook. Several Textbook figures are taken directly from it.

The film demonstrates through the use of radioactive tracers the constancy of macroscopic properties at equilibrium and the dynamic nature of the equilibrium state. Four examples are used, the property in parentheses becoming constant at equilibrium.

1. Population of gold fish in a pair of goldfish bowls connected by a tunnel (population).
2. Gas pressure of bromine gas between two gas bulbs (gas color and pressure).
3. Solubility of I_2 in an alcohol-water mixture (solution color).
4. Reaction of I_2 with water:

   $$3I_2 + 3H_2O = 5I^-(aq) + IO_3^-(aq) + 6H^+(aq)$$

   (solution color).

Next the dynamic nature of equilibrium is demonstrated by allowing equilibrium to be attained and then adding radioactive material. Though the "constant" properties do not change, the radioactive material steadily distributes itself throughout the system. *The conceptual meaning of the tracer experiment* is first illustrated with marked fish. Then, in each example, the dynamic nature is shown.

Background Discussion

The kinetic molecular model was introduced via the billiard ball model in Chapter 2. It has proved extremely useful for relating the material that has been developed in later chapters. We shall find also that the model provides an excellent basis for developing chemical equilibrium. The discussion in the text is presented in a descriptive, qualitative manner suitable for the understanding of the average high school chemistry student. But a deeper understanding of the model is best gained by applying quantitatively some of its predictions; i.e., by solving some problems based on the model. Some equations are presented and discussed in case you wish to do this. No effort is made to derive the equations rigorously because we do not wish to diminish the usefulness of this material.

You are not expected to teach this material as a part of the regular text matter. It is provided primarily as background for you. You may, however, extract selected background material to challenge your better students.

Most chemical reactions occur in a homogeneous phase, usually liquid. Reactions among gases normally are conducted in closed systems. Under such conditions reactants and products remain in the reaction zone. Although reactions in the liquid phase may be conducted in an open vessel, the reactants and products usually remain trapped in the liquid phase. Under such conditions the reaction products combine to reform the reactants; thus the reaction does not proceed to completion but achieves a state of equilibrium.

The chemist is concerned greatly with the extent of chemical reactions, for this knowledge permits him to predict whether a given reaction will be suitable for a specific purpose. Perhaps one of the most universal generalizations of chemistry is: all reactions tend to proceed to equilibrium. We say "tend to proceed" because, for most reactions to reach equilibrium, the necessary activation energy must first be applied. In Chapter 9 you will discuss how chemical equilibrium is achieved kinetically; how equilibrium constants are measured and computed; how equilibrium concentrations can be altered to increase the formation of a desired product; and how equilibrium constant data are used to compute yields.

Up to now you have implied that the driving force of a chemical reaction is the energy released by the reactants in achieving a state of lower energy, and the golf ball analogy (Sec. 9-2.4) supports this assumption. You know, however, that many reactions proceed spontaneously while absorbing energy. Apparently the direction of a chemical reaction is influenced by some factor other than the achievement of a lower energy state.

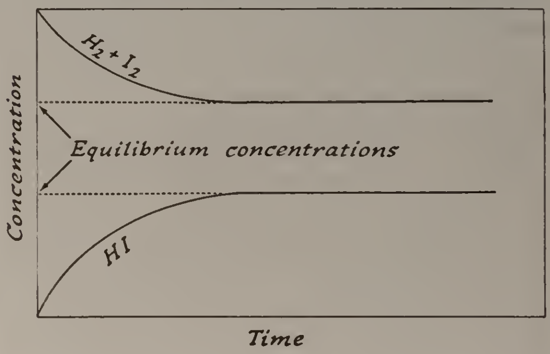
The following sections contain material on these topics:

Why do Reactions Attain Equilibrium?
The Equilibrium Constant
The Relationship between the Equilibrium Constant and Free Energy
The Effect of Some Factors on Equilibrium Constant
The Variation of the Equilibrium Constant with Temperature

WHY DO REACTIONS ATTAIN EQUILIBRIUM?

You may find a graphical representation of how a reaction achieves equilibrium a helpful aid in teaching the concept. An example of the form commonly employed is shown in Figure 9-2. Ob-

Fig. 9-2. **Concentration changes in a system approaching equilibrium. $H_2 + I_2 \rightleftarrows 2HI$**



serve that, at the time of mixing, the rate of formation of HI is quite large and that the rate of consumption of H_2 and I_2 is also large. It follows that the concentrations of H_2 and I_2 will decrease with time, whereas the concentration of HI will increase. Since rate of reaction depends upon the concentration of the reactants, we expect the rate of formation of HI to decrease with time. Furthermore, its rate of decomposition should increase. Since the two rates are in opposition, they must eventually become equal. The state in which the rate of the reverse reaction becomes equal to the rate of the forward reaction is defined as chemical equilibrium.

The student may experience difficulty understanding why products should re-form reactants. He may reason that if products are going to re-form reactants, why do the reactants combine in the first place. This is where you should suggest that the tendency to reach minimum energy is not the only factor that induces chemical reaction.

Normally one expects a reaction to proceed in the direction in which energy is released. If an isolated H_2 molecule reacted with an isolated I_2 molecule to form two isolated HI molecules—that is, two which never collided—the reaction might be completed in the direction of the formation of HI. In an actual reaction, however, moles of H_2 react with moles of I_2 to form moles of HI. This means that billions of billions of both reactant and product molecules are involved. Remember that, although the average energy state of H_2 and I_2 molecules is higher than the average energy state of two HI molecules, reaction does not occur between molecules in the average energy state but between those in an activated state.

THE EQUILIBRIUM CONSTANT

The previous discussion should make the qualitative nature of chemical equilibrium reasonably clear. Now you wish to go further and examine the quantitative aspects. Reaction rate equations are convenient vehicles for deriving equilibrium constant expressions, as is made clear in Sec. 9-2.3. Observe that K is a ratio of the rate constant for the forward reaction divided by the rate constant for the reverse reaction. It follows that K must be related to the basic tendency of the reactants to react. Its value tells the extent to which the reaction has proceeded at equilibrium. The equilibrium constant may be evaluated from a knowledge of the concentrations of the various chemical species at equilibrium.

The utility of the equilibrium constant expression lies in our ability to use it to predict the conditions that will produce a desired product and to calculate what yield can be expected. For example, the equilibrium constant expression (*15*), Textbook, p. 152, shows that, to obtain a large yield of HI, a high concentration of H_2 or of I_2 or of both should be used.

One of the great advantages of the equilibrium constant expression is its universality. It applies to all chemical reactions. The Textbook gave examples of some reactions to which the equilibrium constant expression applies in Table 9-IV, on p. 154. Other examples are listed here in Table 9-I. Observe that the concentrations of the species which are not changed appreciably during reaction are not included in the equilibrium constant expression. The constant concentrations are put "in with" K.

It is because chemical equilibrium is involved in the whole of chemistry that we devote so much time to it. The details of how to apply quantitatively the equilibria listed below are given in the references at the end of the chapter.

THE RELATIONSHIP BETWEEN THE EQUILIBRIUM CONSTANT AND FREE ENERGY

The equilibrium constant is a quantitative measure of the tendency of a reaction to proceed. The equilibrium constant expression can be used to compute the expected extent of reaction from reactants mixed at any initial set of concentration conditions. Because of its great importance, we should like to know the equilibrium constants for as many reactions as possible. From our discussion up to now, the only method of obtaining it consists in carrying out the reac-

Table 9-I. **Examples of the Application of the Equilibrium Constant**

Vapor Pressure	$H_2O(l) \rightleftharpoons H_2O(g)$	$[P_{H_2O}] = K_p$
Solubility	$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{-2}(aq)$	$[Ag^+]^2[CrO_4^{-2}] = K_{sp}$
Extraction	$I_2 \text{ (in } H_2O) \rightleftharpoons I_2 \text{ (in } CS_2)$	$\frac{[I_2 \text{ (in } CS_2)]}{[I_2 \text{ (in } H_2O)]} = K_{ext.}$
Gas Reaction	$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$	$\frac{[P_{H_2O}]^2[P_{Cl_2}]^2}{[P_{HCl}]^4[P_{O_2}]} = K$
Gas Dissociation	$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	$\frac{[P_{PCl_3}][P_{Cl_2}]}{[P_{PCl_5}]} = K_p$
Solid Dissociation	$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	$[P_{CO_2}] = K_p$
Acid Reaction	$H_2SO_3 + H_2O \rightleftharpoons 2H^+(aq) + SO_3^{-2}(aq)$	$\frac{[H^+]^2[SO_3^{-2}]}{[H_2SO_3]} = K_A$
Base Reaction	$NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	$\frac{[NH_4^+][OH^-]}{[NH_3]} = K_B$
Complex Ion Formation	$Cu(OH)_2(s) + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{+2}(aq) + 2OH^-(aq)$	$\frac{[Cu(NH_3)_4^{+2}][OH^-]^2}{[NH_3]^4} = K$
Oxidation-Reduction	$Fe^{+2} + Ce^{+4} \rightleftharpoons Fe^{+3} + Ce^{+3}$	$\frac{[Fe^{+3}][Ce^{+3}]}{[Fe^{+2}][Ce^{+4}]} = K$

tion and measuring the concentrations of the reactants and products at equilibrium. Such a procedure limits the availability of equilibrium constant data, for the equilibrium state of many reactions is difficult to obtain; moreover, it would be most convenient to be able to obtain the equilibrium constant without having to carry out the reaction.

Since the equilibrium constant is independent of the initial concentrations of the reactants—the latter always adjust to the proper equilibrium concentrations—the constant must represent a quantitative measure of the basic tendency of the reaction to proceed. We learned in Chapter 8 that the tendency of a reaction to go must be connected closely with the change in energy which the reactants undergo. Since energy changes often can be conveniently and precisely determined, a knowledge of the exact relationship between equilibrium constant and energy change would aid us materially in obtaining equilibrium constants. The remaining discussion in this section is designed to establish this relationship qualitatively.

In Chapters 7 and 8 we found that most reactions which proceeded readily, once the necessary activation energy was applied, were exothermic. It appears from this observation that the energy released in an exothermic reaction might be used as a measure of the tendency of the reaction to proceed. We know, however, that some reactions which liberate more heat proceed to a smaller extent than do other reactions that liberate less heat. To confuse the picture even more, some endothermic reactions proceed spontaneously. Examples given in Chapter 9 of the

Textbook were the evaporation of water and the dissolution of NH_4Cl in water. The real driving force of a chemical reaction appears to include the achievement of the state of greatest random distribution of energy; that is, the state of least restraint. The Textbook has referred to this kind of energy distribution as the randomness implied by the temperature. The property which measures the degree of randomness of energy distribution is called the *entropy*.

Thus, the reaction tendency is expressed as the competition, or balance, between two tendencies.

$$\begin{pmatrix}\text{Reaction}\\ \text{tendency}\end{pmatrix} = \begin{pmatrix}\text{Tendency}\\ \text{toward}\\ \text{minimum}\\ \text{energy}\end{pmatrix} - \begin{pmatrix}\text{Tendency}\\ \text{toward}\\ \text{maximum}\\ \text{randomness}\end{pmatrix}$$

You have already established that ΔH is a measure of the tendency toward minimum energy. The golf ball analogy hints at the random tendency, which is quantitatively expressed as $T\Delta S$ (temperature × change of entropy). The temperature factor indicates that a greater state of randomness can be achieved as the equilibrium system is heated.

$$\begin{pmatrix}\text{Reaction}\\ \text{tendency}\end{pmatrix} = \Delta H - T\Delta S$$

Net reaction stops when equilibrium is reached—our operational definition of equilibrium. This must mean that the reaction tendency, called free energy (ΔF), is zero. Thus at equilibrium

$$\Delta F = 0 = \Delta H - T\Delta S$$

Incidentally, ΔF, when different from zero, is equal to the maximum useful work that can be derived from the system as it changes toward equilibrium. Since the work must come *out of the system*, useful work is written $+w$. The system *loses* the work, and so ΔF must decrease in a process which can do useful work. Such a process is called spontaneous.

An important example occurs when only electrical work is done. Then $\Delta F = -nE^\circ F$, an equation which we will discuss in the guide for Chapter 12. This equation is the basis for an important way of measuring ΔF, and illustrates why chemists are concerned with E°.

A chemical reaction may be considered to be a process which, together with its surroundings, constitutes a system. In accordance with the analogy made above, ΔF can be used as a measure of the "driving force" of a chemical reaction. Free energy and work are connected: (a) $w = 0$, no work can be obtained, $\Delta F = 0$, the reaction must be at equilibrium; (b) w is positive, the system can do work, ΔF is negative, the reaction can proceed spontaneously; and (c) w is negative, no work can be obtained, ΔF is positive, energy must be supplied to induce the reaction. (The idea that a chemical reaction can do work is well illustrated by burning coal to drive a train.) The ability to use ΔF to predict whether a chemical reaction can proceed makes this one of the most powerful properties available to the chemist. In Chapter 7 you might have been tempted to teach, or at least to imply, that ΔH was a reasonable indication of whether a reaction could proceed spontaneously. You see now that ΔF is the proper guide to spontaneity. It is too complex, however, to present to the high school student. It is true that ΔF and ΔH are frequently close together (whenever $T\Delta S$ is small). Under these conditions ΔH may be taken as a good approximation of the tendency of a reaction to proceed. From the equation, we see also that when $T\Delta S$ is much larger than ΔH, ΔF can be negative even though ΔH is positive; in such cases endothermic reactions will proceed spontaneously. The science which relates energy of reactions and their tendency to proceed is called *thermodynamics*.

We have found that free energy is a measure of the driving force of a chemical reaction. We know that the tendency of a reaction to proceed depends upon the nature of the reactants and their concentrations. It follows that the free energy of a reaction must also depend upon the nature of the reactants and their concentrations. In mathematical terms we say the change in free energy of a reaction is a function of both the nature of the reactants and their concentrations:

$$\Delta F = f(N, C) \qquad (1)$$

where N refers to the nature of the reactants and C to their concentrations. The exact equation derived in thermodynamics and applied to the general reaction $aA + bB = eE + fF$ is

$$\Delta F = \Delta F^\circ + 2.3RT\log\frac{[E]^e[F]^f}{[A]^a[B]^b} \qquad (2)$$

Here ΔF°, called the change in standard free energy, is a constant which depends upon the nature of the reactants. The brackets are the symbol for concentration. We have seen above that the condition $\Delta F = 0$ defines a state of equilibrium; thus under equilibrium conditions equation (*2*) becomes

$$0 = \Delta F^\circ + 2.3RT\log\left(\frac{[E]^e[F]^f}{[A]^a[B]^b}\right)_{\text{eq.}} \qquad (3)$$

In the Textbook, equation (*18*) sets $\left(\frac{[E]^e[F]^f}{[A]^a[B]^b}\right)_{\text{eq.}}$ equal to the equilibrium constant K, thus equation (*2*) can be written

$$\Delta F^\circ = -2.3RT\log K \qquad (4)$$

The discussion in this section was designed to show qualitatively how equation (*4*) was obtained. One of the main uses of this equation is for computing equilibrium constants.

The standard free energy of reaction is usually computed from standard free energies of formation which have been measured and tabulated in books on physical chemistry. *The Handbook of Chemistry and Physics* contains comprehensive tables. The method may be illustrated by computing the equilibrium constant for the dissociation of HI at 25°C, equation (*12*), Textbook, p. 151.

$$\begin{array}{ccccc} 2\text{HI}(g) & \rightleftharpoons & \text{H}_2(g) & + & \text{I}_2(g) \\ 2(0.31) & & (0) & & (0) \end{array} \qquad (5)$$

The free energies of formation are written beneath the reactants. The standard free energy of reaction is ΔF°.

$$\Delta F^\circ = 0 + 0 - 2(0.31) = -0.62 \text{ kcal}$$

Substituting this value of ΔF°, along with the appropriate values of the other terms, yields

$$\begin{aligned} &-2(310 \text{ cal mole}^{-1}) \\ &\quad = (-2.30 \times 1.99 \text{ cal mole}^{-1}\text{ deg}^{-1})(298^\circ \log K) \end{aligned}$$

This equation is satisfied by $K = 2.85$. Observe that K, the equilibrium constant for the dissociation of HI, is much larger at room temperature than the value 1.835×10^{-2} at 698.6°K, given in Table 9-III of the Textbook.

We conclude that (a) HI becomes more stable as the temperature is increased and that (b) HI should be more than half decomposed at room temperature. Hence the reason that HI exists at all at room temperature must be because it decomposes so slowly that equilibrium is not readily achieved.

THE EFFECT OF SOME FACTORS ON EQUILIBRIUM CONSTANT

On p. 262 the simple Arrhenius equation is given as $k = Ae^{-\Delta H^\ddagger/RT}$. Now you can understand that a more correct version is

$$k = Ae^{-\Delta F^\ddagger/RT} = Ae^{-\Delta H^\ddagger/RT}e^{\Delta S^\ddagger/R}$$

For greater readability we write $\exp(-\Delta F^\ddagger/RT)$ instead of $e^{-\Delta F^\ddagger/RT}$, giving

$$\begin{aligned} k &= A\exp(-\Delta F^\ddagger/RT) \\ &= A\exp(-\Delta H^\ddagger/RT)\exp(\Delta S^\ddagger/R) \end{aligned}$$

We can use this equation to show the effect of temperature and catalyst on equilibrium constant. In the Textbook (p. 155) we show that

$$K = \frac{k_{\text{right}}}{k_{\text{left}}} = \frac{k_R}{k_L} = \frac{k_r}{k_l}$$

Let us examine the effect of a catalyst first. We have omitted the symbol $\ddagger$ from each Δ term, although an activated complex is intended, and have used lower case r and l to avoid confusion with R, the gas constant.

$$\begin{aligned} k_r &= \exp(-\Delta F_r/RT) \\ &= \exp(-\Delta H_r/RT)\exp(\Delta S_r/R) \end{aligned}$$

$$\begin{aligned} k_l &= \exp(-\Delta F_l/RT) \\ &= \exp(-\Delta H_l/RT)\exp(\Delta S_l/R) \end{aligned}$$

$$K = \frac{k_r}{k_l} = \frac{\exp(-\Delta H_r/RT)\exp(\Delta S_r/R)}{\exp(-\Delta H_l/RT)\exp(\Delta S_l/R)}$$

When a catalyst is added, *both* ΔH_r and ΔH_l are lowered by an amount ΔH_c, where the subscript c shows that a catalyst is present. The change in entropy, ΔS, is affected in a similar way because a new activated complex, with a different randomness, is involved. Then we write

$$\exp\left(\frac{-\Delta H_r}{RT}\right)\exp\left(\frac{\Delta H_c}{RT}\right)\exp\left(\frac{\Delta S_r}{R}\right)\exp\left(\frac{-\Delta S_c}{R}\right)$$

$$= \exp\left(\frac{-\Delta H_l}{RT}\right)\exp\left(\frac{\Delta H_c}{RT}\right)\exp\left(\frac{\Delta S_l}{R}\right)\exp\left(\frac{-\Delta S_c}{R}\right)$$

$$K_c = \frac{k_r}{k_l} = K\frac{\exp(\Delta H_c/RT)\exp(-\Delta S_c/R)}{\exp(\Delta H_c/RT)\exp(-\Delta S_c/R)} = K$$

The changed factors cancel out, and K is not altered.

For a change in temperature, start by writing

$$\Delta H_r = \Delta H_l + \Delta H$$

We can ignore the ΔS term in

$$K_T = \frac{k_r}{k_l} = \frac{\exp(-\Delta H_r/RT)}{\exp(-\Delta H_l/RT)}$$

$$= \frac{\exp(-\Delta H_l/RT)\exp(-\Delta H/RT)}{\exp(-\Delta H_l/RT)}$$

$$= \exp(-\Delta H/RT)$$

Thus when we change T to $(T + \Delta T)$ we obtain

$$K_{(T+\Delta T)} = \exp[-\Delta H/R(T + \Delta T)]$$

This is *not* equal to K_T.

THE VARIATION OF THE EQUILIBRIUM CONSTANT WITH TEMPERATURE

In the preceding section, we computed, using thermochemical data, the equilibrium constant for the dissociation of HI at room temperature as 2.85. In the Textbook, using experimental equilibrium concentrations measured at 698.6°K, we computed the equilibrium constant for the same reaction to be 1.835×10^{-2}. Can we compare the two computations? Clearly, we are asking whether equilibrium constants at one temperature can be computed from those measured at another temperature. We seek to know how equilibrium constants vary with temperature. One approach to this question is to differentiate equation (*4*) with respect to temperature. This yields

$$\frac{d\Delta F^\circ}{dT} = -2.3R\left(T\frac{d\log K}{dT} + \log K\right)$$

$$\frac{d\Delta F^\circ}{dT} = -2.3RT\frac{d\log K}{dT} - 2.3R\log K \qquad (6)$$

Multiplying by T gives

$$T\frac{d\Delta F^\circ}{dT} = -2.3RT^2\frac{d\log K}{dT} - 2.3RT\log K \qquad (7)$$

Combining this expression with equation (*4*) gives

$$T\frac{d\Delta F^\circ}{dT} = -2.3RT^2\frac{\log K}{dT} + \Delta F^\circ \qquad (8)$$

From thermodynamic theory,

$$T\frac{d\Delta F^\circ}{dT} = \Delta F^\circ - \Delta H^\circ,$$

thus

$$\Delta F^\circ - \Delta H^\circ = -2.3RT^2\frac{d\log K}{dT} + \Delta F^\circ$$

or

$$\frac{d\log K}{dT} = \frac{\Delta H^\circ}{2.3RT^2} \qquad (9)$$

Equation (*9*) defines the variation of the equilibrium constant with temperature. It is called van't Hoff's equation. Observe that if ΔH is positive (that is, if the reaction is endothermic), then the equilibrium constant will be greater at the higher temperature. In contrast, if ΔH is negative (that is, if the reaction is exothermic), then the equilibrium constant will be smaller at the higher temperature. This last rule applies in the dissociation of HI, which, at room temperature, is defined by the equation

$$2HI(g) = H_2(g) + I_2(g) + 12.4\text{ kcal}$$

You can use equation (*9*) to test the predictions regarding the variation of the equilibrium constant with temperature which you studied in the Textbook in relation to Le Chatelier's Principle.

Integrating equation (*9*) between two temperatures, with the assumption that ΔH is constant, gives

$$\log(K_2/K_1) = \frac{\Delta H^\circ}{2.30R}\left(\frac{T_2 - T_1}{T_2T_1}\right) \qquad (10)$$

Equation (*10*) can be used to compute K at one temperature from a knowledge of ΔH and K at another temperature. Unfortunately ΔH is not constant, as has been assumed, but may vary with temperature. It does remain sufficiently constant, however, over small temperature intervals, 50–100°, to permit the use of equation (*10*). A more complicated equation in which ΔH is expressed as a function of temperature must be used in computations involving two widely separated temperatures. More about this must be sought in the references.

Answers to Exercises and Problems

Ex. 9-1. Which of the following systems constitute steady state situations, and which are at equilibrium? For each, a constant property is indicated.

(a) An open pan of water is boiling on a stove. The temperature of the water is constant.
(b) A balloon contains air and a few drops of water. The pressure in the balloon is constant.
(c) An ant-hill follows its daily life. The population of the ant-hill is constant.

Answer

(a) Steady state; water is boiling away, and temperature will remain constant until the water is all gone.
(b) Equilibrium.
(c) Steady state; population is remaining constant, but matter (food and dead ants) are entering and leaving the system.

Ex. 9-2. Does Le Chatelier's Principle predict a change of equilibrium concentrations for the following reactions if the gas mixture is compressed? If so, does the change favor reactants or products?

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Answer

(a) Yes, reactant favored.
(b) No.
(c) Yes, product favored.

Ex. 9-3. For the last two experiments of Table 9-I, numbers 4 and 5, why is $[H_2] = [I_2]$? For experiment 1 what were the initial concentrations of H_2 and I_2 before the reaction occurred to form HI?

Answer

The last two entries have $[H_2] = [I_2]$ because the data come from an experiment in which HI was heated. Equation (*12*) shows that the decomposition gives equal quantities of H_2 and I_2. In experiment #1 we find initial concentrations by using equation (*12*) again. For each mole/liter of HI, we needed 0.5 mole/liter of H_2 and 0.5 mole/liter of I_2. Since, for both H_2 and I_2, the number of moles/liter reacting was

$$\frac{17.671 \times 10^{-3}}{2} = 8.835 \times 10^{-3}$$

we have

$$\text{initial } H_2 = (1.831 + 8.835) \times 10^{-3} \text{ mole/liter} = 10.666 \times 10^{-3} \text{ mole/liter}$$

$$\text{initial } I_2 = (3.129 + 8.835) \times 10^{-3} \text{ mole/liter} = 11.964 \times 10^{-3} \text{ mole/liter}$$

Ex. 9-4. If we assign the equilibrium constant K' to expression (20) and K to expression (21)

$$K' = \frac{[Cu^{+2}][Ag]^2}{[Ag^+]^2[Cu]} \qquad K = \frac{[Cu^{+2}]}{[Ag^+]^2}$$

show that

$$K = K' \frac{[Cu]}{[Ag]^2}$$

Answer

$$K' = \frac{[Cu^{+2}][Ag]^2}{[Ag^+]^2[Cu]}$$

Substituting

$$K = \frac{[Cu^{+2}]}{[Ag^+]^2}$$

into the expression for K' gives

$$K' = K \frac{[Ag]^2}{[Cu]}$$

Now, multiplying by $[Cu]/[Ag]^2$ gives

$$K = K' \frac{[Cu]}{[Ag]^2}$$

Ex. 9-5. Water has a density of one gram per milliliter. Calculate the concentration of water (expressed in moles per liter) in pure water. Now calculate the concentration of water in 0.10 M aqueous solution of acetic acid, CH_3COOH, assuming each molecule of CH_3COOH occupies the same volume as one molecule of H_2O.

Answer

1 liter = 1000 g
1 mole = 18 g

Thus, for pure H_2O,

$$\frac{1000 \text{ g/liter}}{18 \text{ g/mole}} = 55.5 \text{ moles/liter}$$

If the molecules of CH_3COOH and H_2O are assumed to have the same size, then 0.1 mole/liter CH_3COOH will replace 0.1 mole/liter H_2O. Thus 55.5 − 0.1 = 55.4 moles of H_2O will be present in 1 liter of 0.10 M CH_3COOH solution.

Pr. 1. Which of the following are equilibrium situations and which are steady state situations?

(a) A playing basketball team and the bench of reserves. The number of players "in the game" and the number "on the bench" are constant.
(b) The liquid mercury and mercury vapor in a thermometer. Temperature is constant.
(c) Grand Coulee dam and the lake behind it. Water level is constant, though a river flows into the lake.
(d) A well-fed lion in a cage. The lion's weight is constant.

Answer: (a) and (b) are equilibrium situations.

Answer

(a) Equilibrium. There is a fixed number of players (macroscopic property constant) at a time. As fast as new players enter the game, other players leave.
(b) Equilibrium. The system is closed, and temperature alone determines what fraction of molecules are in the liquid or gas phase. The vapor pressure of mercury is very low (about 0.001 mm at 25°C).
(c) Steady state. This open system has water flowing into the lake and being lost by evaporation and over the spillways.
(d) Steady state. Food comes in, and waste goes out. The cage only sounds like a closed system. Closed system means *no* loss or gain of matter.

Pr. 2. Which of the following are equilibrium situations and which are steady state situations?

(a) A block of wood floating on water.
(b) During the noon hour, the water fountain constantly has a line of ten persons.
(c) When a capillary tube is dipped in water, water rises in the capillary (because of surface tension) to a height h and remains constant there.
(d) The capillary system of (c) considered over such a long period that evaporation of water out the end of the capillary cannot be neglected.
(e) At a particular point in the reaction chamber of a jet engine, the gas composition (fuel, air, and products) is constant.

Answer

(a) Equilibrium. A balance exists between force of gravity and buoyancy.
(b) Steady state. People are entering at the rear of the line as fast as they are receiving drinks at the front of the line.
(c) Equilibrium. Though there is an exchange between water molecules in the capillary and those in the container, the height of the column in the capillary remains constant.
(d) Steady state. Though the height of the column remains constant over a long period, it is maintained by an inward flow of water at the bottom, from the container, and by an outward flow at the top, by evaporation.

Notice that this situation is not uncommon in chemistry. A system can be treated as an equilibrium situation for a short time even though it is changing slowly. For example, a mixture of H_2 and O_2 react at room temperature so slowly that pressure equilibrium can be assumed to exist for a period of weeks. Yet over a period of years, the pressure would drop.

(e) Steady state.

Pr. 3. What, specifically, is "equal" in a chemical reaction that has attained a state of equilibrium?

Answer

The rate at which products are being formed equals the rate at which they are being consumed in the reverse reaction. Of course, a similar statement applies to reactants.

Pr. 4. One drop of water may or may not establish a state of vapor pressure equilibrium when placed in a closed bottle. Explain.

Answer

Whether equilibrium is established depends upon the size of the bottle. In a small bottle at ordinary temperature and pressure, equilibrium could probably be established without evaporation of the entire drop. In a large bottle, however, the space above the drop might never become saturated with water vapor before the whole drop evaporated. Hence there would be no liquid present, and liquid-vapor equilibrium would not be reached.

Pr. 5. Why are chemical equilibria referred to as "dynamic"?

Answer

Chemical equilibria are referred to as "dynamic" because they are achieved by a balance between a forward and a reverse reaction. At equilibrium the two reactions are still going on, with the result that the chemicals on either side of the double arrow are being made as fast as they are being used. This might be contrasted to a static equilibrium; e.g., a book on a desk. The desk is pushing on the book and vice versa, but there is no exchange of position or conversion of one into the other.

Pr. 6. What do the following experiments (done at 25°C) show about the state of equilibrium?

(a) One liter of water is added, a few milliliters at a time, to a kilogram of salt which only partly dissolves.

(b) A large salt shaker containing one kilogram of salt is gradually emptied into one liter of water. The same amount of solid dissolves as in (a).

Answer

The state of equilibrium is fixed by temperature, and not by the order in which equilibrium is reached.

Pr. 7. The following chemical equation represents the reaction between hydrogen and chlorine to form hydrogen chloride:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + 44.0\text{ kcal}$$

(a) List four important pieces of information conveyed by this equation.

(b) What are three important areas of interest concerning this reaction for which no information is indicated?

Answer

(a) The equation tells us that:

(i) One mole H_2 reacts with 1 mole Cl_2 to yield 2 moles HCl (1 molecule H_2 + 1 molecule Cl_2 gives 2 molecules HCl).

(ii) The system is at equilibrium.

(iii) All reacting substances in the system are in the gaseous state.

(iv) The reaction is exothermic, liberating 44.0 kcal, or 22 kcal/mole, of $HCl(g)$ formed.

(v) The activation energy for the formation of HCl is less than that for its decomposition.

(b) The equation does not give a clue about:

(i) The equilibrium concentrations.

(ii) The rate at which equilibrium is reached.

(iii) The reaction mechanism.

Pr. 8. How does a catalyst affect the equilibrium conditions of a chemical system?

Answer

A catalyst has no effect upon the equilibrium conditions but affects only the rate at which such conditions are reached.

Pr. 9. In any discussion of chemical equilibrium, why are concentrations always expressed in moles, rather than in grams, per unit volume?

Answer

Moles express concentration in terms of the number of reacting particles. One mole of various reactants can be compared directly, since one mole of any reactant contains the same number of particles. One-gram portions of several reactants do not have an equal number of particles.

Pr. 10. If the phase change represented by

$$\text{heat} + H_2O(l) \rightleftharpoons H_2O(g)$$

has reached equilibrium in a closed system:

(a) What will be the effect of a reduction of volume, thus increasing the pressure?

(b) What will be the effect of an increase in temperature?

(c) What will be the effect of injecting some steam into the closed system, thus raising the pressure?

Answer

(a) The reverse reaction is favored. $H_2O(g)$ goes to $H_2O(l)$, reducing the volume to counteract increased pressure.

(b) Forward reaction favored. The $H_2O(l)$ goes to $H_2O(g)$, absorbing heat to counteract increased temperature.

(c) The reverse reaction is favored, just as in (a).

Pr. 11. Methanol (methyl alcohol) is made according to the following net equation:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) + \text{heat}$$

Predict the effect on equilibrium concentrations of an increase in:

(a) Temperature.
(b) Pressure. *Answer:* (a) Decreases CH_3OH.
(b) Increases CH_3OH.

Answer

(a) According to Le Chatelier's Principle, an increase in the temperature of a system at equilibrium will cause a change that tends to partially counteract the increased temperature. Hence some CH_3OH will decompose to CO and H_2, absorbing heat.

(b) Again, according to Le Chatelier's Principle, new equilibrium concentrations will form so as to partially undo the change imposed on the system. More CH_3OH will form if the pressure is increased. The formation of one mole (CH_3OH) from 3($CO + 2H_2$) will tend to reduce the pressure.

Pr. 12. Consider the reaction:

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g) + 27 \text{ kcal}$$

What effect would the following changes have on the equilibrium concentration of Cl_2? Give your reasons for each answer.

(a) Increasing the temperature of the reaction vessel.
(b) Decreasing the total pressure.
(c) Increasing the concentration of O_2.
(d) Increasing the volume of the reaction chamber.
(e) Adding a catalyst.

Answer

(a) The Cl_2 concentration decreases. Concentrations shift so as to absorb heat. This causes some Cl_2 to react with H_2O to form HCl and O_2, consuming Cl_2.

(b) Decreases. Concentrations shift so as to increase pressure. To do this, the products change to reactants in a mole ratio of 4/5. This consumes Cl_2.

(c) Increases. Concentrations shift so as to consume some of the added O_2, producing more Cl_2.

(d) Decreases. Pressure is reduced, hence the answer to (b) is applicable.

(e) No change. A catalyst changes the rate at which equilibrium concentrations are reached, but not the concentrations themselves.

Pr. 13. Write the equation for the dissociation of HI(*g*) into its elements.

(a) Will HI dissociate to a greater or a lesser extent as the temperature is increased? $\Delta H = -6.2$ kcal/mole HI(*g*).

(b) How many grams of iodine will result if at equilibrium 0.050 mole of HI has dissociated?

Answer

$$2HI(g) = I_2(g) + H_2(g) + 2(6.2) \text{ kcal}$$

(a) According to Le Chatelier's Principle, an increase in temperature of a system at equilibrium will lead to new equilibrium conditions, the attainment of which results in the absorption of heat. In the above reaction, heat is absorbed when HI(*g*) is formed, thus an increase in temperature will result in the formation of more HI(*g*). It will dissociate less.

(b) 0.050 mole of HI forms 0.025 mole of I_2.

$$(0.025 \text{ mole}) = (0.025 \text{ mole})(254 \text{ g/mole}) = 6.4 \pm 2\text{g}$$

Pr. 14. Consider two separate closed systems, each at equilibrium:

(a) HI and the elements from which it is formed,
(b) H_2S and the elements from which it is formed.

What would happen in each if the total pressure were increased? Assume conditions are such that all reactants and products are gases.

Answer

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Since the number of moles of reactants equals the number of moles of product, pressure will have no effect on equilibrium concentrations.

(b) $8H_2(g) + S_8(g) \rightleftharpoons 8H_2S(g)$

Since nine moles of reactants produce only eight moles of product, an increase in pressure will produce more $H_2S(g)$. Of course, at sufficiently high temperatures, $S_8(g)$ breaks apart, eventually to S(*g*), but the reaction between $H_2(g)$ and S(*g*) gives the same pressure effect.

Pr. 15. Each of the following systems has come to equilibrium. What would be the effect on the equilibrium concentration (increase, decrease, no change) of each substance in the system when the listed reagent is added?

Reaction	Added Reagent
(a) $C_2H_6(g) \rightleftharpoons H_2(g) + C_2H_4(g)$	$H_2(g)$
(b) $Cu^{+2}(aq) + 4NH_3(g) \rightleftharpoons Cu(NH_3)_4^{+2}(aq)$	$CuSO_4(s)$
(c) $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$	$AgCl(s)$
(d) $PbSO_4(s) + H^+(aq) \rightleftharpoons Pb^{+2}(aq) + HSO_4^-(aq)$	$Pb(NO_3)_2$ solution
(e) $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ + heat	heat

Answer: (a) C_2H_6 (increase); H_2 (increase); C_2H_4 (decrease).

Answer

(a) C_2H_6 (increase); H_2 (increase); C_2H_4 (decrease).

(b) Cu^{+2} (increase); NH_3 (decrease); $Cu(NH_3)_4^{+2}$ (increase).

(c) Ag^+ (no change); Cl^- (no change); AgCl (no change).

(d) $PbSO_4$ (increase); $H^+(aq)$ (increase); Pb^{+2} (increase); HSO_4^- (decrease).

(e) CO (increase); O_2 (increase); CO_2 (decrease).

Notice that an important point is made in this problem that deserves discussion. For example, in question (a), the addition of H_2 shifts the equilibrium so as to *partially* counteract the imposed change. Thus the equilibrium will shift to consume *some* of the added H_2 *but never all.* Hence there is a net *increase* in H_2 pressure, though not as much as there would have been had a new equilibrium not been established as predicted by Le Chatelier's Principle. The consumption of H_2 is shown, of course, in the decrease of C_2H_4 and in the increase of C_2H_6.

Pr. 16. Nitric oxide, NO, releases 13.5 kcal/mole when it reacts with oxygen to give nitrogen dioxide. Write the equation for this reaction and predict the effect of

(i) raising the temperature, and of

(ii) increasing the concentration of NO (at a fixed temperature) on:

(a) the equilibrium concentrations;

(b) the numerical value of the equilibrium constant;

(c) the speed of formation of NO_2.

Answer

$2NO + O_2 \rightleftharpoons 2NO_2$ $\Delta H = -27.0$ kcal

(a) (i) Since the reaction is exothermic, increasing temperature will favor greater concentration of NO and O_2 at equilibrium.

(ii) Increasing NO will favor an increase in the concentration of NO_2 and a decrease in O_2 at equilibrium.

(b) (i) The numerical value of K changes with temperature; since increasing the temperature favors reactants, it must lower the value of K.

(ii) Increasing the concentration of NO favors the forward reaction but does not alter the numerical value of K for a given reaction.

(c) (i) Increasing the temperature increases the rate of formation of NO_2.

(ii) Increasing the concentration of NO increases the rate of formation of NO_2.

Pr. 17. Given: $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) + 23$ kcal

(a) For this reaction, discuss the conditions that favor a high equilibrium concentration of SO_3.

(b) How many grams of oxygen gas are needed to form 1.00 gram of SO_3?

Answer: 0.200 gram of O_2.

Answer

(a) High pressure. All substances are gaseous, and there are $1\frac{1}{2}$ moles on the left compared to one mole on the right.
High concentration of SO_2 and/or oxygen.
Low temperature. Since this reaction is exothermic, lowering the temperature favors a greater equilibrium concentration of $SO_3(g)$, for this change produces heat to counteract the lowered temperature.

(b) One mole of SO_3 requires $\frac{1}{2}$ mole of O_2.

$$(1\text{ g }SO_3)\left(\frac{1.00}{80}\right) = 0.0125\text{ mole}$$

$$(0.0125\text{ mole})(\tfrac{1}{2})(32\text{ g }O_2/\text{mole}) = 0.200\text{ g }O_2$$

Pr. 18. Given:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (closed system)

At a fixed temperature, what effect would adding more $CaCO_3$ have on the concentration of CO_2 in the region above the solid phase? Explain.

Answer

None. The K for this reaction depends only upon the concentration of CO_2, as long as temperature does not change and as long as both $CaCO_3$ and CaO are present. It does not depend upon how much solid is present.

Pr. 19. Given:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \text{(closed system)}$$

at 450°C, $K = 50.0$ for the above reaction. What is the equilibrium constant of the reverse reaction at 450°C?

Answer

$$K = \frac{[HI]^2}{[H_2][I_2]} = 50.0 \text{ (forward reaction)}$$

$$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{50.0} = 0.02 \text{ (reverse reaction)}$$

Pr. 20. Write the expression indicating the equilibrium law relations for the following reactions.

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(b) $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$
(c) $Zn(s) + 2Ag^+(aq) \rightleftharpoons Zn^{+2}(aq) + 2Ag(s)$
(d) $PbI_2(s) \rightleftharpoons Pb^{+2}(aq) + 2I^-(aq)$
(e) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

Answer

(a) $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$
(b) $K = \dfrac{[CO_2][NO]}{[NO_2][CO]}$
(c) $K = \dfrac{[Zn^{+2}]}{[Ag^+]^2}$
(d) $K = [Pb^{+2}][I^-]^2$
(e) $K = \dfrac{[HCN][OH^-]}{[CN^-]}$

Pr. 21. Equilibrium constants are given for several systems below. In which case does the reaction as written occur to the greatest extent?

Reaction	K
(a) $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$	1.8×10^{-5}
(b) $CdS(s) \rightleftharpoons Cd^{+2}(aq) + S^{-2}(aq)$	7.1×10^{-28}
(c) $H^+(aq) + HS^-(aq) \rightleftharpoons H_2S(aq)$	1×10^7

Answer

Only in reaction (c) is the K greater than 1, and hence this reaction occurs to the greatest extent. Such a large K indicates a considerable concentration of products as compared to reactants at equilibrium. All the other K's given indicate that product concentrations are much less than reactant concentrations at equilibrium.

Pr. 22. In the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

at 448°C the partial pressures of the gas at equilibrium are as follows:

$[HI] = 4 \times 10^{-3}$ atm;
$[H_2] = 7.5 \times 10^{-3}$ atm;
$[I_2] = 4.3 \times 10^{-5}$ atm.

What is the equilibrium constant for this reaction?

Answer

$$K_p = \frac{(7.5 \times 10^{-3})(4.3 \times 10^{-5})}{(4 \times 10^{-3})^2} = 0.02 = 2 \times 10^{-2}$$

Pr. 23. Reactants A and B are mixed, each at a concentration of 0.80 mole/liter. They react slowly, producing C and D: $A + B \rightleftharpoons C + D$. When equilibrium is reached, the concentration of C is measured and found to be 0.60 mole/liter. Calculate the value of the equilibrium constant.

Answer: $K = 9.0$.

Answer

$$K = \frac{[C][D]}{[A][B]}$$

$[C] = 0.60$ mole/liter $= [D]$
$[A] = 0.80 - 0.60 = 0.20$ mole/liter
$[B] = 0.80 - 0.60 = 0.20$ mole/liter

$$K = \frac{[0.60][0.60]}{[0.20][0.20]} = 9.0$$

Pr. 24. The water gas reaction

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

was carried out at 900°C with the following results:

Trial No.	Partial pressure at equilibrium, atm			
	CO	H_2O	CO_2	H_2
1	0.352	0.352	0.648	0.148
2	0.266	0.266	0.234	0.234
3	0.186	0.686	0.314	0.314

(a) Write the equilibrium constant expression.
(b) Verify that the expression in (a) is a constant, using the data given.

Answer

(a) $K = \dfrac{[CO][H_2O]}{[CO_2][H_2]}$

(b) Trial 1; $K = 1.291$.
Trial 2; $K = 1.290$.
Trial 3; $K = 1.293$.
To the significant figures consistent with the data, these are all equal to 1.29.

Pr. 25. Select from each of the following pairs the more random system.

a	A brand new deck of cards arranged according to suit and number.
a′	The same deck of cards after shuffling.
b	A box full of sugar cubes.
b′	Sugar cubes thrown on the floc..
c	A hay stack.
c′	Stacked fire wood.

Answer

a′ is more random than a.
b′ is more random than b.
c is more random than c′.

Pr. 26. For each of the following reactions, state:

(i) whether the tendency toward minimum energy favors reactants or products;
(ii) whether the tendency toward maximum randomness favors reactants or products.
(a) $H_2O(l) \rightleftharpoons H_2O(s) \quad \Delta H = -1.4$ kcal
(b) $H_2O(l) \rightleftharpoons H_2O(g) \quad \Delta H = +10$ kcal
(c) $CaCO_3(s) + 43\text{ kcal} \rightleftharpoons CaO(s) + CO_2(g)$
(d) $I_2(s) + 1.6\text{ kcal} \rightleftharpoons I_2$ (in alcohol)
(e) $4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s) + 400$ kcal

Answer

(a) (i) Product;
(ii) reactant.
(b) (i) Reactant;
(ii) product.
(c) (i) Reactants;
(ii) products (because of randomness of gas).
(d) (i) Reactant;
(ii) product (because of randomness of solution).
(e) (i) Products;
(ii) reactants (because of randomness of gas).

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1–7 are based on the following reaction, which takes place in a closed container in the presence of a suitable catalyst.

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad \Delta H = -23 \text{ kcal/mole } SO_2$$

1. How does the rate of the forward reaction compare to the rate of the reverse reaction at equilibrium?

   Answer: They are the same.

2. What is the effect of adding some additional $SO_2(g)$ after the system has reached equilibrium?

   Answer
   The addition of more $SO_2(g)$ destroys the existing equilibrium, causing the system to change; the $SO_3(g)$ concentration is increased, and the $O_2(g)$ concentration is decreased until a new equilibrium is established.

3. If the pressure of the system is increased by reducing the volume (temperature and amounts of gases remaining constant) the pressure of each component goes up. How will the equilibrium shift, and what further effect will this have on the $SO_3(g)$ concentration? Why?

   Answer
   The $SO_3(g)$ concentration would be still higher after the new equilibrium is established. According to Le Chatelier's Principle, the system will shift to compensate for the disturbing factor. In this situation, increasing the pressure favors the reaction which tends to reduce the pressure. Relatively speaking, there are $1\frac{1}{2}$ volumes of reactants to one volume of product. The formation of more $SO_3(g)$ would have the effect of relieving some of the added pressure but increases the $SO_3(g)$ pressure still more.

4. What effect should increasing the temperature have on this reaction if pressure remains constant?

   Answer
   Since the reaction producing $SO_3(g)$ is exothermic; an increase in temperature should cause a new equilibrium, with more $SO_2(g)$ and $O_2(g)$ present at equilibrium than before.

5. What effect does a catalyst have on the rate of the forward reaction?

   Answer
   A catalyst increases the rate of the forward reaction.

6. What effect does a catalyst have on the rate of the reverse reaction?

   Answer
   A catalyst increases the rate of the reverse reaction.

7. Compare the equilibrium concentration of $SO_3(g)$ without a catalyst to the equilibrium concentration of $SO_3(g)$ with a catalyst. Explain.

   Answer
   They are the same. The presence of a catalyst increases the rates of reaction but does not alter the equilibrium concentrations.

8. Write the equilibrium law relations for the following reactions.

   (a) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$

   (b) $4Al(s) + 3O_2(g) \rightleftharpoons 2Al_2O_3(s)$

   Answer

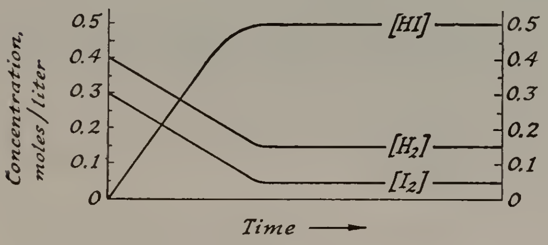
   (a) $K = \dfrac{[CO_2][H_2O]^2}{[CH_4][O_2]^2}$

   (b) $K = \dfrac{1}{[O_2]^3}$

9. A large number of pennies is arranged with each coin heads-up in a box. The box is closed and shaken. Predict what will be found when the box is opened. Explain.

Answer
Many coins will show tails when the box is opened. The tendency toward maximum randomness favors a disorderly arrangement, and the various arrays have about the same energy requirements.

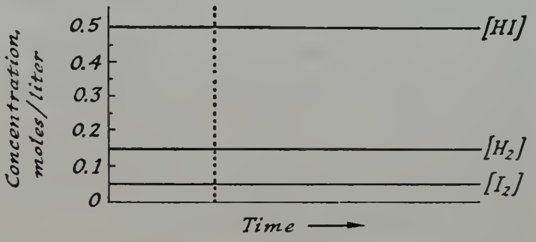
Questions 10–14 relate to the following diagram, which shows how the concentration of each of the products and reactants changes [$H_2(g) + I_2(g) = 2HI(g) + 3.0$ kcal] as the reaction proceeds until equilibrium is finally established for temperature T_1 and pressure P_1.



For each of questions 10–12, choose, from the descriptions I–V, those which best describe the chart represented in each question. In each case the system is initially at equilibrium, but at the time marked by the broken line some change in condition is made.

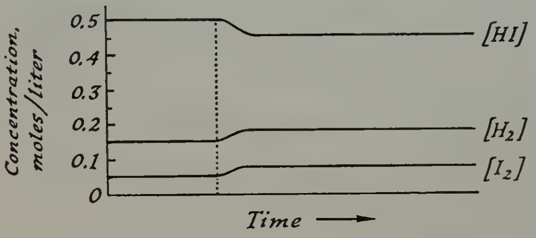
I. The temperature is increased to T_2 while the pressure is maintained at P_1.
II. The temperature is increased to T_2, and the pressure is increased to P_2 by adding an inert gas.
III. H_2 is added to the system (T_1 and P_1 maintained).
IV. The total pressure is increased to P_2 by adding an inert gas while the temperature is maintained at T_1.
V. A catalyst is added to the system with all other factors remaining constant.

10.



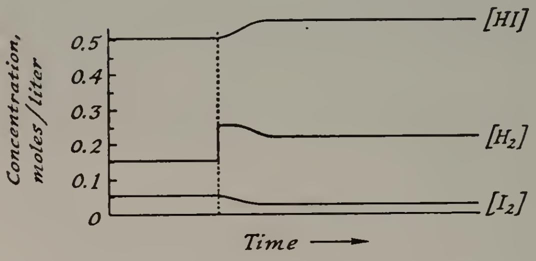
Answer: IV and V.

11.



Answer: I and II.

12.



Answer: III.

13. Which of the following will change the value of the equilibrium constant for the reaction between $H_2(g)$ and $I_2(g)$?

(1) Adding a catalyst;
(2) Increasing the pressure (temperature constant);
(3) Increasing the temperature;
(4) Increasing the concentration of the reactants;
(5) Increasing the concentration of the products.

Answer: (3).

14. Calculate the value of the equilibrium constant for the reaction. Use the equi-

librium concentrations given in the first chart.

Answer

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(5 \times 10^{-1})^2}{(0.15)(0.05)} = 33$$

15. What weight of HI(*g*) is formed in a mixture of 0.10 mole of $H_2(g)$ and 0.20 mole of $I_2(g)$? Temperature and pressure are such that 20% of the H_2 is converted into HI.

Answer

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The equation shows that H_2 and I_2 react in the molar ratio of 1/1.

Moles of H_2 reacting = (0.10)(0.20) = 0.02

Moles of HI formed

$$= (0.02 \text{ mole } H_2)\left(\frac{2 \text{ moles HI}}{1 \text{ mole } H_2}\right) = 0.04$$

$$(0.04 \text{ mole HI})\left(128 \frac{\text{g}}{\text{mole HI}}\right)$$

$$= 5.12 \text{ g HI or } 5.1 \text{ g}$$

CHAPTER

10

SOLUBILITY EQUILIBRIA

Intent and Approach

There are two lines of approach in this chapter. One consists in stressing the individual character of ions. That is, they are not "almost like" their parent element, with just a charge to distinguish them. They are entirely separate chemical species. And as such their properties are not dependent upon the source compound. The other approach consists in making an immediate application of the equilibrium law to problems of a practical kind. The student can see the importance of the questions "How much dissolves?" and "Will a precipitate form, or will it dissolve?"

This chapter provides a general survey of ionic reactions and how their behavior can be predicted. The major goals of the chapter include:

1. Applying the equilibrium constant to solubility reactions (K_{sp}).
2. Establishing the concept of ions as separate chemical species whose behavior is entirely independent of the source of the ion.
3. Contrasting the solubility of molecular and ionic solids.

After studying this chapter, the student should be able to write the equilibrium expression for any reaction and be able to decide whether a precipitate will form by using a trial ion product. For the simpler *AB* case he should be able to calculate the solubility in pure water.

Outline

1. The dissolving of a molecular crystal (iodine) is used to illustrate the dynamic nature of solubility equilibria (10-1.1). The two opposing rates are discussed (10-1.2).
2. The opposing effects of the tendencies toward maximum randomness and minimum energy are used to explain the solubility of a solid in different solvents (10-1.3) and of two gases in water (10-1.4).
3. The formation of electrolytes is related to the periodic table (10-2.1).
4. General solubility rules are given for a number of compounds in water. These rules are related to the periodic table (10-2.2).
5. Quantitative solubility calculations are introduced in Sec. 10-2.3 and expanded in Secs. 10-2.4 and 10-2.5. The equilibrium constant for such a reaction is called the solubility product, K_{sp}.

New Concepts

1. Ions are separate chemical species whose behavior is independent of the ion's source.
2. Solubility rules can be used to predict the occurrence of some chemical reactions.
3. Quantitative calculations of solubility are based on equilibrium constant.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
Review Expts. 11 and 12 S 10-1/10-1.2 (pp. 163–165)	1	Discussion		1	2		Solubility as an equilibrium process
S 10-1.3/10-2 (pp. 165–169) Start Expt. 16	2	Discussion Expt. 16	1–2		3	4	Factors affecting solubility
End Expt. 16 S 10-2.1/10-2.2 (pp. 169–173)	3	Discussion	3–5	5, 6, 9–**11**	7, 12, **13**, **16**	8,* 14, 15	Qualitative view of solubility
S 10-2.3/10-2.6 (pp. 173–176)	4	Discuss Expt. 16 and S 10-2.1/10-2.6	6–10		17, 19, 22, 23	18, **20**, 21	Quantitative view, K_{sp}
Review	5	Work Problems			26, 27	24, 25	
	6	Test on Ch. 8–10					

Note: Experiments 17 and 18 (Chapter 11) require advance preparation.

* Boldface indicates problems whose answers are given in the Textbook.

Development

SOLUBILITY: A CASE OF EQUILIBRIUM (10-1)

The Solubility of Iodine in Ethyl Alcohol (10-1.1)

The Dynamic Nature of Solubility Equilibrium (10-1.2)

These sections are to focus the student's attention on the equilibrium reactions which determine the solubility. The material is not new, but constitutes a review of the principles presented in the film EQUILIBRIUM, restated specifically for dissolving. Section 10-1.2 also contains a fuller explanation about why the "concentration" of a solid does not appear in the expression for K (see equations (*7*) and (*8*) in the Textbook). Through this review, a sharper contrast is made between the properties of aqueous ionic and molecular solutions.

The Factors That Fix Solubility of a Solid (10-1.3)

Solubility of a Gas in a Liquid (10-1.4)

These sections represent specific application of the ideas of energy and randomness discussed in Chapters 7 and 9. For your purposes the material in *The Relationship between the Equilibrium Constant and Free Energy* (p. 292) is useful.

It is important to choose your words carefully in explaining these sections. Trouble comes from two sources. First, the names for the opposing factors—maximum randomness and minimum energy—can be confused, and the two adjectives need to be used with precision. The second source of difficulty is that these opposing tendencies have opposite effects on the solubility of gases and on the solubility of solids. Note that *a system always establishes equilibrium in the same way—by tending toward maximum randomness and minimum energy*. This universal regularity should be stressed in order that specific cases can be considered with the regularity as a firm basis.

In discussing Sec. 10-1.3, under *The Effect of Temperature* (Textbook, p. 165), help the student avoid making the wrong interpretation—that a rise in temperature *always* favors solution. The first sentence specifies that higher temperature *always* favors "the more random state." This remark applies to the entire system, with solid plus solvent as one state and solution (or solid plus solution as the other).

AQUEOUS SOLUTIONS (10-2)

Expt. 16, DETERMINATION OF THE SOLUBILITY PRODUCT CONSTANT OF SILVER ACETATE, $AgCH_3COO$,
fits here. See p. 315 for guide.

Types of Compounds That Are Electrolytes (10-2.1)

An important concept to stress here is that the ion is a separate chemical entity. Emphasize that its properties differ completely from those of the materials from which it comes. This can be related to the use of Ba^{+2} (from several sources) as a test for SO_4^{-2}, or of Ag^+ for Cl^-. This point can be quickly and effectively made by demonstrating a few precipitations.

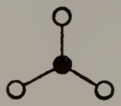
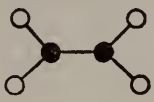
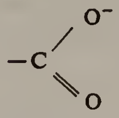
Teachers who have struggled in the past with the attempt to make somewhat fine distinctions between the terms ionization and dissociation will appreciate the emphasis on the two major ways in which ions in solution can and do arise. This has been done without introducing new and unnecessary terms at this point.

It is sometimes (erroneously) concluded that a substance which forms an ionic solution in water also forms an ionic solid. The HCl example is given specifically to show this isn't true. You can rely fairly well on the converse, however; an ionic solid will form an ionic solution.

This is probably a good place to discuss polyatomic ions. Describe one as a charged group of atoms which remain together. They can carry either a positive or negative charge, and the student has seen a number of examples already. The most common are listed below, together with their shapes. The student isn't ready for much information on bonding or structures yet.

the twenty most common metals, the table correlates the behavior of over 200 compounds. In Expt. 11 the student observed only 6 (or 12) compounds. Emphasize that this is an example of the usefulness of a generalization. The figures show how the solubilities of several common anions are related to the periodic table.

POLYATOMIC IONS

ION	BONDING FORMULA	SHAPE
OH^-, CN^-		linear
SCN^-		linear
NO_3^-, CO_3^{-2}		planar, equilateral triangle
H_3O^+		presumed to be pyramidal
SO_4^{-2}, PO_4^{-3} ClO_4^-, NH_4^+		tetrahedral
$(OOCCOO)^{-2}$ oxalate ion		each  is a planar, equilateral triangle

A Qualitative View of Aqueous Solubilities (10-2.2)

This material should be presented as the result of many experiments such as Expt. 11. Solubility rules are not mysterious laws to memorize, but provide a convenient way to express a multitude of experiments. For instance, Textbook Table 10-I, if applied to all the metallic elements (roughly 80), gives a guide to the solubility of about 900 compounds. Even if we consider only

The Equilibrium Law (10-2.3)

Calculation of the Solubility of Cuprous Chloride in Water (10-2.4)

Present the solubility product constant as simply a special name for the equilibrium constant of one particular reaction—a slightly soluble material dissolving in an ionizing solvent. Most students flounder on the next step—finding the concentration of ions to substitute in the K_{sp} expression. Emphasize, therefore, that every problem, to be workable, must contain enough information to permit calculation of the moles/liter for each ion. Of course, in some problems ("What is the solubility of AgCl if the $K_{sp} = 1.7 \times 10^{-10}$?") the whole point is to calculate the moles/liter from the solubility product constant. Practice is valuable here, hence you should assign several problems and work examples in class.

Although the point is a small one, we suggest that you avoid using the letter x as a symbol. It can be confused with the multiplication sign, especially in equilibrium problems, where exponential notation is often used, such as 1×10^{-3}. Use y, s, or the symbol for the ion concentration, e.g., $[Cl^-]$.

The units have been omitted from K_{sp} values. This is commonly done and should cause no confusion. They are always derived from ion concentrations in moles/liter.

Students often find it hard to develop the proper appreciation for solubility equilibria. You can use the experimental approach to prevent them from considering the problems in this chapter mere exercises in arithmetic. A series of test tube experiments will suffice. The following demonstration is an example.

Add two volumes of 1 M $AgNO_3$ to one volume of 1 M K_2CrO_4, shake, and let settle. Decant a small portion of the supernatant liquid, and add a few drops of 1 M KCl to it. The white precipitate shows that chromate ions did not precipitate silver ions completely from solution. It follows also that a smaller concentration of Ag^+ is required to precipitate AgCl than is required to precipitate Ag_2CrO_4. The idea can be reinforced by adding a few drops of 1 M $AgNO_3$ to a solution which is 1 M with respect to both HCl and K_2CrO_4; AgCl will precipitate first. Another variation of the experiment is to precipitate Ag_2CrO_4 and then add HCl to the resulting mixture. Continued addition of HCl will cause yellow Ag_2CrO_4 to dissolve and white AgCl to precipitate. Experiments of this kind will convince the student that an equilibrium exists between a precipitate and its dissolved ions. See the *Supplementary Materials* section for another example.

After you have established that an equilibrium exists between a precipitate and its dissolved ions, you will want to demonstrate the reciprocal relation between the concentrations of the ions in solution. The goal is to be sure that the student understands how a change in the concentration of one ion will affect the concentration of another ion. To illustrate this relationship prepare a saturated solution of AgCl. Decant two portions of the clear liquid. Add a few drops of 1 M HCl to one, and a few drops of 1 M $AgNO_3$ to the other. The cloudiness produced in each portion shows that the solubility of AgCl can be decreased by adding either Ag^+ or Cl^-. It follows from the discussion above that for a reaction defined by the equation

$$MA = M^+(aq) + A^-(aq) \qquad (1)$$

and represented by the equilibrium constant expression

$$[M^+][A^-] = K_{sp} \qquad (2)$$

a high concentration of one common ion requires a small concentration of the other. That the product of the two concentrations should be a constant is no longer surprising.

Will a Precipitate Form? (10-2.5)

The student should also understand how to use the K_{sp} to decide whether a precipitate will form in a particular mixture. Keep the terms "solubility product" (the equilibrium value of concentration product) separate from "ion product" (just the product of ion concentrations as they would exist if nothing happened). The ion product comes straight from the stated problem, and the prediction follows from a comparison of the ion product with the K_{sp}.

EXPERIMENT 16 DETERMINATION OF THE SOLUBILITY PRODUCT CONSTANT OF SILVER ACETATE, $AgCH_3COO$

PURPOSE. To determine a solubility product constant experimentally, as an introduction to solubility equilibria.

PRELAB DISCUSSION. The three solutions should be clearly marked as to method of preparation, and the marking should be made clear to students before the experiment is started. In each solution, excess solid should be clearly visible in the bottom of the stock bottle; the amount of this excess solid will vary from bottle to bottle. Remind the student that the method is similar to that used in Expt. 7.

TIMING. Do this experiment early in Chapter 10, before assigning a discussion of Sec. 10-2.3.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

100 ml of solution I, II, or III (lab hint 1)
20 cm copper wire (B and S #16)
acetone rinse bath
emery cloth or steel wool
wash bottle
100 ml graduate (lab hint 2)
250 ml beaker
balance (±0.01 g)

TIME REQUIRED. This experiment will require twenty minutes from each of two classes. Procedures *a–c*, first period; *d–e*, second period.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. Prepare three saturated solutions of silver acetate from different starting concentrations. Make them a few days before use.

   Make solution I by using 16 grams of silver acetate for each liter to be prepared. The silver acetate may either be purchased or prepared in the lab. Warm the solution to 40°C until *almost all* the solid has dissolved (solubility at 40°C is 14.1 grams/liter). A supersaturated solution may form unless some solid is present as the solution cools to room temperature. For each liter of solutions II and III, mix 500 ml of each component, made as follows:

Solution	$AgNO_3$	*g/500 ml*	$NaCH_3COO$	*(anhydrous) g/500 ml*	*or*	*(trihydrate) g/500 ml*
II	0.2 *M*	17	0.2 *M*	8.2		13.6
III	0.3 *M*	25.5	0.3 *M*	12.3		20.4

   If no solid forms, seed the solution with a small crystal of silver acetate. Do not heat.

   The solutions should be prepared in large enough quantity to provide each student with a 100 ml sample of one of the three. The samples may be easily dispensed by using a siphon arrangement with the pickup tube well above the solid phase, in order that the student will obtain a sample free of any solid.

   The solubility curve for silver acetate is quite steep (1.21 grams/100 ml at 30°; 1.04 grams/100 ml at 20°), hence all solutions should be at the same temperature if students are going to compare results.

Solubility also increases as the concentration of $Na^+(aq)$ and $NO_3^-(aq)$ is increased. This may be evident in solutions II and III. The solubility product is apparently not well known and is listed in various sources as being in the range 2×10^{-3} to 6×10^{-3} (about room temperature).

If you wish to have closer agreement of the solubility product constants from the three solutions you may reduce the concentrations of II and III somewhat in order that there will be less $Na^+(aq)$ and $NO_3^-(aq)$, but a supersaturated solution may result during preparation.

Still closer agreement is possible if all the students obtain the K_{sp} from a single solution (for example, Solution I), but this defeats part of the purpose of the experiment. See the answer under Calculation 5.

2. A clean 100 ml graduate may be placed next to each of the three solutions for the student's use in order that each will not need to have a 100 ml graduate in his desk.
3. You may wish to provide an alternate experiment for more capable students. Solutions containing an excess of one ion may be supplied in addition to the three described in detail above.
4. The silver can be washed and reclaimed by dissolving it in the appropriate amount of 6 *M* HNO_3. If it is to be used in Expt. 7, the H^+ concentration must be low enough in the final solution so that $Cu(s)$ will not react with HNO_3 to produce NO. It is perhaps better to crystallize $AgNO_3(s)$ from the solution after partial evaporation. Alternatively, AgCl may be precipitated for use in Expt. 2 or 25.

CALCULATIONS. Sample data included here are averages from a 1962 trial school.

1. Calculate the number of moles of $Cu(s)$ which reacted with the silver ions.

Answer

$$\text{Moles Cu}(s) = \frac{\text{g Cu}(s)\text{ reacted}}{63.5\text{ g/mole}}$$

	Solutions Tested		
	I	*II*	*III*
Wt of Cu reacting	0.20 ± 0.02 g	0.22 ± 0.02 g	0.23 ± 0.02 g
Moles of $Cu(s)$	$3.2 \times 10^{-3} \pm 10\%$	$3.5 \times 10^{-3} \pm 10\%$	$3.6 \times 10^{-3} \pm 10\%$

2. Recalling the relationship between $Ag^+(aq)$ and $Cu(s)$ obtained in Experiment 7, how many moles of silver ions, $Ag^+(aq)$, were present in the 100 ml sample? What is the concentration of the silver ions in moles per liter?

Answer

$$\text{Moles Ag}^+ = 2(\text{moles Cu}(s)\text{ reacted})$$

	Solutions Tested		
	I	*II*	*III*
moles $Ag^+(aq)$/100 ml	$6.4 \times 10^{-3} \pm 10\%$	$7.0 \times 10^{-3} \pm 10\%$	$7.2 \times 10^{-3} \pm 10\%$
moles/liter	$6.4 \times 10^{-2} \pm 10\%$	$7.0 \times 10^{-2} \pm 10\%$	$7.2 \times 10^{-2} \pm 10\%$

3. What is the concentration of the acetate ions also present, expressed in moles per liter?

   Answer: Since Ag^+ and CH_3COO^- react in a molar ratio of 1/1 to form $AgCH_3COO(s)$, and since the initial molar concentrations of each of these ions were equal as they were mixed to form the saturated solution, the concentration of the acetate ions will be the same as for the silver ions.

4. Calculate the value of the K_{sp} for silver acetate at room temperature.

   Answer

$$K_{sp} = [Ag^+][CH_3COO^-]$$

	Solutions Tested		
		II	*III*
K_{sp}	$(4.1 \pm 0.8) \times 10^{-3}$	$(4.9 \pm 1.0) \times 10^{-3}$	$(5.2 \pm 1.0) \times 10^{-3}$

5. Compare your results with those of other students who used the other saturated solutions of silver acetate which contained different amounts of the solid, $AgCH_3COO(s)$. What do you conclude about the comparative results?

   Answer: The K_{sp} is generally constant for the three solutions. There may be some difficulty here if the solutions are not prepared carefully and if the experiment is not done carefully, *or* if the K_{sp} is listed without the rather large uncertainty. Since the K_{sp} is based on a concentration of $Ag^+(aq)$ that has an uncertainty of ±10%, the values calculated in 4 will not be expected to be accurate to within more than ±20%. Direct the students to look at other K_{sp} values in the Textbook, which often differ by many powers of 10. The variation of K_{sp} with temperature should be made clear to the student, since some of the differences obtained may be due to this, even though an attempt is made to keep the temperature constant.

   The influence of other ions in solution need not be discussed.

QUESTIONS AND EXERCISES

1. Propose another method for determining the concentration of $Ag^+(aq)$ in the saturated solution—either by using the same experimental method or a different one.

   Answer: The silver could be weighed as in Expt. 7 to determine the $[Ag^+]$.

2. If 100 ml of 0.02 M $AgNO_3$ and 100 ml of 0.02 M $NaCH_3COO$ were mixed, would a precipitate be expected to form? Use the average value for the K_{sp} of silver acetate obtained by members of your class in their calculations.

   Answer: After mixing, the concentration of the ions will be:

$$\begin{aligned} [Ag^+] &= 0.01\ M \\ [CH_3COO^-] &= 0.01\ M \\ [Ag^+][CH_3COO^-] &= (1 \times 10^{-2})(1 \times 10^{-2}) = 1 \times 10^{-4} \end{aligned}$$

   Since this value (1×10^{-4}) is less than the K_{sp}, no precipitate would be expected.

3. Suppose that some solid sodium acetate, $NaCH_3COO$, were added to a saturated solution of silver acetate which is in equilibrium with some $AgCH_3COO(s)$. After the sodium acetate has dissolved, what will be the effect of the increased concentration of the acetate ion on the equilibrium

$$AgCH_3COO(s) \rightleftharpoons Ag^+(aq) + CH_3COO^-(aq)$$

Answer: Increasing the $CH_3COO^-(aq)$ would shift the equilibrium to use up this substance, producing more $AgCH_3COO(s)$ and removing $Ag^+(aq)$ ions from solution.

4. Calculate the $Ag^+(aq)$ ion concentration if the acetate ion concentration in the solution in Question 3 is 1.0 *M*. Is this result in agreement with the prediction you made in Question 3?

Answer: Using $K_{sp} = 5.0 \times 10^{-3}$, we obtain

$$[Ag^+][CH_3COO^-] = 5.0 \times 10^{-3}$$

$$[Ag^+] = \frac{5.0 \times 10^{-3}}{1.0} = 5.0 \times 10^{-3} \text{ mole/liter}$$

This is in agreement with the prediction in Question 3, since the result is less than the number of moles of $Ag^+(aq)$/liter found in the experiment (7×10^{-2}).

POSTLAB DISCUSSION. Calculation 5 (comparison of results) is very important. It is worth discussing the calculations in some detail, since they are basic to the understanding of the K_{sp}.

Supplementary Materials

In *J. Chem. Education*, **36**, 45 (1959), J. R. Schwenk gives a series of reactions showing solubility reactions of silver. The series takes this course:

$$\underset{\text{colorless}}{Ag^{+}}\ \text{(from nitrate)} \xrightarrow{CO_3^{-2}} \underset{\text{cream}}{Ag_2CO_3} \xrightarrow{OH^{-}} \underset{\text{brown}}{Ag_2O} \xrightarrow{Cl^{-}}$$

$$\underset{\text{white}}{AgCl} \xrightarrow{NH_4OH} \underset{\text{colorless}}{Ag(NH_3)_2^{+}} \xrightarrow{Br^{-}} \underset{\text{pale yellow}}{AgBr} \xrightarrow{S_2O_3^{-2}}$$

$$\underset{\text{colorless}}{Ag(S_2O_3)_2^{-3}} \xrightarrow{I^{-}} \underset{\text{yellow}}{AgI} \xrightarrow{CN^{-}} \underset{\text{colorless}}{Ag(CN)_2^{-}} \xrightarrow{S^{-2}}$$

$$\underset{\text{black}}{Ag_2S} \xrightarrow[\text{hot}]{Na_2CO_3} \text{Ag metal}$$

You can use this as a review. You should, however, skip lightly over the three complex ions. We will study them in Chapter 22.

Background Discussion

We have learned that, for reaction to occur, molecules must collide. Usually too few molecules of a pair of solids get close enough together to collide with sufficient energy to react. This is why reactions among solids are usually quite slow. Chemists increase the speed of reaction between solids by first dissolving them—usually in water, where the reacting species (molecules or ions) are always hydrated. In most instances the chemist will be concerned with putting reagents in solution (dissolving) or removing products from solution (precipitating a solid, separating a liquid, or evolving a gas). These are the important processes in analysis and synthesis. The chemist will want to know what factors influence solubility, reaction between dissolved particles, and chemical equilibrium in solution. The Textbook discusses a number of specific equilibria which are important in aqueous solution. We shall want to apply our knowledge of reaction rates and chemical equilibrium, gained in the study of the last two chapters, to predict the direction, rate, and extent of reaction in solution.

The major index of reaction will be the equilibrium constant. Several problems are solved to illustrate how the constant can be used to compute solubility. You will want the student to recognize the special names, such as solubility product, which are commonly applied to constants. Later he will study K_w and K_A as other specific equilibrium constants.

The topics discussed are

The Role of the Solvent
Solubility Equilibria
Quantitative Prediction of Solubility
The Nature of Solution Processes

THE ROLE OF THE SOLVENT

The professional chemist must be concerned with the properties of many solvents. In high school chemistry, owing both to the limitation of time and to the complexity of treatment, you will examine only one solvent in detail—water. Recall that water possesses several properties unexpected for a compound of such small molecular weight. If we assume the van der Waals forces in water to be of the magnitude of those that exist in hydrocarbons, then the boiling point of water is about what we would expect for a compound having a molecular weight of 100 (C_7H_{16}, M.W. 100, b.p. = 98.4°C). If only forces of this nature existed, water would surely have a boiling point less than that of H_2S, -60.8°C. The high boiling point and other unusual properties of water (melting point, heat of melting, heat of vaporization) are related to the tendency of its molecules to clump together and form large molecular aggregates. This property is explained in terms of hydrogen bonding, which you will discuss in Chapter 17.

In addition to forming hydrogen bonds, water has a dipole moment resulting from the O—H bonds, which form an angle of about 105°. Because of their dipole character, water molecules align themselves in a more or less regular manner when they form larger molecular aggregates in the liquid. This arrangement greatly enhances the effect of their dipole moment, giving water a high *dielectric constant*. This constant is really part of the full equation for the attractive force between two charges. Its inclusion is often not apparent because the proportion given is for a vacuum having a dielectric constant equal to unity. Dielectric constant is found to enter the denominator of the equation; hence one can see that the larger the constant, the smaller the force of attraction between charged particles.

When substances are dissolved in water three processes may occur, according to the nature of the substance: (1) the molecules may simply separate and become hydrated (alcohol in water); (2) the ions may separate and become hydrated (NaCl in water); or (3) the molecules may form ions which become hydrated (HCl in water). Substances which simply dissolve probably do so according to a process by which their molecules form hydrogen bonds with water molecules. Salts separate into ions because, as mentioned above, the electrostatic attraction between the ions is overcome by the attraction to water. The reason that molecules of some substances dissociate in water to form ions is a bit more subtle. Background for understanding this will be given later in Chapters 15–17.

SOLUBILITY EQUILIBRIA

The Textbook lists several solubility rules in Table 10-I. You should encourage the student to make maximum use of these. It might prove interesting, however, to take an overview of solubility. The extent to which a solid substance will dissolve is governed by minimum energy and maximum randomness. For solids, randomness always favors dissolution because the solid is ordered and the solution is disordered. Insofar as energy is concerned, whether a substance will dissolve in water depends upon the energy the substance possesses as a solid and the energy it possesses when dispersed in water. We expect the state of lowest energy to be the preferred one. The solid state (not dissolved) will be favored by high interionic attraction, low hydration energy, and efficient packing in the crystal lattice. The magnitude of interionic attraction will be greater with larger charge on the ion and smaller ionic size. Most solids containing covalent bonds have low solubility in water because the energy required to pull the molecules away from each other is greater than the energy released when the molecules become hydrated. Dissolution is favored by low interionic attraction in the solid and high hydration energy of the dissolved ions or molecules.

QUANTITATIVE PREDICTION OF SOLUBILITY

The rules developed above will enable you to make rough qualitative predictions of solubility. You may wonder how quantitative predictions are made. Direct measurements can be carried out by weighing the dissolved solid per liter. Many salts, however, are so slightly soluble that direct measurements become difficult to perform. For many such substances thermodynamic calculations of the K_{sp} can be made. Recall the equation that was presented on p. 294.

$$\Delta F = \Delta H - T\Delta S \qquad (3)$$

If ΔH and ΔS of a solution are known, or can be computed from available data, ΔF of the solution can be computed. Using equation (*3*) discussed on p. 295, we obtain the relation between free energy and the solubility product constant,

$$\Delta F = -2.3RT \log K_{sp} \qquad (4)$$

This is another example of the utility of the free energy function.

You will recall that the dissolution of NH_4Cl was given as an example of a spontaneous endothermic process. Many examples of such processes are found among solution phenomena. We can offer an explanation of this behavior in terms of equation (*3*). Remember that a spontaneous process requires a negative value of ΔF and that ΔF will be negative if $T\Delta S$ is sufficiently large, even if ΔH is positive. It follows that, if T is sufficiently high, most substances will be soluble, and the solubility of most substances will increase with temperature. In terms of our definition of entropy as the property which measures the degree of randomness of the energy distribution in a system, the solution of solids will be accompanied by an increased entropy (the particles have much more available space in solution). We are not surprised then that many solution processes are endothermic.

THE NATURE OF SOLUTION PROCESSES

A detailed consideration of solubility phenomena should involve the analysis of two terms: the change in heat content, or ΔH for the process; and the change in entropy, or ΔS for the process. Let us picture an ionic solid dissolving, and imagine breaking the process into separate energy terms, each of which represents the making or breaking of various bonds or the alteration of various intermolecular or interionic attractions. Then if we add up the energy terms associated with each of the separate steps, we can get ΔH for the process of solution.

Let us analyze ΔH for the process involved in dissolving a crystalline solid such as NaCl. We may consider a *number of hypothetical steps* involving energy terms, each of which can be pictured easily from our model. Such an analysis helps us to see which bonds or interactions are of significance for the process being considered, but it does not imply that solution proceeds by the steps used for the analysis. The net equation is:

$$\mathrm{NaCl}(s) + \text{water} \rightleftharpoons \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

where $\mathrm{Na}^+(aq)$ and $\mathrm{Cl}^-(aq)$ represent the ions in a water solution. The following steps may be conveniently assumed:

1. Vaporization of NaCl produces gaseous molecules of NaCl.

   $$\mathrm{NaCl}(s) \rightleftharpoons \mathrm{NaCl}(g) \qquad \Delta H_1 = 40 \text{ kcal/mole}$$

   This is an endothermic process, the heat being the heat of sublimation.
2. Adding enough energy to break the bond produces neutral atoms:

   $$\mathrm{NaCl}(g) \rightleftharpoons \mathrm{Na}(g) + \mathrm{Cl}(g) \qquad \Delta H_2 = 120 \text{ kcal/mole}$$

   This is an endothermic process, the observed heat being the bond energy.
3. Ionization of the sodium atom is shown by the reaction

   $$\mathrm{Na}(g) \rightleftharpoons \mathrm{Na}^+(g) + e^- \qquad \Delta H_3 = 118 \text{ kcal/mole}$$

   This reaction is endothermic, the observed heat being the ionization energy.
4. Ionization of the chlorine atom follows the reaction

   $$\mathrm{Cl}(g) + e^- \rightleftharpoons \mathrm{Cl}^-(g) \qquad \Delta H_4 = -90 \text{ kcal/mole}$$

   This is the first exothermic step, and it releases about 90 kcal (less heat than step 3 absorbs).
5. Now let's dissolve these two ions in water.

   $$\mathrm{Na}^+(g) \rightleftharpoons \mathrm{Na}^+(aq) + \Delta H_{5a}$$
   $$\mathrm{Cl}^-(g) \rightleftharpoons \mathrm{Cl}^-(aq) + \Delta H_{5b}$$

   Adding all of the heats, we must get ΔH for the overall process, which is usually only a few kcal (for NaCl it is -1 kcal).

$$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_{5a} + \Delta H_{5b} = \text{heat of solution}$$

$$(+40) + (+120) + (+118) + (-90) + \Delta H_{5a} + \Delta H_{5b} = -1 \text{ kcal/mole}$$

$$\Delta H_{5a} + \Delta H_{5b} = -180 \text{ kcal/mole}$$

We see that the sum of ΔH_{5a} and ΔH_{5b} is exothermic by almost 200 kcal. This is the result of two processes:

(a) When a positive ion dissolves, it interacts with the negative ends of the water molecules.

(b) When a negative ion dissolves, it interacts with the positive ends of the water molecules.

The heat change for the overall process involves the sum of the heat terms for each of the above three steps. Since the large energy needed to pull the positive and negative ions apart in step (1) must be provided by the interaction of positively and negatively charged ions with the charged ends of the solvent, it is clear why salts dissolve most readily in polar solvents (solvents having a positive and negative end). Nonpolar molecules do not interact strongly with the ions (as in step 5) to provide energy for the endothermic steps, thus the process becomes prohibitively endothermic.

To get an estimate of ΔS for the process from our model is much more difficult and involves a statistical study of the disorder of the system. In general the second term $(-T\Delta S)$ for a solution process is negative and may dominate *slightly* endothermic processes but *not* strongly endothermic ones.

For substances like paraffin and gasoline, in which nonpolar molecules are held together loosely, the ΔH (solution) is small, and the prime driving force is $(-T\Delta S)$. The most direct explanation of $T\Delta S$ is that it measures the disorder in a system. If we go from an ordered system such as two components in separate bottles to a disordered system in which the two components are randomly mixed in a solution, the $T\Delta S$ value is positive, and $(-T\Delta S)$, appearing in our equation for ΔF, is negative. This makes ΔF more negative; and our driving force for the process, greater.

Answers to Exercises and Problems

Ex. 10-1. The heat of solution of iodine in benzene is +4.2 kcal/mole (heat is absorbed). Assuming the increase in randomness is the same when iodine dissolves in liquid benzene as it is in ethyl alcohol and in CCl_4, justify the prediction that the solubility of I_2 in benzene is higher than in CCl_4 but lower than in alcohol.

Answer

$$I_2(s) + 1.6\text{ kcal} \rightleftharpoons I_2\,(in\ alcohol)$$
$$I_2(s) + 4.2\text{ kcal} \rightleftharpoons I_2\,(in\ benzene)$$
$$I_2(s) + 5.8\text{ kcal} \rightleftharpoons I_2\,(in\ CCl_4)$$

The heat absorbed as I_2 dissolves in benzene is less than the heat absorbed when it dissolves in CCl_4. This means that for benzene there is less of an energy effect opposing the tendency toward randomness, hence the solubility in benzene will be higher than in CCl_4. Since the heat absorbed for benzene solution is greater than for ethyl alcohol, there is more of an energy effect opposing the tendency toward randomness, and as a result the solubility in benzene will be lower than in ethyl alcohol.

Ex. 10-2. From the heat of solution of chlorine in water, −6.0 kcal/mole (heat evolved), how do you expect the solubility of chlorine at one atmosphere pressure and 20°C to compare with that of oxygen and nitrous oxide, N_2O?

Answer

$$O_2(g) \rightleftharpoons O_2(aq) \qquad \Delta H = -3.0\text{ kcal/mole }O_2$$

$$N_2O(g) \rightleftharpoons N_2O(aq) \qquad \Delta H = -4.8\text{ kcal/mole }N_2O$$

$$Cl_2(g) \rightleftharpoons Cl_2(aq) \qquad \Delta H = -6.0\text{ kcal/mole }Cl_2$$

More heat is evolved per mole dissolved for chlorine than for either O_2 or N_2O. Hence there is a larger tendency toward minimum energy in the solution of Cl_2 than for either O_2 or N_2O. Since this larger energy effect (favoring dissolving) opposes about the same randomness effect, the solubility of Cl_2 will be higher than either O_2 or N_2O.

Ex. 10-3. Using the periodic table as a guide, predict which of the following compounds form ionic solutions in water: silicon carbide, SiC; magnesium bromide, $MgBr_2$; carbon tetrabromide, CBr_4; chromic chloride, $CrCl_3$.

Answer

$MgBr_2$ and $CrCl_3$. Compounds containing elements from the opposite sides of the periodic table can be expected to form ionic solutions in water. The compounds $MgBr_2$ and $CrCl_3$ each comprise a metallic element (left side) and a nonmetallic element (right side). These two should form ionic solutions. The other two compounds each contain only nonmetallic elements, and hence are not expected to give ionic solutions.

Ex. 10-4. Use Figures 10-4, 10-5, and 10-6 to decide the solubility of each of the compounds listed below. Write "sol" if the compound is soluble and "low" if it has low solubility.

$Mg(NO_3)_2$, $MgCl_2$, $MgSO_4$, $Mg(OH)_2$, $MgCO_3$,
$Ca(NO_3)_2$, $CaCl_2$, $CaSO_4$, $Ca(OH)_2$, $CaCO_3$,
$Sr(NO_3)_2$, $SrCl_2$, $SrSO_4$, $Sr(OH)_2$, $SrCO_3$.

Answer

$Mg(NO_3)_2$ sol	$MgCl_2$ sol	$MgSO_4$ sol	$Mg(OH)_2$ low	$MgCO_3$ low
$Ca(NO_3)_2$ sol	$CaCl_2$ sol	$CaSO_4$ low	$Ca(OH)_2$ low	$CaCO_3$ low
$Sr(NO_3)_2$ sol	$SrCl_2$ sol	$SrSO_4$ low	$Sr(OH)_2$ sol	$SrCO_3$ low

Ex. 10-5. Decide the formula of each of the following compounds and indicate those with low solubility in water. Silver carbonate; aluminum chloride; aluminum hydroxide; cuprous chloride (the chloride of Cu^+); cupric chloride (the chloride of Cu^{+2}); ammonium bromide.

Answer

silver carbonate	Ag_2CO_3	low solubility
aluminum chloride	$AlCl_3$	
aluminum hydroxide	$Al(OH)_3$	low solubility
cuprous chloride	$CuCl$	low solubility
cupric chloride	$CuCl_2$	
ammonium bromide	NH_4Br	

Ex. 10-6. Write the equation for the dissolving of calcium sulfate, $CaSO_4$, and the solubility product expression.

Answer

$CaSO_4(s) \rightleftharpoons Ca^{+2}(aq) + SO_4^{-2}(aq)$

$K = [Ca^{+2}][SO_4^{-2}]$

Ex. 10-7. Write the equation for the dissolving of silver chromate, Ag_2CrO_4, and the solubility product expression. Silver chromate dissolves to give Ag^+ and CrO_4^{-2} ions.

Answer

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{-2}(aq)$

$K = [Ag^+]^2[CrO_4^{-2}]$

Ex. 10-8. Calculate the solubility, in moles per liter, of calcium sulfate in water, using the solubility product given in Table 10-II.

Answer

$CaSO_4(s) \rightleftharpoons Ca^{+2}(aq) + SO_4^{-2}(aq)$

$K_{sp} = [Ca^{+2}][SO_4^{-2}]$

From Table 10-II, $K_{sp} = 2.4 \times 10^{-5}$. If the solubility is s moles per liter, the concentrations of Ca^{+2} and SO_4^{-2} are each equal to s.

$[Ca^{+2}] = [SO_4^{-2}] = s$

$K_{sp} = (s)(s) = (s)^2$

$(s)^2 = 2.4 \times 10^{-5} = 24 \times 10^{-6}$

$(s) = 4.9 \times 10^{-3}$ mole/liter

Ex. 10-9. A 50 ml volume of 0.04 M $Ca(NO_3)_2$ solution is added to 150 ml of 0.008 M $(NH_4)_2SO_4$ solution. Show that a trial value of the calcium sulfate ion product is 6×10^{-5}. Will a precipitate form?

Answer

The Ca^{+2} ion is diluted from a volume of 50 ml to 200 ml. Hence, its concentration is reduced by the factor

$$\frac{50\text{ ml}}{50\text{ ml} + 150\text{ ml}} = \frac{50}{200} = \frac{1}{4}$$

$[Ca^{+2}] = \frac{1}{4}(0.04\ M) = 0.01\ M = 1 \times 10^{-2}\ M$

The SO_4^{-2} ion is diluted from 150 ml to 200 ml. Its concentration is reduced by the factor $\frac{150}{200} = \frac{3}{4}$.

$[SO_4^{-2}] = \frac{3}{4}(0.008\ M) = 0.006\ M = 6 \times 10^{-3}\ M$

The trial product is

$[Ca^{+2}][SO_4^{-2}] = (1 \times 10^{-2})(6 \times 10^{-3}) = 6 \times 10^{-5}$

Since 6×10^{-5} is a larger number than $K_{sp} = 2.4 \times 10^{-5}$, a precipitate *will* form.

Ex. 10-10. Use Figures 10-5 and 10-6 or Table 10-I to decide which of the following soluble salts would permit a separation of magnesium and lead through a precipitation reaction: sodium iodide, NaI; sodium sulfide, Na_2S; sodium carbonate, Na_2CO_3.

Answer

The ion Pb^{+2} forms an iodide of low solubility, PbI_2, whereas Mg^{+2} does not. The salt NaI *could* be used to separate $Pb^{+2}(aq)$ from $Mg^{+2}(aq)$.

Pb^{+2} but not Mg^{+2} forms a compound of low solubility with sulfide ion, S^{-2}. The salt Na_2S *could* be used to separate $Pb^{+2}(aq)$ from $Mg^{+2}(aq)$.

Both Pb^{+2} and Mg^{+2} form compounds of low solubility with CO_3^{-2}. The salt Na_2CO_3 *cannot* be used to separate $Pb^{+2}(aq)$ from $Mg^{+2}(aq)$.

Pr. 1. Sugar is added to a cup of coffee until no more sugar will dissolve. Does addition of another spoonful of sugar increase the rate at which the sugar molecules leave the crystal phase and enter the liquid phase? Will the sweetness of the liquid be increased by this addition? Explain.

Answer

The addition increases the area of solid, hence it does increase the rate at which molecules dissolve. The sweetness of the liquid is *not* increased, however, because the added solid increases the rate at which molecules leave the solution by the same amount that it increases the rate at which they enter the solution. Equilibrium is unaffected by the added solid.

Pr. 2. In view of the discussion of the factors that determine the rate of dissolving (Section 10-1.2), propose two methods for increasing the rate at which sugar dissolves in water.

Answer

1. Granulate or pulverize the sugar to increase the surface area.
2. Raise the temperature to increase the rate at which molecules leave the crystal surface.

Note that stirring is also effective if the rate of dissolution is so rapid that a saturated layer of liquid forms near the crystal surface. Under these circumstances, the rate of diffusion in the liquid is the rate-determining step, rather than the rate at which molecules leave the surface. Thus by replacing the saturated liquid close to the crystal, one can speed its solution.

Pr. 3. When a solid evaporates directly (without melting), the process is called **sublimation**. Evaporation of "dry ice" (solid CO_2) is a familiar example. Two other substances that sublime are FCN and ICN.

$$\mathrm{FCN}(s) \rightleftharpoons \mathrm{FCN}(g) \qquad \Delta H = +5.7 \text{ kcal}$$
$$\mathrm{ICN}(s) \rightleftharpoons \mathrm{ICN}(g) \qquad \Delta H = +14.2 \text{ kcal}$$

(a) In sublimation, does the tendency toward maximum randomness favor solid or gas?
(b) In sublimation, does the tendency toward minimum energy favor solid or gas?
(c) The vapor pressure of solid FCN is 760 mm at 201°K. In view of part *b*, would you expect solid ICN to have a lower or higher vapor pressure than solid FCN at this same temperature, 201°K?

Answer

(a) A gas is more random than a solid. Randomness favors the gas phase.
(b) Heat is absorbed during sublimation. Minimum energy favors the solid phase.
(c) Since solid ICN is more favored by ΔH than is solid FCN, the equilibrium vapor pressure will be lower. The randomness effects are about the same at equal pressures. In fact, the vapor pressure of solid ICN reaches 760 mm only after the temperature is raised to 413°K.

Pr. 4. Liquid chloroform, $CHCl_3$, and liquid acetone, CH_3COCH_3, dissolve in each other in all proportions (they are said to be **miscible**).

(a) When pure $CHCl_3$ is mixed with pure acetone, is randomness increased or decreased?
(b) Does the tendency toward maximum randomness favor reactants or product in the reaction:

$$\mathrm{CHCl_3}(l) + \mathrm{CH_3COCH_3}(l) \rightleftharpoons 1{:}1 \text{ solution} \qquad \Delta H = -495 \text{ cal}$$

(c) Considering the sign of ΔH shown in part *b*, does the tendency toward minimum energy favor reactants or product?
(d) In view of your answers to parts *b* and *c*, discuss the experimental fact that these two liquids are miscible.

Answer

(a) Since two kinds of molecules are mixed in the solution, it is more random than the pure liquids, each of which consists of only one kind of liquid.
(b) Tendency toward maximum randomness favors the more random state, the solution.
(c) $\Delta H = -495$. The negative sign means heat is evolved. Hence, the tendency toward minimum energy favors products.
(d) The fact that the two liquids dissolve in all proportions is consistent with the fact that tendencies to maximum randomness and minimum energy work together, *both* favoring the solution.

Pr. 5. Which of the following substances can be expected to dissolve in the indicated solvent to form, primarily, ions? Which would form molecules?

(a) Sucrose in water
(b) RbBr in water
(c) $CHCl_3$ in water
(d) $CsNO_3$ in water
(e) HNO_3 in water
(f) S_8 in carbon disulfide, CS_2
(g) ICl in ethyl alcohol

Answer

Ions are expected from

(b) RbBr,
(d) $CsNO_3$,
(e) HNO_3.

Molecules are expected from

(a) Sucrose
(c) $CHCl_3$,
(f) S_8,
(g) ICl.

Notice that the question is not concerned with the amount that dissolves. Thus $CHCl_3$ has only limited solubility in water, but the amount that does dissolve remains in molecular form.

Pr. 6. Which of the substances listed in Problem 5 would be called electrolytes?

Answer: (b), (d), (e).

Pr. 7. Assume the following compounds dissolve in water to form separate, mobile ions in solution. Write the formulas and names for the ions that can be expected.

(a) HI
(b) $CaCl_2$
(c) Na_2CO_3
(d) $Ba(OH)_2$
(e) KNO_3
(f) NH_4Cl

Answer

(a) $H^+(aq)$, hydrogen ion; $I^-(aq)$, iodide ion.
(b) $Ca^{+2}(aq)$, calcium ion; $Cl^-(aq)$, chloride ion.
(c) $Na^+(aq)$, sodium ion; $CO_3^{-2}(aq)$, carbonate ion.

(d) $Ba^{+2}(aq)$, barium ion; $OH^-(aq)$, hydroxide ion.
(e) $K^+(aq)$, potassium ion; $NO_3^-(aq)$, nitrate ion.
(f) $NH_4^+(aq)$, ammonium ion; $Cl^-(aq)$, chloride ion.

Pr. 8. Write the equation for the reaction that occurs when each of the following electrolytes is dissolved in water.

(a) Lithium hydroxide (solid)
(b) Nitric acid (liquid)
(c) Potassium sulfate (solid)
(d) Sodium nitrate (solid)
(e) Ammonium iodide (solid)
(f) Potassium carbonate (solid)
Answer: (a) $LiOH(s) \longrightarrow Li^+(aq) + OH^-(aq)$.

Answer

(a) $LiOH(s) \longrightarrow Li^+(aq) + OH^-(aq)$
(b) $HNO_3(l) \longrightarrow H^+(aq) + NO_3^-(aq)$
(c) $K_2SO_4(s) \longrightarrow 2K^+(aq) + SO_4^{-2}(aq)$
(d) $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3^-(aq)$
(e) $NH_4I(s) \longrightarrow NH_4^+(aq) + I^-(aq)$
(f) $K_2CO_3(s) \longrightarrow 2K^+(aq) + CO_3^{-2}(aq)$

Pr. 9. What would you expect to happen if equal volumes of 0.1 *M* $MgSO_4$ and 0.1 *M* $ZnCl_2$ were mixed together?

Answer

Nothing. The two volumes would merely mix, and no precipitates would form. All combinations of the ions give soluble substances.

Pr. 10. Predict what would happen if equal volumes of 0.2 *M* Na_2SO_3 and 0.2 *M* $MgSO_4$ were mixed. If a reaction takes place write the net ionic equation.

Answer

A precipitate of $MgSO_3$ would form.

$$Mg^{+2}(aq) + SO_3^{-2}(aq) \rightleftharpoons MgSO_3(s)$$

Pr. 11. Using Figures 10-4 to 10-6 (or Table 10-1), make a statement about the solubilities of the compounds containing the following ions.

Anion	Cations
(a) Carbonate, CO_3^{-2}	alkali ions, Li^+, Na^+, K^+, Rb^+, Cs^+
(b) Carbonate, CO_3^{-2}	alkaline earth ions, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}
(c) Sulfide, S^{-2}	alkaline earth ions, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}
(d) Hydroxide, OH^-	the cations of the fourth row of the periodic table
(e) Chloride, Cl^-	the cations of the fifth row of the periodic table

Answer: (a) All alkali carbonates are soluble.
(b) All alkaline earth carbonates have low solubilities.

Answer

(a) All alkali carbonates are soluble.
(b) All alkaline earth carbonates have low solubilities.
(c) All alkaline earth sulfides are soluble.
(d) All hydroxides of the fourth-row cations have low solubility except K^+. (Note that Se, Br, and Kr do not form cations.)
(e) All chlorides of the fifth-row cations have high solubility except Ag^+.

Pr. 12. Write the empirical formulas for each of the following compounds, and indicate which have low solubilities.

(a) Silver sulfide
(b) Potassium sulfide
(c) Ammonium sulfide
(d) Nickel sulfide
(e) Ferrous sulfide (Fe^{+2})
(f) Ferric sulfide (Fe^{+3})

Answer

(a) Ag_2S (low)
(b) K_2S
(c) $(NH_4)_2S$
(d) NiS (low)
(e) FeS (low)
(f) Fe_2S_3 (low)

Pr. 13. Write net ionic equations for any reactions that will occur upon mixing equal volumes of 0.2 *M* solutions of the following pairs of compounds.

(a) Silver nitrate and ammonium bromide
(b) $SrBr_2$ and $NaNO_3$
(c) Sodium hydroxide and aluminum chloride
(d) NaI and $Pb(NO_3)_2$
(e) Barium chloride and sodium sulfate
Answer: (a) $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$.

Answer

(a) $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$
(b) No solids will form.
(c) $Al^{+3}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$
(d) $Pb^{+2}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$
(e) $Ba^{+2}(aq) + SO_4^{-2}(aq) \longrightarrow BaSO_4(s)$

Pr. 14. What ions could be present in a solution if samples of it gave:

(a) A precipitate when either $Cl^-(aq)$ or $SO_4^{-2}(aq)$ is added?
(b) A precipitate when $Cl^-(aq)$ is added but none when $SO_4^{-2}(aq)$ is added?
(c) A precipitate when $SO_4^{-2}(aq)$ is added but none when $Cl^-(aq)$ is added?

Answer

(a) $Pb^{+2}(aq)$ must be present.
(b) One or more of $Cu^+(aq)$, $Ag^+(aq)$, and Hg_2^{+2} must be present.
(c) One or more of $Ca^{+2}(aq)$, $Sr^{+2}(aq)$, $Ba^{+2}(aq)$, and $Ra^{+2}(aq)$ must be present.

Pr. 15. What cations from the fourth row of the periodic table could be present in a solution with the following behavior?

(a) No precipitate is formed with hydroxide ion.
(b) A precipitate forms with hydroxide ion and with sulfate ion.
(c) A precipitate forms with hydroxide ion and with sulfide ion.
(d) A precipitate forms with carbonate ion, none with sulfide ion.

Answer

(a) $K^+(aq)$.
(b) $Ca^{+2}(aq)$.
(c) Any cation in the fourth row except $K^+(aq)$ or $Ca^{+2}(aq)$.
(d) $Ca^{+2}(aq)$.

Pr. 16. The solubility of silver chloride is so low that all but a negligible amount of it is precipitated when excess sodium chloride solution is added to silver nitrate solution. What would be the weight of the precipitate formed when 100 ml of 0.5 *M* NaCl is added to 50.0 ml of 0.100 *M* $AgNO_3$?

Answer: 0.715 gram.

Answer

50.0 ml of 0.100 *M* $AgNO_3$ contain

$$(0.0500\ \text{liter})(0.100\ \text{mole/liter}) = 5.00 \times 10^{-3}\ \text{mole}\ Ag^+(aq)$$

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Hence 5.00×10^{-3} mole AgCl will form. The weight of this number of moles is

$$(5.00 \times 10^{-3}\ \text{mole})(143\ \text{g/mole}) = 0.715\ \text{g}$$

Pr. 17. Write the solubility product expression for each of the following reactions.

(a) $BaSO_4(s) \rightleftharpoons Ba^{+2}(aq) + SO_4^{-2}(aq)$
(b) $Zn(OH)_2(s) \rightleftharpoons Zn^{+2}(aq) + 2OH^-(aq)$
(c) $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{+2}(aq) + 2PO_4^{-3}(aq)$

Answer

(a) $K_{sp} = [Ba^{+2}][SO_4^{-2}]$
(b) $K_{sp} = [Zn^{+2}][OH^-]^2$
(c) $K_{sp} = [Ca^{+2}]^3[PO_4^{-3}]^2$

Pr. 18. Write the solubility product expression applicable to the solubility of each of the following substances in water.

(a) Calcium carbonate
(b) Silver sulfide
(c) Aluminum hydroxide

Answer

(a) $K_{sp} = [Ca^{+2}][CO_3^{-2}]$
(b) $K_{sp} = [Ag^+]^2[S^{-2}]$
(c) $K_{sp} = [Al^{+3}][OH^-]^3$

Pr. 19. The solubility product of AgCl is 1.4×10^{-4} at 100°C. Calculate the solubility of silver chloride in boiling water.

Answer

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
$K_{sp} = [Ag^+][Cl^-]$
but here
$[Ag^+] = [Cl^-]$
$1.4 \times 10^{-4} = [Ag^+]^2$
$[Ag^+] = \sqrt{1.4 \times 10^{-4}} = 1.2 \times 10^{-2}\ M$
Solubility $= 1.2 \times 10^{-2}\ M$

Pr. 20. Experiments show that 0.0059 gram of $SrCO_3$ will dissolve in 1.0 liter of water at 25°C. What is K_{sp} for $SrCO_3$?

Answer: 1.6×10^{-9}.

Answer

$SrCO_3(s) = Sr^{+2}(aq) + CO_3^{-2}(aq)$

For every mole dissolved, one mole of Sr^{+2} ions and one mole of CO_3^{-2} ions are formed.

Moles $SrCO_3(s)$ dissolved

$$= \frac{0.0059\ \text{g/liter}}{148\ \text{g/mole}} = 4.0 \times 10^{-5}\ \text{mole/liter}$$

$$K_{sp} = [Sr^{+2}][CO_3^{-2}] = (4.0 \times 10^{-5})^2 = 1.6 \times 10^{-9}$$

Pr. 21. How many milligrams of silver bromide dissolve in 20 liters of water? (Use the data given in Table 10-II.)

Answer

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$
$K_{sp} = [Ag^+][Br^-] = 5.0 \times 10^{-13} = 50 \times 10^{-14}$
$[Ag^+] = [Br^-]$
$[Ag^+]^2 = 50 \times 10^{-14}$

$[Ag^+] = 7.0 \times 10^{-7}\ M$
In 20 liters, there will be $20 \times 7.0 \times 10^{-7} = 1.4 \times 10^{-5}$ mole AgBr.
In 20 liters, there will be $(1.4 \times 10^{-5}$ mole$)(188$ g/mole$) = 2.63 \times 10^{-3}$ gram AgBr.
In 20 liters, 2.63 milligrams AgBr dissolve.

Pr. 22. To one liter of 0.001 M H_2SO_4 is added 0.002 mole of solid $Pb(NO_3)_2$. As the lead nitrate dissolves, will lead sulfate precipitate?

Answer

$PbSO_4(s) \rightleftharpoons Pb^{+2}(aq) + SO_4^{-2}(aq)$

$K_{sp} = [Pb^{+2}][SO_4^{-2}] = 1.3 \times 10^{-8}$

$$[Pb^{+2}] = \frac{0.002 \text{ mole}}{\text{liter}}$$

$$[SO_4^{-2}] = \frac{0.001 \text{ mole}}{\text{liter}}$$

If all the $Pb(NO_3)_2$ dissolves, the trial product of ion concentrations is

$$(2 \times 10^{-3})(1 \times 10^{-3}) = 2 \times 10^{-6}$$

This is *larger* than K_{sp}; hence these concentrations cannot continue to exist; some $PbSO_4(s)$ will precipitate, removing ions until the actual product of ion concentrations equals $K_{sp} = 1.3 \times 10^{-8}$.

Pr. 23. Suppose 10 ml of 1.0 M $AgNO_3$ is diluted to one liter with tap water. If the chloride concentration in the tap water is about 10^{-5} M, will a precipitate form?

Answer

$K_{sp} = [Ag^+][Cl^-] = 1.7 \times 10^{-10}$

$$[Ag^+] = \frac{(0.010 \text{ liter})(1.0 \text{ mole/liter})}{1.0 \text{ liter}} = 0.010\ M$$

$[Cl^-] = 10^{-5}\ M$

Trial product: $[Ag^+][Cl^-] = (10^{-2})(10^{-5}) = 10^{-7}$. This exceeds $K = 1.7 \times 10^{-10}$. Hence a precipitate will form.

Pr. 24. The test described in Problem 23 does *not* give a precipitate if the laboratory distilled water is used. What is the maximum chloride concentration that could be present?

Answer

A precipitate will form if the chloride concentration exceeds the value which makes the the product $[Ag^+][Cl^-]$ equal to K_{sp}.

$[Ag^+] = 1.0 \times 10^{-2}$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.7 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.7 \times 10^{-8}$$

$[Cl^-]$ cannot exceed $1.7 \times 10^{-8}\ M$ in the distilled water.

Pr. 25. Will a precipitate exist at equilibrium if $\frac{1}{2}$ liter of a $2 \times 10^{-3}\ M$ $AlCl_3$ solution and $\frac{1}{2}$ liter of a $4 \times 10^{-2}\ M$ solution of sodium hydroxide are mixed and diluted to 10^3 liters with water at room temperature? ($K_{sp} = 5 \times 10^{-33}$.)

Answer

Half a liter of $2 \times 10^{-3}\ M$ $AlCl_3$ contains 1×10^{-3} mole of Al^{+3}.

$$[Al^{+3}] = \frac{1 \times 10^{-3}}{10^3} = 1 \times 10^{-6}\ M$$

Half a liter of $4 \times 10^{-2}\ M$ NaOH contains 2×10^{-2} mole of OH^-.

$$[OH^-] = \frac{2 \times 10^{-2}}{10^3} = 2 \times 10^{-5}\ M$$

$$\begin{aligned}[Al^{+3}][OH^-]^3 &= (1 \times 10^{-6})(2 \times 10^{-5})^3 \\ &= 8 \times 10^{-21}\end{aligned}$$

The solubility product for $Al(OH)_3$ is 5×10^{-33}, which is much smaller than 8×10^{-21}, thus a precipitate will form.

Pr. 26. Use Figures 10-5 and 10-6 or Table 10-I to decide which of the following soluble substances would permit a separation of aqueous magnesium and barium ions. For those that are effective, write the equation for the reaction that occurs.

(a) Ammonium carbonate
(b) Sodium bromide
(c) Potassium sulfate
(d) Sodium hydroxide

Answer

(a) No separation; both cations precipitate.
(b) No separation; neither cation precipitates.
(c) Separation possible.

$$Ba^{+2}(aq) + SO_4^{-2}(aq) \rightleftharpoons BaSO_4(s)$$

(d) Separation possible.

$$Mg^{+2}(aq) + 2OH^-(aq) \rightleftharpoons Mg(OH)_2(s)$$

Pr. 27. To a solution containing 0.1 *M* of each of the ions Ag^+, Cu^+, Fe^{+2}, and Ca^{+2} is added 2 *M* NaBr solution, giving precipitate *A*. After filtration, a sulfide solution is added to the solution, and a black precipitate forms, precipitate *B*. This precipitate is removed by filtration, and 2 *M* sodium carbonate solution is added, giving precipitate *C*. What is the composition of each precipitate, *A*, *B*, and *C*?

Answer

A is a mixture of AgBr and CuBr.
B is FeS.
C is $CaCO_3$.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Given 2×10^{-3} *M* solutions of $Pb(NO_3)_2$ and Na_2SO_4, determine the following:

1. What ions will be present in each of the solutions? And in what concentrations?

   Answer
   $Pb^{+2}(aq)$, $NO_3^{-}(aq)$ in the first, and $Na^{+}(aq)$ and $SO_4^{-2}(aq)$ in the second.

   $$[Pb^{+2}] = 2 \times 10^{-3} \text{ mole/liter}$$
   $$[NO_3^{-}] = 4 \times 10^{-3} \text{ mole/liter}$$
   $$[Na^{+}] = 4 \times 10^{-3} \text{ mole/liter}$$
   $$[SO_4^{-2}] = 2 \times 10^{-3} \text{ mole/liter}$$

2. Which ions are most likely to form a precipitate if the solutions are mixed?

   Answer: $Pb^{+2}(aq)$ and $SO_4^{-2}(aq)$.

3. Would you expect a precipitate to form when equal volumes of the two solutions are mixed? ($K_{sp} = 1.3 \times 10^{-8}$.)

   Answer: Yes.

   $$[Pb^{+2}][SO_4^{-2}] = (2 \times 10^{-3})(2 \times 10^{-3}) = 4 \times 10^{-6}$$

   A precipitate is expected to form when the product of the maximum possible ion concentrations is greater than the K_{sp}.

4. Write an equilibrium equation for the most probable reaction when equal volumes of the two solutions are mixed together.

   Answer
   $$Pb^{+2}(aq) + SO_4^{-2}(aq) = PbSO_4(s)$$

5. What is the equilibrium concentration of Ag^{+} ions in a saturated aqueous solution of AgCl made by shaking AgCl with water? ($K_{sp} \approx 1 \times 10^{-10}$.) Show calculations.

   Answer
   $$AgCl(s) = Ag^{+}(aq) + Cl^{-}(aq)$$
   $$1 \times 10^{-10} = [Ag^{+}][Cl^{-}]$$
   $$[Ag^{+}] = [Cl^{-}] = (1 \times 10^{-10})^{1/2} = 1 \times 10^{-5} \text{ mole/liter}$$

6. Which of the following pairs of ions would be expected to form precipitates when dilute solutions are mixed? Write formulas for the precipitates formed.
   (1) Na^{+}, SO_4^{-2};
   (2) Ba^{+2}, CO_3^{-2};
   (3) NH_4^{+}, CO_3^{-2};
   (4) Fe^{+3}, OH^{-};
   (5) Pb^{+2}, Cl^{-};
   (6) Na^{+}, S^{-2};
   (7) Ca^{+2}, PO_4^{-3}.

   Answer
   (2) $BaCO_3$.
   (4) $Fe(OH)_3$.
   (5) $PbCl_2$.
   (7) $Ca_3(PO_4)_2$.

7. Why does the solid species *not* appear in *K* for dissolving the solid?

   Answer
   The rates of dissolving and precipitating are both proportional to the surface area of the solid. When these two rates are equal (at equilibrium), then area cancels, and the concentration of the solid species does not appear in the equation.

8. The equilibrium constant for the reaction, $HBrO(aq) = H^{+}(aq) + BrO^{-}(aq)$ is 2×10^{-9}. Determine the $[H^{+}]$ in a 0.05 *M* solution of hypobromous acid, HBrO.

   Answer

   $$K = \frac{[H^{+}][BrO^{-}]}{[HBrO]} = 2 \times 10^{-9}$$

   Let
   $y = [H^{+}] = [BrO^{-}]$
   Then
   $0.05 - y = [HBrO]$
   and
   $$\frac{y^2}{0.05 - y} = 2 \times 10^{-9}$$

Since y will likely to be small compared to 0.05 we will neglect it. Then

$y^2 = (2 \times 10^{-9})(5 \times 10^{-2}) = 10 \times 10^{-11}$

$y = (1 \times 10^{-10})^{1/2} = 1 \times 10^{-5}$ mole/liter

which is indeed small compared to 0.05.

9. Consider the following equilibria for gases.

$$H_2S(g) \rightleftharpoons H_2S(aq) + 4.6 \text{ kcal/mole } H_2S$$
$$SO_2(g) \rightleftharpoons SO_2(aq) + 8.6 \text{ kcal/mole } SO_2$$

Assuming the randomness factor to be about the same for each, which of the gases will have the lower solubility in water?

Answer: H_2S.

10. Which of the following would be expected to form ionic solutions in water?
(1) CO_2,
(2) CCl_4,
(3) C,
(4) O_2,
(5) NaI.

Answer: (5).

11. The compound HCN gives CN^- (cyanide ion) when dissolved in water. Given the clue that CN^- behaves somewhat as halide ions do, write formulas for the following compounds, and indicate those you would expect to have low solubility in water:
(a) ammonium cyanide,
(b) barium cyanide,
(c) silver cyanide.

Answer

(a) NH_4CN; (b) $Ba(CN)_2$; (c) AgCN, for which a low solubility is expected.

12. Suppose you wish to separate Ba^{+2} from Co^{+2}. Which of these reagents could be successfully used: NaCl, Na_2CO_3, NaOH.

Answer

NaOH, since $Co(OH)_2$ precipitates, whereas $Ba(OH)_2$ does not.
Na_2CO_3 forms solids with both.
NaCl forms a solid with neither.

13. Consider the reactions

$$CO_2(s) \rightleftharpoons CO_2(g) \qquad \Delta H = 6.03$$
$$BrCN(s) \rightleftharpoons BrCN(g) \qquad \Delta H = 11.3$$

and use the data in Textbook problem 3, taking randomness effects to be similar in all these reactions.
(a) Discuss why the vapor pressure of CO_2 is about the same as that of FCN at 201°K.
(b) What is the vapor pressure of BrCN relative to the vapor pressure of other compounds?

Answer

(a) The heat absorbed by CO_2 in subliming is about equal to that by FCN, thus their opposing tendencies give about the same K, or nearly equal vapor pressures.
(b) The vapor pressure of BrCN should be intermediate to those of FCN and ICN.

14. Write the solubility product expression for the dissolution of each of the following solids.
(1) PdS,
(2) Ag_3PO_4,
(3) chromic carbonate,
(4) gallium hydroxide.

Answer

(1) $K_{sp} = [Pd^{+2}][S^{-2}]$.
(2) $K_{sp} = [Ag^+]^3[PO_4^{-3}]$.
(3) $K_{sp} = [Cr^{+3}]^2[CO_3^{-2}]^3$.
(4) $K_{sp} = [Ga^{+3}][OH^-]^3$.

CHAPTER

11

AQUEOUS ACIDS AND BASES

Intent and Approach

This chapter continues the discussion of equilibrium, now applied to the important and complementary classes: acids and bases. After first establishing the difference between strong and weak electrolytes, we take up the ionization of water and the special role of $H^+(aq)$ and $OH^-(aq)$—all in terms of dynamic equilibrium. We then give the experimental, or operational, definition of acids and bases, discuss the nature of $H^+(aq)$, and consider a titration. This material sets the stage for the treatment of acid strength, during which we use the equilibrium constant as a quantitative measure. Next we mention some broader aspects of the behavior and definition of acids (Brønsted Theory). The chapter ends with an important discussion of kinds of definitions, applied here to acids. Having gone through this chapter, a student should be able to calculate $H^+(aq)$ from a given $OH^-(aq)$, or vice versa, and to work problems involving the relationship between K_A, hydrogen ion, and acid concentrations.

Outline

1. The concept of electrolyte strength is introduced and is then used to show that water is a weak electrolyte (Sec. 11-1.1). Variation of strength with temperature is taken up in Sec. 11-1.2 (reduced type).
2. The study of ionic equilibrium in water and of how it is shifted by the addition of ion-producing solutes reveals the role of $H^+(aq)$ and $OH^-(aq)$ (Sec. 11-1.3).
3. Five characteristic properties of acids are given in Sec. 11-2.1 and are related to the release of $H^+(aq)$ ions.
4. The distinguishing properties of bases are listed (11-2.2) and explained as a reaction with $H^+(aq)$ (Sec. 11-2.3). A summary is given in Sec. 11-2.4.
5. Three possible models for the hydrated hydrogen ion are considered. Although $H^+(aq)$ is generally used, this section shows why H_3O^+ is chosen when convenient, as in discussing the Brønsted Theory of acids and bases (Sec. 11-2.5) (reduced type).
6. Through the use of the reaction between $H^+(aq)$ and $OH^-(aq)$ the equilibrium calculations made in Sec. 11-1.3 are extended to acid–base reactions or titrations (Sec. 11-2.6). The pH notation is treated briefly (Sec. 11-2.7) (reduced type).
7. The distinction of weak electrolytes is applied directly to acids, and K_A is defined as a measure of relative strength (Sec. 11-3.1).
8. An experimental method for determining K_A is given, and is used to illustrate typical calculations (Sec. 11-3.2)..
9. The proton competition that can develop between weak acids is introduced and broadens into the Brønsted definition of acids (Sec. 11-3.3).
10. Operational and conceptual definitions are illustrated and contrasted (Sec. 11-3.5).

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
S 11-1/11-1.3* (pp. 179–182)	1	Discussion	1–3	1		2	Strong and Weak Electrolytes, Water
Expt. 17	2	Expt. 17 Demonstration 5					Heat of Acid–Base Reaction
S 11-2/11-2.4 (pp. 183–185)	3	Discussion		3	4, 5		Properties and Definitions
Expt. 18	4	Expt. 18					Indicators
S 11-2.5/11-2.7* (pp. 185–189)	5	Discussion	4		6,† 8–10, 22, 23	7	Titration, *p*H, Nature of $H^+(aq)$
S 11-3/11-3.2* (pp. 190–193)	6	Discussion	5	11, 12	13–15	16, 17	Acid Strength and Equilibrium
Expt. 19	7	Expt. 19					Le Chatelier's Principle
S 11-3.3/11-3.5 (pp. 193–195)	8	Discussion		**18**	**19, 20, 24**	21	Brønsted Theory
Review	9	Review FILM, ACID–BASE INDICATORS					

Note: Experiments 17 and 18 require numerous solutions prepared in advance.
* Includes fine print material. You must decide the assignment for your class.
† Boldface indicates problems whose answers are given in the Textbook.

New Concepts

1. Strength of electrolytes—that is, extent of ionization.
2. Definition of a group of chemicals by properties of an ion common to all: acids as a source of $H^+(aq)$.
3. Concentration changes during approach to equilibrium: titration.
4. The differences and advantages of conceptual and operational definitions.

Development

ELECTROLYTES—STRONG AND WEAK (11-1)

The distinction made here is best shown by selecting examples from the ends of the spectrum, as is done in the Textbook. The primary basis for the classification is a conductivity test. Remind the student that he saw you demonstrate this test. Nothing more need be done here.

Water: A Weak Electrolyte (11-1.1)

This section establishes that water does dissociate to ions and introduces K for the reaction. The equilibrium ion product for water, K_w, is quite important, primarily for the idea of balance that it expresses. Hydrogen and hydroxide ion concentrations are dependent upon each other. A simple equation of this type is already known to the student. Area of a rectangle is the product of length and width. For example, $l \times w = 100$ cm². If the area is to be constant, we can choose l or w, but not both. If one is made larger, the other must decrease to keep area constant at 100 cm².

The same holds for the *product* $[H^+][OH^-]$. It is a constant, and one concentration cannot arbitrarily rise. A firm grasp of this interconnection will help not only in Expt. 19 but in several later sections of the Textbook. The analogy is not, however, limited to K_w, or even to acid–base reactions. It is true for all equilibria.

The inclusion of $[H_2O]$ with K to give K_w is identical in concept to deriving K_{sp} from K by combining it with the concentration of solid. In Sec. 11-3.1 we will define K_A and relate it to K_w and K in Textbook equation (*7*).

The Change of K_w with Temperature (11-1.2) (reduced type)

This section gives a combined application of ΔH considerations and Le Chatelier's Principle to the equation for K_w.

The Special Roles of $H^+(aq)$ and $OH^-(aq)$ in Water (11-1.3)

In this section you will find the examples to use in stressing the connection between $[H^+]$ and $[OH^-]$ discussed above. The student must grasp this connection. Some of these examples for a simple substance in water will be used later (Sec. 11-2.6) to help explain the reaction between an acid and a base.

EXPERIMENTAL INTRODUCTION TO ACIDS AND BASES (11-2)

Properties of Aqueous Solutions of Acids (11-2.1)

Expt. 17, THE HEAT OF SOME ACID-BASE REACTIONS,
fits here. See p. 341 for guide.

The demonstration, part of Expt. 17, should give ample evidence for the conductivity of acids (and bases), a property true for all ionic solutions; it shows the presence of ions but doesn't identify acids or bases. The presence of ions is one facet of the definition. *Solutions of acids contain ions.*

You can show the liberation of hydrogen in a quick test. Along with the stated (not proved) fact that all acids are found by analysis to contain hydrogen, this test helps establish that hydrogen (or its ion) is characteristic of all acids.

The litmus test is, of course, easy to show, but the color change results from a chemical change in a compound whose structure is too complex to show. Moreover, it does not give, directly, any information about the nature of the acidic solution. Present it as a quick and easy test for acids. Here is a mnemonic device for remembering the color of litmus:

RED in
ACID solution

BLUE in
BASE solution

The typical taste of acids can be identified in vinegar (acetic acid) and sour milk (lactic acid). The footnote offers a basis for a short set of remarks about safety in the laboratory. Emphasize that tasting, or sometimes smelling, unknown substances is *not* for amateurs. Professionals use these tests with extreme caution.

The Textbook outlines the suggested approach well. It follows the method of Chapter 1. Notice that it leads to a *postulate* which states that we can identify an acid by its ability to release protons. This is a conceptual definition (a type which the student will study in Sec. 11-3.5). A great many tests of the postulate have been performed, and the results taken as a body establish the usefulness of the postulated description of an acid.

Properties of Aqueous Solutions of Bases (11-2.2)

This section goes easily once the idea of describing and defining a chemical class by its properties is well planted in the student's mind. Use the same kind of argument as for acids. Demonstration 5 and Expt. 17 give some data.

An Explanation of the Properties of Bases (11-2.3)

One question that may arise is "Why are no acids formed by reaction with water—somewhat as Na_2CO_3 and NH_3 give bases?" Actually there are; SO_2 and CO_2 are examples of acid-forming compounds. The production of $H^+(aq)$, however, is not clear hence they are not suitable as first examples. There is no need to go into a discussion of acidic and basic oxides as such. To do so would require more chemistry than the student has so far; for this reason it is taken up in Chapters 20 and 21.

Acids and Bases: Summary (11-2.4)

This section contains the definitions and explanations from Secs. 11-2.1–11-2.3.

Expt. 18, THE DETERMINATION OF THE HYDROGEN ION CONCENTRATION OF SOLUTIONS USING INDICATORS, fits here. See p. 346 for guide.

The Nature of $H^+(aq)$ (11-2.5) (reduced type)

This section opens with some remarks about the presence of ions in liquid phases. The presence of ions in aqueous solution is quite easy to establish for many substances. Yet these same substances must usually be heated to a rather high temperature to melt and produce ions in the liquid phase. These facts mean that the hydrated ion is an important species—important because it is likely to occur. For this reason we use a special symbol—the (aq) part of $M^+(aq)$—to show there are some water molecules clustered around the ion. These are strongly held and move with the ion—they are really part of the ion. An individual molecule of water is not indefinitely attached to one particular ion. There is some "changing of partners" caused by collisions, but the M^+ ion is constantly surrounded.

This section is devoted to three possible ways the water may be arranged around a proton. There is no definitive experimental evidence as yet, but the evidence that does exist favors $H_9O_4^+$ rather than H_3O^+. Part of the reason for the absence of a distinct result is that the species changes with temperature and other conditions that affect the interaction between oxygen and the proton. This interaction is called hydrogen bonding and is treated in Chapter 17. Note the section on $H^+(aq)$ in *Background Discussion.*

Acid–Base Titrations (11-2.6)

Up to this point the student has been preparing for the rest of the chapter. He has particularized equilibrium concepts to the acid–base case and developed a clearer picture of hydrated ions, especially $H^+(aq)$. So far, however, he has not considered an acid and base in the same solution. This is now put before him as a series of calculations (like those in Sec. 11-1.3) of $[H^+]$ and $[OH^-]$.

You can make a plot of the data in Textbook Table 11-II to show $[H^+]$ versus added OH^-. The point is to dramatize the fast change near the equal molar point and to help illustrate why indicators work in Expt. 18.

*p*H (11-2.7) (reduced type)

We have treated *p*H rather lightly because our small use of it would not be worth the effort required to teach logarithms. If your class already has facility with logarithms, you may choose to present the *p*H method. Actually, acidity can be expressed easily in concentration units, and, indeed, that method is more straightforward. It also fits better with the equilibrium calculations the student needs to make. Your handling of Expt. 18 will depend upon the choice you make about presenting *p*H. See *Purpose*, p. 346 for details.

STRENGTHS OF ACIDS (11-3)

Weak Acids (11-3.1)

The student will, if he has any idea of acids at all, consider them as corrosive materials capable of eating through almost anything. To accept the coming sections he must use the more well-defined equilibrium expression of strength. You should instill the idea that this "strength" is not a matter of concentration (which we are not really discussing now) but one related to the tendency for ions to exist at equilibrium. For acids this means the tendency to release $H^+(aq)$. It is important for the student to realize that *hydrogen ions are all alike*. There are *not* weak and strong types of $H^+(aq)$. "Strong" merely means the acid supplies essentially all the $H^+(aq)$ it can potentially supply. "Strong" and "weak" are qualitative designations of the same information contained in K_A, referring to the extremes of very large and very small K_A.

The equilibrium constant for ion formation, producing $H^+(aq)$, is given the special symbol K_A. This section shows values of K_A for some common substances. The production of $H^+(aq)$ from some substances is more favored than from others, for the reasons described in Chapter 9. Emphasize that K_A converts acid strength into a quantitative concept.

Equilibrium Calculations of Acidity (11-3.2) (part in reduced type)

The two samples illustrate the level of competence expected. These are really no different from problems in the previous chapter. The same ideas are applied to equilibria involving proton donation, or acidity. Note that the determination of K_A in the example gives direct support to Expt. 18.

Competition for H^+ Among Weak Acids (11-3.3)

Introduce the idea of *proton transfer* by combining some equations the student has already seen. You should make sure the student understands proton exchange and the *necessary* result that a new acid and base are produced. A less sophisticated way to say this is that if a compound has a proton and gives it away (acts as an acid), the proton can then be taken back (the new compound formed acts as a base).

The notation HB for an acid is picked to show the base contained in the acid.

$$HB_1 \rightleftharpoons H^+ + B_1^-$$

As is true of any equilibrium, there are really two opposing reactions involved in this one equation.

Hydronium Ion in the Proton Transfer Theory of Acids (11-3.4)

This section contains another version of the important idea that *water* reacts as an *acid* or a *base*! The student can claim that water fits only one of our defining properties given earlier. It does contain hydrogen, but so do sugar, benzene, and natural gas. There are these arguments to advance: (1) In liquid water, there are some ions present; it conducts, although feebly. (2) We can detect the presence of $H^+(aq)$ and $OH^-(aq)$ ions in pure liquid water, but we cannot for the other substances named. To produce these ions, water molecules must have released protons—acted as an acid. (3) There is evidence that the proton is hydrated; that is, the water molecule must be able to accept a proton—act as a base.

Contrast of Acid-Base Definitions (11-3.5)

Operational and conceptual definitions of acids are defined by using an analogy from sports. Then they are applied to acids and bases. The usefulness of the two kinds of definition is not limited to acids. They can be (and are) applied to nearly any situation. This is really just a more formalized example of an idea you gave the student in Expt. 1. It is a way of keeping experimental fact separate from interpretation. Indeed, we could call these experimental and interpretive definitions.

This particular kind of distinction is one which is valuable outside science and represents the kind of training that every citizen needs. It is a part of the "scientific attitude" that all students can benefit from whether they ever become practicing scientists or not. Therefore, this section is probably as important for its "social" impact as for its "chemical" content.

Film, ACID-BASE INDICATORS,
fits here. See p. 353 for summary.

EXPERIMENT 17 THE HEAT OF SOME ACID-BASE REACTIONS

PURPOSE. To establish the exothermic reaction $H^+(aq) + OH^-(aq) \rightleftharpoons HOH$ as an introduction to the study of acids and bases.

PRELAB DISCUSSION. This is an investigation of the predominant species reacting when aqueous solutions of various acids and bases are mixed. The introduction in the Laboratory Manual reminds students of Expt. 13 and directs them to consider the heat involved when other acids and bases react.

Point out that all reactions to be studied take place in solutions and that they will have mixed the solutions quickly and measure the temperature immediately after mixing, since the reaction is rapid. It will not be necessary to include the heat absorbed by the glass. See lab hints 3 and 4. Tell the students to calculate the number of calories by assuming that the density of each solution is 1 gram/ml and that one calorie is used to heat each gram one degree centigrade.

TIMING. This experiment should follow Sec. 11-1 (pp. 179–182). Note that Demonstration 5 is to be done after this experiment but in the same period.

EQUIPMENT NEEDED (PER STUDENT)

2 containers for solutions (Erlenmeyer flasks or beakers, 100 ml)
1 250-ml beaker as calorimeter (see lab hint 5)
1 thermometer, −10°C to 110°C
100 ml graduates or 100 ml volumetric flasks (see lab hint 3)

You will need the solutions listed below. The number of milliliters listed is the amount for one complete set, which involves six measurements; presumably each will be done by one out of each six students. If *each* student in the class is to do a single part, multiply these volumes by five for a class of 30.

Important note: See lab hint 1 for preparation of solutions.

100 ml 1 *M* HCl (85.5 ml conc. reagent/liter)
200 ml 1 *M* CH_3COOH (56.9 ml conc. reagent/liter)
200 ml 1 *M* HNO_3 (64.0 ml conc. reagent/liter)
100 ml 0.5 *M* H_2SO_4 (28.0 ml conc. reagent/liter)
300 ml 1 *M* $NaOH$ (40.0 g solid/liter)
300 ml 1 *M* KOH (56.1 g solid/liter)

The equipment needed for the demonstration is given on p. 344.

TIME REQUIRED. You will need twenty minutes for the experiment and fifteen minutes for the demonstration. The dispensing of the solutions and the measurement of volumes must be conveniently set up and the students prepared ahead of time. This will allow time in one period for calculation, exchange of data, and demonstration. Any of these parts—the actual experiment, the calculation, the exchange of data—may be done on a different day.

PRECAUTIONS. In addition to the usual laboratory precautions. warn the students about keeping even dilute sulfuric acid off clothing. All of these solutions are irritating to the skin.

LABORATORY HINTS

1. Since the results of each section are to be compared, it is essential that the concentrations of the reactants be comparable. The acids can and should be made up accurately from the stock concentrated acids. The bases, which are a little more difficult to mix accurately, should be somewhat more concentrated (about 1.1 *M*) in order to guarantee that there will be 0.1 mole

available in the 100 ml to react with the acid. All solutions should be prepared the day before to allow them to come to room temperature.

Be sure to check the concentrations beforehand. If the HCl, CH_3COOH, and HNO_3 are fresh, reagent-grade acids from recently opened bottles, you should have little difficulty. Since KOH converts easily to carbonate when exposed to air, it must be taken from a recently opened container.

2. With a number of classes doing this experiment, the required volumes may be rather large, since for many of the solutions a liter will be needed for each period. We suggest a siphon-type dispensing arrangement from stock bottles (5 liters or more).
3. You will not need a 100 ml volumetric flask or a 100 ml graduate for each student. Place a labeled one with each stock bottle for use only with that solution. This will avoid the need for rinsing between uses. The student should measure each solution into a beaker or flask to avoid having to measure volumes at his lab desk.
4. Remind the student to record the temperature of each solution (*rinsing* and *drying* the thermometer before transfer) before, as well as after, mixing. The temperature is to be read to 0.2°C, which requires careful observation.
5. Coffee cups made of polystyrene foam make excellent calorimeters. You may need to reduce the volumes to 50 ml acid and 50 ml base.

SAMPLE DATA TABLE AND CALCULATIONS

Each student will have only one of the combinations, hence this table represents combined results from six students.

TRIAL	ACID *A*	BASE *B*	INITIAL TEMP (AV OF $A + B$) (°C)	FINAL TEMP (°C)	Δt (°C)	FINAL VOLUME (ml)	HEAT ABSORBED BY SOLUTION* (cal)	MOLES OF H_2O PRODUCED BY REACTION	ΔH (KCAL/MOLE H_2O)
1	HCl	KOH	23.5	30.0	6.5	200	1300	0.1	13
2	CH_3COOH	NaOH	24.1	30.0	5.9	200	1180	0.1	12
3	HNO_3	NaOH	24.1	30.8	6.7	200	1340	0.1	13
4	HNO_3	KOH	24.2	30.0	5.8	200	1160	0.1	12
5	CH_3COOH	KOH	24.6	31.0	6.4	200	1280	0.1	13
6	H_2SO_4	NaOH	23.8	30.6	6.8	200	1360	0.1	14
Expt. 13	HCl	NaOH	—	—	3.2	200	640	0.048	13

Note: The uncertainties have been omitted from this table, but since the Δt is ±0.4°C, or about 7%, the molar heats are all known to about ±1 kcal.

* Calculated essentially as in Expt. 5, cal = $\text{ml} \times \frac{\text{g}}{\text{ml}} \times \frac{1\ \text{cal}}{(\text{g})(°\text{C})} \times °\text{C}$. Assume the density of all solutions is 1.0 gram/ml.

Demo. 5, ELECTRICAL CONDUCTIVITY OF ACIDS AND BASES, fits here. See p. 344 for guide.

RECORD OF RESULTS AS INDICATED

1. Write equations for each of the reactions performed by you and your classmates. Write the formulas for the strong electrolytes in ionic form and the formulas for the weak electrolytes in molecular form to indicate the reacting species present. Include the molar heat for each reaction.

Equations: An example for a strong acid and a strong base is given in the procedure. Example for a weak acid and strong base:

$$CH_3COOH + Na^+(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + Na^+(aq) + H_2O + 12\ \text{kcal}$$

2. What regularities do you observe about the ΔH values obtained for the reactions involving various acids and bases? What do all of the equations have in common?

   Regularities observed: The ΔH is similar for all the reactions. All the reactions involve the formation of the same amount of water.

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O + (13 \pm 1\ \text{kcal})$$

3. The values of ΔH for the various reactions will be collected and tabulated by your teacher or by a designated member of your class. Study the tabulated results, and note the average values for each combination of acid and base.

   Make any generalizations possible about the ΔH values the class obtained when strong electrolytes reacted compared to those obtained for reactions which involved a weak electrolyte.

   Answer: Considering data from an entire class (5 determinations of each molar heat), you will note that ΔH for reactions in which both acid and base are strong electrolytes will be higher (about 13 kcal) than in reactions (with CH_3COOH) in which one of the reactants is a weak electrolyte (about 12 kcal). Since the uncertainty of any one student's measurements is about ±1 kcal, the trend may not appear in the data from a single set of measurements.

4. Attempt a theoretical explanation of the differences and similarities in the ΔH values based upon the energy involved in making and breaking chemical bonds.

   Answer: Since less energy is liberated when one of the reactants is a weak electrolyte, we may account for this by assuming some energy is needed to break bonds before a reaction between $H^+(aq)$ and $OH^-(aq)$ occurs. With strong electrolytes, bonds within a molecular species do not need to be broken prior to the exothermic reaction.

$$H^+(aq) + OH^-(aq) \rightleftharpoons HOH$$

5. On the basis of your present knowledge of strong and weak acids, answer the Question to Wonder About at the end of Expt. 12.

   Answer: The demonstration should suggest that HCl is strong and CH_3COOH weak. Thus the observation in Expt. 12 that 6 *M* CH_3COOH behaves about the same as 1 *M* HCl is rationalized. When you have made the summary of class data suggested below, you can comment that the low ΔH for CH_3COOH may be partially due to its weakness, which gives a slower reaction and more chance to lose heat.

POSTLAB DISCUSSION. As indicated in the answer to question 3, the accumulation of data from an entire class (or from several classes) is very important. The principal point of the experiment concerns the similarities, rather than the differences, in the molar heat of the reaction. The student should realize that the reaction of H^+ with OH^- is the important one and that other ions do not matter.

Here are some average molar heats obtained from this experiment at 1961–1962 trial schools. Each value is an average of 12–15 tests.

HCl and KOH	12.9 kcal/mole of water	H_2SO_4 and NaOH	13.5
CH_3COOH and NaOH	12.1	HCl and NaOH	13.0
HNO_3 and NaOH	12.7		

DEMONSTRATION 5 ELECTRICAL CONDUCTIVITY OF ACIDS AND BASES

PURPOSE. To demonstrate relative conductivity, which is used as a basis for inferring degree of ionization. This, in turn, is used to define "weak" and "strong" electrolytes, as the terms are applied to acids and bases. This fits nicely with Sec. 11-1 of the text.

TIMING. This demonstration should be done after Expt. 17, but *before* the questions are assigned. The experiment and demonstration should be done in one period.

EQUIPMENT NEEDED. Conductivity apparatus described in Demonstration 3 (p. 157).

50 ml each of the 6 solutions used in Expt. 17, diluted to 0.1 *M*
50 ml H_2SO_4 diluted to 0.02 *M*
50 ml $Ba(OH)_2$ (0.4 g/100 ml)
8 small beakers or bottles to contain solutions

TIME REQUIRED. This demonstration will take about fifteen minutes.

DEMONSTRATION

PART I

Test the conductivity of each of the solutions used in Expt. 17 (diluted to 0.1 *M*), and test the conductivity of distilled water. Have each student record the results in his notebook, classifying each solution as a good conductor (strong electrolyte) or as a poor conductor (weak electrolyte).

PART II

Test the conductivity of the following:

A. Strong acid with a strong base.

1. Recall the conductivity of 0.1 *M* solutions of HCl and NaOH just measured.
2. Mix the two solutions together, and test the conductivity of half of the resulting solution.
3. Have the students write the overall equation and then the net ionic equation for the reaction

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

B. Weak acid with a strong base.

1. Recall the conductivity of 0.1 *M* solutions of acetic acid and NaOH just measured.
2. Mix the two solutions together, and test the conductivity of half of the resulting solution.
3. Write the net ionic equation

$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + HOH$$

C. Acid with a base to form a slightly soluble salt.

1. Test the conductivity of a 0.02 *M* solution of sulfuric acid and of a 0.02 *M* solution of $Ba(OH)_2$.
2. Titrate the 0.02 *M* $Ba(OH)_2$ solution with the 0.02 *M* H_2SO_4, using phenolphthalein indicator. At the same time, observe the relative conductivity of the solution. At the end point, the light will go out. After that, slowly add an excess of acid, and follow the conductivity.
3. Write the net ionic equation

$$Ba^{+2}(aq) + 2OH^-(aq) + 2H^+(aq) + SO_4^{-2}(aq) \rightleftharpoons BaSO_4(s) + 2H_2O(l)$$

EXERCISES

1. Write equilibrium equations for the following compounds dissolved in water (saturated solutions). Underline the substances favored in the equilibrium.

   (a) NaCl
   (b) $\mathrm{Ba(OH)_2}$
   (c) $\mathrm{Na_2SO_4}$
   (d) $\mathrm{BaSO_4}$

   Answer: (a) $\mathrm{NaCl}(s) \rightleftharpoons \underline{\mathrm{Na^+}}(aq) + \underline{\mathrm{Cl^-}}(aq)$
   (b) $\mathrm{Ba(OH)_2}(s) \rightleftharpoons \underline{\mathrm{Ba^{+2}}}(aq) + \underline{\mathrm{2OH^-}}(aq)$
   (c) $\mathrm{Na_2SO_4}(s) \rightleftharpoons \underline{\mathrm{2Na^+}}(aq) + \underline{\mathrm{SO_4^{-2}}}(aq)$
   (d) $\underline{\mathrm{BaSO_4}}(s) \rightleftharpoons \mathrm{Ba^{+2}}(aq) + \mathrm{SO_4^{-2}}(aq)$

2. Write equations for the dissociation of the following acids in aqueous solution. Underline the substances favored in the equilibrium.

   (a) $\mathrm{HCl}(l)$
   (b) $\mathrm{H_2SO_4}(l)$
   (c) $\mathrm{HNO_3}(l)$
   (d) $\mathrm{CH_3COOH}(l)$

   Answer: (a) $\mathrm{HCl}(l) \rightleftharpoons \underline{\mathrm{H^+}}(aq) + \underline{\mathrm{Cl^-}}(aq)$
   (b) $\mathrm{H_2SO_4}(l) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{HSO_4^-}(aq) \rightleftharpoons \underline{\mathrm{2H^+}}(aq) + \underline{\mathrm{SO_4^{-2}}}(aq)$
   (c) $\mathrm{HNO_3}(l) \rightleftharpoons \underline{\mathrm{H^+}}(aq) + \underline{\mathrm{NO_3^-}}(aq)$
   (d) $\underline{\mathrm{CH_3COOH}}(l) \rightleftharpoons \mathrm{CH_3COO^-}(aq) + \mathrm{H^+}(aq)$

EXPERIMENT 18 THE DETERMINATION OF THE HYDROGEN ION CONCENTRATION OF SOLUTIONS USING INDICATORS

PURPOSE. To give experience in observing relative strengths of acid solutions and base solutions; to give a simple method for determining the equilibrium constant of a weak acid; and to introduce a simple titration. Optional questions 2 and 3 should be used only if Sec. 11-2.7 (*p*H) is to be included.

PRELAB DISCUSSION. Tell the students that there are many dyes whose colors change with $[H^+]$. We have selected some that are convenient for the concentrations used in this experiment.

Emphasize the need for careful measurement in preparing the standards. Mention also the need for careful rinsing of glassware before use. See notes under *Time Required.*

TIMING. This experiment should follow Sec. 11-2 but precede Sec. 11-3, in which the ionization constant of acetic acid is given.

EQUIPMENT NEEDED (PER PAIR). Indicator solutions in dropper bottles (several sets per class; each set needs only about 10 ml of the indicator solution). See lab hint 1.

Orange IV (0.1 g in 100 ml water)
Methyl Orange (0.1 g in 100 ml water)
Indigo Carmine (0.25 g in 100 ml 50% ethanol)
Alizarin Yellow R (0.1 g in 100 ml water)
phenolphthalein (1 g in 100 ml 50% ethanol)
6 ml 0.1 *M* HCl (8.6 ml conc. reagent/liter) (see lab hint 2)
7 ml 0.1 *M* NaOH (4 g NaOH/liter) (see lab hint 2)
set of unknowns (see lab hint 3) (5 ml of an unknown for each student)
6 ml 0.1 *M* acetic acid (5.7 ml conc. reagent/liter)
5 ml 1.0 *M* acetic acid (56.9 ml conc. reagent/liter)
10 ml graduated cylinder
medicine dropper (calibrated in Expt. 10)
22 test tubes, 13 × 100 mm (each student needs 8 for the color standards and 3 for the rest of the experiment)
marking pencils or labels
litmus paper
distilled water

TIME REQUIRED. The experiment requires one or two 45–50 minute periods. It can be done quite rapidly if the students understand what they are to do and if the various solutions are conveniently located such that there is little waiting. The standards fade overnight, and although they may be brought back by adding another drop of indicator, it is probably wise to do the entire experiment in one day. The students should check the day before to be sure that they have enough clean test tubes and that they understand the directions.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. The indicators selected are those that give distinct color change in the ranges we are particularly interested in. There are many other indicators possible, but if too many sets of standards are prepared the students become confused. The ranges for those suggested are

	$[H^+]$ range	*p*H range	Color change
Orange IV (Tropeolin 00)	500 to 6×10^{-4}	1.3–3.2	R–Y
Methyl Orange (Orange III, Tropeolin D)	800 to 4×10^{-6}	3.1–4.4	R–OY
Alizarin Yellow R	100 to 1×10^{-12}	10–12	Y–R
Indigo Carmine (sodium indigo disulfonate)	25 to 1×10^{-13}	11.6–13	B–Y

(R = red; Y = yellow; OY = orange-yellow; B = blue.)

The Indigo Carmine should be dark blue when freshly prepared. If it fades in use, add more. If these indicators are not available, others may be substituted (see handbooks.)

2. Directions are given for each student to prepare dilutions for 0.01, 0.001, and 0.0001 *M* acid and base. If you are short of time you may supply some or all of these.
3. The H+ concentration of the following unknowns is within the range of the indicators discussed in the foregoing:

	$[H^+]$	*p*H	Acid	To Make 100 ml Solution
	3×10^{-2}	1½	0.05 *M* oxalic acid	0.63 g $C_2H_2O_4 \cdot 2H_2O$
Orange IV	10^{-2}	2	0.03 *M* citric acid	0.7 g $C_6H_8O_7 \cdot H_2O$
	3×10^{-3}	2½	1 *M* acetic acid	5.7 ml conc. CH_3COOH
	10^{-3}	3	0.1 *M* potassium hydrogen phthalate and 0.1 *M* hydrochloric acid	2 g $C_6H_4COOHCOOK$ and 10 ml 1 *M* HCl
	3×10^{-4}	3½	0.03 *M* potassium hydrogen tartrate	0.63 g $C_2H_5O_4COOK$
Methyl Orange	10^{-4}	4	0.05 *M* potassium hydrogen phthalate	1 g $C_6H_4COOHCOOK$
	3×10^{-5}	4½	0.1 *M* sodium acetate and acetic acid	1.36 g $CH_3COONa \cdot 3H_2O$ and 10 ml 1 *M* CH_3COOH
	10^{-10}	10	0.1 *M* sodium hydrogen carbonate and 0.1 *M* sodium carbonate	0.84 g $NaHCO_3$ and 1.24 g $Na_2CO_3 \cdot H_2O$
Alizarin Yellow R	3×10^{-11}	10½	saturated magnesium hydroxide	about 0.001 g MgO
	3×10^{-12}	11½	0.05 *M* sodium carbonate	0.62 g $Na_2CO_3 \cdot H_2O$
Indigo Carmine	10^{-12}	12	0.03 *M* trisodium phosphate	1.3 g $Na_3PO_4 \cdot 12H_2O$
	3×10^{-12}	12½	saturated calcium hydroxide	about 0.1 g $Ca(OH)_2$

CALCULATIONS. Calculate the equilibrium constant for acetic acid, CH_3COOH.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Use the value for $[H^+]$ determined in IV c. You may assume that the concentration of the acetate ion, $[CH_3COO^-]$, is equal to the $[H^+]$ and that the concentration of acetic acid, $CH_3COOH(aq)$, is essentially that of the solution you used, 0.1 *M* or 1 *M*.

Answer: The $[H^+]$ for the 0.1 *M* acetic acid corresponded to that in the 0.001 *M* HCl. Therefore the $[H^+]$ is 10^{-3}, and the $[CH_3COO^-]$ is also 10^{-3}. The $[CH_3COOH]$ is 10^{-1}. (Remind the students of the conductivity demonstration, which showed very few ions present for a weak acid, and point out that, since such a small amount is subtracted from 10^{-1}, this value is not changed significantly.) Thus

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{10^{-3} \times 10^{-3}}{10^{-1}} = 10^{-5}$$

The accepted value at 25°C is 1.8×10^{-5}.

For the 1 *M* acetic acid the concentration of H^+ corresponded to a value between that of the 0.01 *M* and the 0.001 *M* HCl. The student may use either of these and get a constant of 10^{-6} or 10^{-4}. Class discussion of these results should indicate the intermediate value of 10^{-5}.

QUESTIONS

1. Predict qualitatively the effect of each of the following experiments on the above equilibrium.
   (a) Some of the salt sodium acetate, which contains the ions $Na^+(aq)$ and $CH_3COO^-(aq)$, is dissolved in the 0.1 *M* acetic acid solution. Would the $[H^+]$ increase or decrease?
   (b) Some sodium hydroxide solution is added drop by drop to the 0.1 *M* CH_3COOH.

   Answer: (a) The $[H^+]$ would decrease. The student may reason on the basis of a shift in equilibrium, using Le Chatelier's Principle.

   $$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

   If the concentration of one of the products is increased, the equilibrium will shift to favor the reactant, and this would eliminate some of the H^+. On the other hand, the student may use the equilibrium constant just calculated,

   $$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 10^{-5}$$

   and show that any increase in $[CH_3COO^-]$ must result in an increase in $[CH_3COOH]$ and a decrease in $[H^+]$.

   (b) The $[H^+]$ would decrease. The student has seen this in Part V, and he also knows the reaction

   $$H^+ + OH^- \rightleftharpoons HOH$$

2. How do you explain the results noted in Part V, where you compared the volume of 0.1 *M* NaOH required to react with equal volumes of 0.1 *M* HCl and 0.1 *M* CH_3COOH?

   Answer: The same volume was used in each case, indicating that although there may not be as many hydrogen ions in the solution, there is the same amount of H^+ in 0.1 *M* CH_3COOH as in 0.1 *M* HCl.

3. The $H^+(aq)$ concentration of a 1 *M* solution of benzoic acid is 8×10^{-3} *M*.
   (a) What percent of the benzoic acid, C_6H_5COOH, is ionized in this aqueous solution?
   (b) Predict what volume of 1 *M* NaOH would be required to react with 10 ml of 1 *M* C_6H_5COOH. Assume that the reaction will be carried to the point where phenolphthalein turns pink, as in Part V.

   Answer: (a) If 8×10^{-3} mole of H^+ is produced from one mole of benzoic acid, the percent ionized is

   $$\frac{8 \times 10^{-3} \text{ mole}}{1 \text{ mole}} \times 100 = 0.8\%$$

   (b) 10 ml of 1 *M* C_6H_5COOH would contain 0.01 mole of H^+ and would require 0.01 mole of OH^-, which would be supplied by 10 ml of 1 *M* NaOH.

OPTIONAL QUESTIONS (*Use only if Sec. 11-2.7 is assigned.*)

1. Calculate the $H^+(aq)$ concentration of each of the solutions prepared in Parts II a, b, c, and d. Use the relation $[H^+][OH^-] = 10^{-14}$.

Answer: In Part II the OH^- concentrations were 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4}. The corresponding H^+ concentrations are 10^{-13}, 10^{-12}, 10^{-11}, and 10^{-10}.

2. The *p*H of a solution is a shorthand way of designating the hydrogen ion concentration, $[H^+]$. For example, when the $[H^+] = 0.1\ M$ or $10^{-1}\ M$ the *p*H is 1. Note that the *p*H is simply the exponent to which 10 is raised (the logarithm) with the sign changed. What is the *p*H of each of the standard solutions prepared in Parts I a, b, c, and d and Parts II a, b, c, and d?

Answer

Solution in Part	*p*H
I a	1
b	2
c	3
d	4
II a	13
b	12
c	11
d	10

3. What is the *p*H of your unknown solution?

Answer: See values given in lab hint 3.

EXPERIMENT 19 APPLYING LE CHATELIER'S PRINCIPLE TO SOME REVERSIBLE CHEMICAL REACTIONS

PURPOSE. To illustrate Le Chatelier's Principle by using an equilibrium dependent upon $[H^+]$ and to give an illustration of the equilibrium $H^+ + OH^- \rightleftharpoons HOH$.

PRELAB DISCUSSION. Little discussion of this experiment is needed. Remind the students to consider the reacting species involved in each step of the experiment.

TIMING. This experiment is most effective if done at the end of Chapter 11, just preceding Sec. 11-3.5.

EQUIPMENT NEEDED (PER STUDENT)

About 5 ml each of K_2CrO_4 and $K_2Cr_2O_7$ and 2 ml each of the other solutions (all these should be in dropper bottles):

0.1 *M* K_2CrO_4 (19.4 g K_2CrO_4/liter)
0.1 *M* $K_2Cr_2O_7$ (29.4 g $K_2Cr_2O_7$/liter)
1 *M* NaOH (40 g NaOH/liter)
1 *M* HCl (85.5 ml conc. HCl/liter)
0.1 *M* $Ba(NO_3)_2$ (26.1 g $Ba(NO_3)_2$/liter)
1 *M* CH_3COOH (56.9 cc ml glacial acid/liter)
1 *M* HNO_3 (64 ml conc. HNO_3/liter)
1 *M* H_2SO_4 (55.5 ml conc. H_2SO_4/liter)
1 *M* KOH (56.1 g KOH/liter)
1 *M* NH_3 (66.3 ml conc. NH_4OH/liter)
Saturated $Ca(OH)_2$ (approx. 3.6 g $Ca(OH)_2$/liter)
C_2H_5OH

6 13 × 100-mm test tubes

TIME REQUIRED. The student will need one full laboratory period (45–50 minutes) to complete all of the procedures and answer the questions. It is advisable for the student to attempt to answer the questions while still in the laboratory in case he needs to repeat any procedure for which he obtained doubtful results.

PRECAUTIONS. Observe the usual laboratory precautions.

LABORATORY HINT. Have many sets of reagents available in dropper bottles in order that time will not be wasted by students waiting for reagents.

EXPECTED RESULTS

PART I

$$2CrO_4^{-2}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{-2}(aq) + H_2O \qquad K = 3.0 \times 10^{14}$$

(a) $CrO_4^{-2}(aq)$, yellow; $Cr_2O_7^{-2}(aq)$, orange.
(b) When NaOH solution is added, $Cr_2O_7^{-2}(aq)$ becomes yellow. The color then matches that of the $CrO_4^{-2}(aq)$.
(c) When HCl solution is added, $CrO_4^{-2}(aq)$ becomes orange. The color then matches that of the $Cr_2O_7^{-2}(aq)$.
(d) Adding NaOH solution to (c) reverses the color change.
(e) Adding HCl solution to (b) reverses the color change.

PART II

(a) A yellow, dense precipitate forms;

$$Ba^{+2}(aq) + CrO_4^{-2}(aq) \rightleftharpoons BaCrO_4(s) \qquad K_{sp} = 2 \times 10^{-10}$$

(b) No precipitate forms;

$$Ba^{+2}(aq) + Cr_2O_7^{-2}(aq) \longrightarrow \text{no precipitate}$$

(c) The precipitate dissolves, and the yellow solution changes to orange.
(d) The color changes to yellow, and a precipitate forms.

(e) In step (c) add sodium hydroxide to reverse the change, and in step (d) add hydrochloric acid.
(f) A heavy precipitate forms with $CrO_4^{-2}(aq)$, and a light precipitate forms with $Cr_2O_7^{-2}(aq)$.

PART III (OPTIONAL)

The color changes show that $CrO_4^{-2}(aq)$ is converted to $Cr_2O_7^{-2}(aq)$ with CH_3COOH, HNO_3, and H_2SO_4. The reverse happened with $Ca(OH)_2$, KOH, and NH_3. No change is observed with C_2H_5OH.

QUESTIONS FOR PART I

1. What can you conclude about the reaction $2CrO_4^{-2}(aq) \longrightarrow Cr_2O_7^{-2}(aq)$ and its dependence upon hydrogen ions, $H^+(aq)$, as noted in Steps (c) and (e)? Balance this equation by adding the proper number of $H^+(aq)$ ions and H_2O molecules to the appropriate side of the equation.

   Answer: The addition of $H^+(aq)$ to the reaction causes the equilibrium concentration of $Cr_2O_7^{-2}(aq)$ to increase:

$$2H^+(aq) + 2CrO_4^{-2}(aq) \rightleftharpoons Cr_2O_7^{-2}(aq) + H_2O(l)$$

2. What can you conclude about the reverse reaction $Cr_2O_7^{-2}(aq) \longrightarrow 2CrO_4^{-2}(aq)$ and its dependence on hydroxide ions, $OH^-(aq)$, as noted in Steps (b) and (d)? Balance the equation by adding the proper number of $OH^-(aq)$ ions and H_2O molecules to the appropriate side of the equation.

   Answer: The addition of $OH^-(aq)$ causes the equilibrium concentration of $CrO_4^{-2}(aq)$ to increase:

$$2OH^-(aq) + Cr_2O_7^{-2}(aq) \rightleftharpoons 2CrO_4^{-2}(aq) + H_2O(l)$$

QUESTIONS FOR PART II

1 From your observations in Step (f) what can you conclude about the relative equilibrium concentrations of $CrO_4^{-2}(aq)$ ion in each of the solutions 0.1 *M* $K_2Cr_2O_7$ and 0.1 *M* K_2CrO_4?

   Answer: There are $CrO_4^{-2}(aq)$ ions in each, but the concentration in $K_2Cr_2O_7$ is much less than in K_2CrO_4.

2. Use the equations you balanced in questions 1 and 2 of Part I to explain the results you obtained in Steps (c), (d), and (e) of Part II.

   Answer: In (a) and (b) we learn that $BaCr_2O_7(s)$ is much more soluble than is $BaCrO_4(s)$. Since adding $OH^-(aq)$ favors the formation of $CrO_4^{-2}(aq)$, we find that $BaCrO_4(s)$ forms when $OH^-(aq)$ is present. Adding $H^+(aq)$ favors the formation of $Cr_2O_7^{-2}$, and we find that adding $H^+(aq)$ dissolves this precipitate.

3. Make a statement summarizing your results with the chromate ion-dichromate ion equilibrium, which includes the application of the Principle of Le Chatelier.

   Answer: Using the equations

$$2OH^-(aq) + Cr_2O_7^{-2}(aq) \rightleftharpoons 2CrO_4^{-2}(aq) + H_2O(l)$$
$$2H^+(aq) + 2CrO_4^{-2}(aq) \rightleftharpoons Cr_2O_7^{-2}(aq) + H_2O(l)$$

   we can see that adding $H^+(aq)$ to the first is the same as removing $OH^-(aq)$ and that adding $OH^-(aq)$ to the second is the same as removing $H^+(aq)$. Thus the eqilibrium is shifted to counteract the imposed change—to form more $CrO_4^{-2}(aq)$ if either $OH^-(aq)$ is added or $H^+(aq)$ is removed and to form more $Cr_2O_7^{-2}(aq)$ when the reverse happens.

QUESTIONS FOR PART III

1. (a) Which substances in solution caused the color to change from that of $Cr_2O_7^{-2}(aq)$ ion to that of the $CrO_4^{-2}(aq)$ ion?
   (b) Which substances in solution caused the reverse color change?

   Answer: (a) $Ca(OH)_2$, KOH, NH_3.
   (b) CH_3COOH, HNO_3, H_2SO_4.

2. What ionic species do the solutions you listed in 1a have in common? Answer the same question for the solutions listed in 1b.

   Answer: All the solutions in 1a contain $OH^-(aq)$, and those in 1b contain $H^+(aq)$.

3. Give an explanation of the results you noted
   (a) When ethyl alcohol, C_2H_5OH, was added.
   (b) When the solution of aqueous ammonia, $NH_3(aq)$, was added.

   Answer: (a) Since no change was noted with C_2H_5OH we may conclude that it produces no $H^+(aq)$ or $OH^-(aq)$ in solution.
   (b) The observed change was that given by compounds containing $OH^-(aq)$, thus we may conclude that this change is evidence for the reaction

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

4. On the basis of your conclusion made in question 2, predict some additional substances which in solution might have the same effect on the CrO_4^{-2}-$Cr_2O_7^{-2}$ equilibrium as those you categorized in questions 1a and 1b.

   Answer: Solutions having the same effect as those in 1a would be any which have $OH^-(aq)$ in solution. Among the possibilities are NaOH, LiOH, RbOH, and CsOH. The student may also mention $Ba(OH)_2$ and $Ca(OH)_2$ but may recognize that these would give precipitates of $BaCrO_4(s)$ and $CaCrO_4(s)$.

   Solutions having the same effect as those in 1b would be any which have $H^+(aq)$ in solution. Possibilities include oxalic acid, sulfurous acid, the halogen acids, and phosphoric acid.

POSTLAB DISCUSSION. Question 3 for Part II should provide the principal basis for discussion. Place emphasis on the $H^+(aq) + OH^-(aq)$ equilibrium. You may wish to write

$$Cr_2O_7^{-2}(aq) + OH^-(aq) \rightleftharpoons 2CrO_4^{-2}(aq) + H^+(aq)$$

This is a good opportunity to mention the importance of the equilibrium between $H^+(aq)$ and $OH^-(aq)$ in biological systems as well as in many industrial processes.

Supplementary Materials

Books

1. A. R. Olson, C. W. Koch, and G. C. Pimentel, *Introductory Quantitative Chemistry*, Freeman, San Francisco (1955). See Chapter 11, especially pages 173–191. This material on titration is suggested for your use or for use by an interested student working with some guidance. The use of equivalent weights and the millimole will be new to him and will need explanation.
2. C. A. VanderWerf, *Acids, Bases, and the Chemistry of the Covalent Bond*, Reinhold, New York (1961), pp. 11–37a.
3. H. H. Sisler, *Chemistry in Non-aqueous Solvents*, Reinhold, New York (1961). Good background reading for teachers and able students.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

ACID–BASE INDICATORS

A CHEM Study film
Running Time: 19 minutes

This film was made in collaboration with Dr. J. A. Campbell. It is most suitable for presentation at the conclusion of the chapter. The film summarizes certain concepts covered previously [$H^+(aq)$ effects on indicators], applies some of them to new situations (equilibrium constants of indicators), and advances others beyond the material in the Textbook (proton transfer). A preview will help you fit the film to your needs.

Background Discussion

There are three major parts to the following discussion:

Definitions of Acids and Bases
Strengths of Acids and Bases—
Ionization Constants for Acids
The Nature of $H^+(aq)$

DEFINITIONS OF ACIDS AND BASES

Have any students asked you yet, "What is *the correct* definition for an acid?" If not, just wait; they *will.* The operational concepts of acids and bases originated with the alchemists. Many of the operational criteria described in the Textbook were listed by Robert Boyle in the heyday of the phlogiston theory. Perhaps it will seem strange that a concept so old, so common, and so useful should be plagued by at least four separate sets of definitions of an acid. It is legitimate, of course, to wonder whether there is a *best* definition of an acid.

A number of respected chemists have referred, in their writings, to the *true* definition of an acid. Somewhat more introspective scientists, including men who originated some of our current theories, have been careful to avoid such emphasis upon opinion and have placed the different systems in their proper place as *conceptual aids* used to describe experimental results. In the latter framework we can (and do) have a number of different sets of definitions of acids and bases. It seems reasonable to identify as "best" that set of definitions which interprets the pertinent experimental facts in the *simplest* and *most consistent* way. You will immediately note that this statement contains a built-in "fudge factor." The scheme which interprets the facts most simply is a matter of opinion; therefore scientists are liable to become as emotional in their views on this topic as they are in many other areas of chemistry. Most chemists agree, however, that the different systems can be arranged in order of increasing generality of application. We want to consider a number of different schemes in this light. For presentation to the students of this course, we will consider only the first two sets of definitions, the Arrhenius and the Brønsted-Lowry, since we are working primarily with water solutions. But if we were working with nonprotonic solvents or fused salts, we would find other systems, such as the Lewis theory or the solvent system, more appropriate. The selection of systems depends upon the experimental problem. Let's be dogmatic; there is no *one* correct set of definitions for either acids or bases. Various schemes are defined in subsequent sections. Different experiments are best treated in terms of whichever definition is simplest.

The Arrhenius Definitions

The Arrhenius definitions are applicable only in water solution; they constitute one of the oldest, most restrictive, and probably simplest, sets of definitions. They deserve emphasis because of the singular importance of the chemistry of aqueous solutions on this planet.

Acid: A chemical entity which gives hydrated hydrogen ion, $H^+(aq)$, in water solution, e.g., HCl, HSO_4^-, H_2SO_4, HNO_3, CH_3COOH.

Base: A chemical entity which gives hydrated hydroxide ion, $OH^-(aq)$, in water solution, e.g., $NaOH$, KOH, $Ba(OH)_2$, $[(CH_3)_4N]OH$ (tetramethylammonium hydroxide).

Salt: A substance, other than water, resulting from the neutralization of an acid by a base. Salts have also been defined as substances, other than compounds giving $H^+(aq)$ or $OH^-(aq)$, which crystallize in an ionic lattice, e.g., $NaCl$, K_2SO_4, $Ba(NO_3)_2$, K_3PO_4.

Neutralization: The reaction of an acid and a base in water to give a salt and water (*all ions aquated*):

$$Na^+ + OH^- + H^+ + Cl^- \rightleftharpoons \underbrace{Na^+ + Cl^-}_{\text{ions of salt}} + HOH$$

$$Ba^{+2} + 2OH^- + 2H^+ + 2NO_3^- \rightleftharpoons \underbrace{Ba^{+2} + 2NO_3^-}_{\text{ions of salt}} + 2HOH$$

Hydrolysis: A reaction between a compound and water in which the water molecule is split to give $OH^-(aq)$ or $H^+(aq)$, the other ion combining with the compound.

$$AlCl_3(s) + H_2O(l) \rightleftharpoons Al(OH)^{+2}(aq) + H^+(aq) + 3Cl^-(aq)$$

$$AsCl_3(l) + H_2O(l) \rightleftharpoons H_3AsO_3(aq) + 3H^+(aq) + 3Cl^-(aq)$$

$$H_3AsO_3(aq) \rightleftharpoons H^+(aq) + H_2AsO_3^-(aq)$$

Comments: The foregoing definitions are straightforward and generally familiar to you. Except for the definition of hydrolysis, they are presented in the Textbook and will be used as a *point of reference* in considering subsequent sets of definitions. Equilibrium constants described later are applicable.

The Brønsted-Lowry Definitions

They are applicable in all solvents which can give up or accept a proton. This theory is broader than the Arrhenius theory in that it considers reactions in $NH_3(l)$, CH_3OH, CH_3COOH, and many other protonic solvents *as well as water.* Water, *the* solvent in the Arrhenius theory, is now only one of many solvents which can be used in the Brønsted-Lowry system.

Acid: A cation, anion, or neutral molecule which can *donate a proton* to another (acceptor) species. The acid can be a neutral molecule,

$$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

$$HCl(g) + NH_3(l) \rightleftharpoons NH_4^+(l\ NH_3) + Cl^-(l\ NH_3)$$

an anion,

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{-2}(aq)$$

or a cation,

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O$$

Base: A cation, anion, or neutral molecule which can accept a proton from a Brønsted-Lowry acid. For example, the H_2O and the OH^- shown on the left in the illustrations of acids are functioning as bases. Other examples can be cited:

$$Na^+(aq) + \underset{\text{base anion}}{CN^-(aq)} + HOH(l) \rightleftharpoons HCN(aq) + Na^+(aq) + OH^-(aq)$$

$$HCl(g) + \underset{\substack{\text{neutral}\\ \text{base}}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

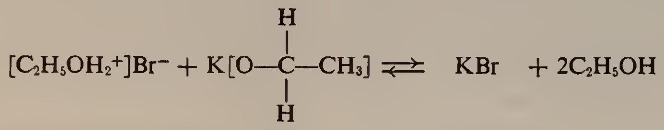
$$H_3O^+ + \underset{\text{base cation}}{[Al(H_2O)_5OH]^{+2}} \rightleftharpoons [Al(H_2O)_6]^{+3} + H_2O$$

As a consequence of this set of definitions, the process of hydrolysis described separately in the Arrhenius definitions is now only another acid–base process. (See the reaction for NaCN.) You will also notice that NaOH, classed as a base in the Arrhenius theory, is now considered as a salt which contains the base OH^-. The prime difference between NaOH and NaCN in this scheme is that the base OH^- in the salt NaOH is stronger than the base CN^- in the salt NaCN. Note the greater generality of the Brønsted-Lowry scheme.

Salt: The same definition holds as in the Arrhenius scheme.

Neutralization: The same definition holds as in the Arrhenius scheme. Neutralization is the reaction of acid and base. Reactions can take place in solvents other than water, as the following equations show.

$$\underset{\text{acid}}{NH_4Br(l\ NH_3)} + \underset{\text{base}}{KNH_2(l\ NH_3)} \rightleftharpoons \underset{\substack{\text{salt, also}\\ \text{a base}}}{KBr(l\ NH_3)} + \underset{\text{acid}}{2NH_3(l)}$$



$$\underset{\substack{\text{HBr in ethyl}\\ \text{alcohol}}}{[C_2H_5OH_2^+]Br^-} + \underset{\substack{\text{potassium}\\ \text{ethoxide}}}{K[O{-}\underset{\substack{|\\ H}}{\overset{\substack{H\\ |}}{C}}{-}CH_3]} \rightleftharpoons \underset{\substack{\text{salt, also}\\ \text{a base}}}{KBr} + \underset{\text{alcohol}}{2C_2H_5OH}$$

Solvolysis: The specific process for breaking a water molecule can now be generalized to include solvent molecules other than water. The general term *solvolysis*, rather than the more specific *hydrolysis*, is used. For example, reactions in liquid ammonia are comparable to those in water:

$$\mathrm{AlBr_3}(s) + 2\mathrm{NH_3}(l) \rightleftharpoons \mathrm{Al(NH_2)^{+2}}(l\ NH_3) + 3\mathrm{Br^-}(l\ NH_3) + \mathrm{NH_4^+}(l\ NH_3)$$

$$\mathrm{OPF_3}(g) + \mathrm{NH_3}(l) \rightleftharpoons \mathrm{OP(NH_2)_3}(l\ NH_3) + 3\mathrm{NH_4F}(s)$$

Comments: Although the Brønsted-Lowry definitions are more widely applicable, the formalism becomes somewhat more restrictive, and, as a result, details of terminology become more important. You may have noticed that this set of definitions implies something about the actual mechanism of proton transfer, yet in most reactions we know nothing of the mechanism involved. We identify only initial reactants and final products, and there is even some uncertainty about the products, since we don't really know how many H_2O molecules are associated with each ion in solution. We write H_3O^+ as a matter of convenience, but there is little evidence to support this particular formula. We could write $[H(H_2O)_n{}^+]$ as a more exact representation of the situation. The mechanistic aspect is recognized as part of our formalism. The Brønsted-Lowry concept can also be utilized outside of solution, as the reaction $\mathrm{NH_3}(g) + \mathrm{HCl}(g) \rightleftharpoons \mathrm{NH_4Cl}(s)$ suggests. One of the big advantages of the Brønsted-Lowry concept is that it recognizes and emphasizes the role of the solvent in ionization processes. From experiment we know that

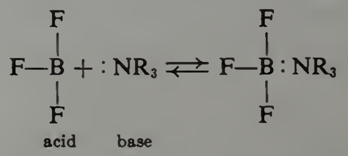
$$\mathrm{HCl}(g) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$
$$\mathrm{HCl}(g) + \text{toluene} \longrightarrow \text{no reaction}$$

The solvent *is* important.

The Lewis Definitions

The definitions proposed by G. N. Lewis are applicable in protonic as well as nonprotonic solvents and are equally applicable to reactions carried out in the absence of solvents. The formalism centers around the concept of the electron pair and the nebulous relation between bond type and acid–base behavior.

Acid: Any anion, cation, or neutral molecule that has an operationally incomplete electronic configuration and which can accept one or more *electron pairs* to form a coordinate bond. Among the simplest examples are these:



$$\mathrm{BF_3} + :\mathrm{NR_3} \rightleftharpoons \mathrm{F_3B}:\mathrm{NR_3}$$

acid base

$$\mathrm{SnCl_4} + 2\mathrm{Cl^-} \rightleftharpoons \mathrm{SnCl_6^{-2}}$$

acid base

Base: Any anion, cation, or neutral molecule which can donate an electron pair to form a coordinate bond. You will notice that, in the two examples above, the basic trialkylamine "donates" or shares an electron pair with BF_3 to give the compound F_3BNR_3, in which the F_3B and NR_3 are joined by a coordinate bond. Note that an ultimate grouping of eight electrons around the acid is *not* demanded in the Lewis system, since in the second example the Sn^{+4} shares *twelve* electrons with the six chloride ions surrounding it.

Salt: This term is not really as applicable in the Lewis system as it is in the earlier systems. If a salt must be defined, it is called an ionic solid.

Neutralization: The reaction between equivalent quantities of acid and base. The product can be a salt or any coordination compound. (The term neutralization is not really used in reference to Lewis acid–base reactions). The reaction between copper(II) ion and ammonia to form $[Cu(NH_3)]^{+2}$ is an acid–base reaction in this system.

Solvolysis: This term has no special significance in this system.

Comments: It will be noticed that the electron pair system includes all types of acid–base behavior described in all of the earlier systems. As first proposed by Lewis, the system was largely operational in character, and centered around observations of the type described. It interprets a large amount of data effectively. Confusion relative to its use may arise when attempts to interpret electron distribution and bond type are superimposed upon Lewis' original operational definition. For example, some people have noted that an electron pair may not really bind Cl^- to $AlCl_3$ in the complex $AlCl_4^-$, but the binding may be an electrostatic attraction between one Al^{+3} ion and four Cl^- ions. If this is true, then the process

$$AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$$

falls outside the strict Lewis definition of acid–base processes, since we can't identify a shared electron pair. Such problems, of course, are man-made and are not inherent in the *operational* application of the system. But the concepts of acid–base behavior *are* operational in character, and difficulties arise when we try to impose strict interpretations of electron distribution upon the definitions. Unfortunately, the pertinent data that would allow proper consideration of the questions raised are usually unavailable.

The Solvent System Definitions

The solvent system definitions are applicable in protonic as well as nonprotonic solvents. The primary emphasis is upon the solvent used, not upon the proton transfer.

Acid: Any cation, anion, or neutral molecule giving a *cation that is characteristic of the solvent.* In water, H^+ is the characteristic cation of the solvent, since water is assumed to ionize according to the equilibrium $HOH \rightleftharpoons H^+ + OH^-$. In liquid NH_3, the cation that characterizes the solvent is again H^+, since NH_3 is assumed to ionize according to the process $NH_3 \rightleftharpoons H^+ + NH_2^-$. In the nonprotonic solvent nitrosyl chloride, NOCl, the cation NO^+ is characteristic of the solvent, since the formal process $NOCl \rightleftharpoons NO^+ + Cl^-$ is assumed.

Base: Any cation, anion, or neutral molecule giving an *anion that is characteristic of the solvent.* The equations for the ionization processes in HOH, NH_3, and NOCl indicate that compounds containing ionizable or reactive OH^-, NH_2^-, and Cl^- will each be bases in the respective solvents HOH, NH_3, and NOCl.

Salt: As before, a salt is defined as an ionic solid.

Neutralization: Again, this is a process involving chemical interaction of equivalent quantities of acid and base to give a salt and one mole of the solvent.

In water:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightleftharpoons HOH + Na^+(aq) + Cl^-(aq)$$

In liquid NH_3 (each species is in liquid NH_3):

$$H^+ + Br^- + K^+ + NH_2^- \rightleftharpoons NH_3 + K^+ + Br^-$$

In liquid NOCl (each species is in liquid NOCl):

$$NO^+ + AlCl_4^- + [(CH_3)_4N]^+ + Cl^- \rightleftharpoons NOCl + [(CH_3)_4N]AlCl_4$$

Solvolysis: The specific processes for protonic molecules such as H_2O and NH_3 can now be generalized to include nonprotonic solvents. Solvolysis now implies any process which promotes breaking the solvent molecule into its ions, one of which is usually tied up chemically. Compare the following examples.

$$AlCl_3(s) + HOH(l) \rightleftharpoons [AlOH]^{+2}(aq) + H^+(aq) + 3Cl^-(aq)$$

$$AlCl_3(s) + NH_3(l) \rightleftharpoons [AlNH_2]^{+2}(solv) + H^+(solv) + 3Cl^-(solv)$$

$$AlCl_3(s) + NOCl \rightleftharpoons [AlCl_4]^-(solv) + NO^+(solv)$$

In each reaction the cation that characterizes the solvent is generated as a result of a process which formally appears to break the solvent molecule into a positive and a negative ion.

Comments: You will recognize that this system resembles the Brønsted-Lowry system but is broadened to apply to many solvents, not just water. We also achieve an increase in the formalism of the system. We now have to assume ionization of our solvents according to set patterns, and we must assume ionic mechanisms even though such an assumption may be unproved or highly doubtful. Note that all examples considered in the Arrhenius and Brønsted-Lowry systems are automatically included in the Solvent system definitions. As a means of correlating information and predicting products from reactions, this scheme has much to recommend it, but we must be careful in accepting a literal interpretation of the description of the processes considered.

Summary of Acid–Base Systems*

We can summarize what has been stated in the foregoing as follows:

	Acid	Base	Formation of Acid or Base
Arrhenius	contains H^+	contains OH^-	Ionization in water.
Brønsted-Lowry	donates H^+	accepts H^+	Donation in water.
Lewis	accepts an electron pair	donates an electron pair	Acid and base molecules come together. Can be in any solvent, but none required.
Solvent-system	gives a solvent cation	gives a solvent anion	Donation in solvent.

The first three are progressively more general. The first specifies the composition of acids, bases, and solvents; the second stipulates the solvent and, in part, the acid composition; the third implies something about acids (electron-accepting capacity) and bases (donating capacity).

STRENGTHS OF ACIDS AND BASES—IONIZATION CONSTANTS FOR ACIDS

The Textbook covers K_A for simple ionization theory of acids. The following paragraphs develop the corresponding relation for the Brønsted-Lowry view. Such material is not needed in most classes but will be helpful for interested students. The problem of the "concentration of water," dealt with very briefly in the Textbook, receives additional treatment here.

What determines the strength of an acid? Since we can't agree as to what an acid is, it should not be surprising to find that we are even more uncertain about acid strength when considered in general terms. One thing is abundantly clear, *the concept of acid strength can be defined only in terms of some rather arbitrarily selected experimental parameters.* Parameters appropriate to all systems of acids and bases have not been found, but if we restrict our interest to aqueous solutions of acids and bases, the situation becomes more encouraging. For purposes of discussion let us select a modification of the Brønsted-Lowry scheme and discuss the general acid HB in water, where B^- is any anion. The appropriate equation is then

$$HB(s, l, \text{ or } g) + (n + m)H_2O(l) = H^+(H_2O)_n(aq) + B^-(H_2O)_m(aq)$$

Both ions, H^+ and B^-, owe their stability in aqueous solution to a strong interaction with the solvent, called aquation. In the equation, we show explicitly the H_2O molecules in the first hydration sphere, these being considered to be bound much more strongly than any others. Both for $H^+(H_2O)_n$ and $B^-(H_2O)_m$, the values of n and m are unknown. We shall investigate the effect on the equilibrium expression to include, specifically, the hydration. We shall concentrate on $H^+(H_2O)_n(aq)$—since our interest is in acids at this point—by suppressing in the equation the hydration of $B^-(aq)$, even though there is no experimental evidence that the aquation of B^- (or other anions and cations) is less important than that of H^+. Hence we write

$$HB(s, l, \text{ or } g) + nH_2O(l) = H^+(H_2O)_n(aq) + B^-(aq)$$

Since we can't be sure how many water molecules will be associated with each proton, we have indicated our uncertainty by writing n as the number of water molecules involved. As you will see, the number of water molecules is unimportant, but it *is* important to recognize that

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* This is a generalized Brønsted-Lowry definition.

water serves as the reference base in all cases. We are comparing all acids by using a standard base. This simplifies our comparison tremendously. Another simplifying assumption lies in our decision to use the ionization process in the solvent water as a measure of acid strength. If we are willing to accept the aforementioned limitations, the problem of relative acid strength is subject to direct experimental attack. The concentration of cation and anion can be determined from measurements of conductivity, and the concentration of nonionized HB can be determined from stoichiometry. The concentration relationships at equilibrium can be expressed directly by the equilibrium constant for our defining equation:

$$K' = \frac{[H^+(H_2O)_n][B^-]}{[H_2O]^n[HB]}$$

We note in the above relationship the quantity $[H_2O]^n$; it is the only quantity not specifically mentioned in our discussion of measurement. What is the concentration of water in an aqueous solution? What is the value of n? Let's consider the second question first. The absolute value of n escapes us at the present time ($n = 4$ seems to have stronger support than $n = 1$), but we feel safe in assuming that n is the same for the proton, regardless of its source. That is, *the number of water molecules around an H⁺ ion will be the same whether the proton comes from HCl, H_2SO_4, or HNO_3, etc., in water solution.* Let's look at the first question now. The laws of stoichiometry will permit us to estimate the "concentration" of water in various solutions in terms of number of moles of water per liter of solution. Several representative calculations are summarized in Table I. Examine carefully the columns set in boldface type in Table 11-I. You will note that the "concentration" of water in all solutions is relatively constant and changes only about 3.5% as we go from pure water to 1.0 M H_2SO_4. In more dilute solutions, changes are trivial. As a simplification, let us neglect these small changes in the concentration of water and write

$$K' = \frac{[H^+(H_2O)_n][B^-]}{[H_2O]^n[HB]} = \frac{[H^+(H_2O)_n][B^-]}{C^n[HB]}$$

where C is now the concentration of water and is assumed to be constant at about 55.5* moles/liter.

We can simplify the previous equation.

$$K' \times C^n = \frac{[H^+(H_2O)_n][B^-]}{[HB]} = K_A = \frac{[H^+(aq)][B^-]}{[HB]}$$

We find then that, for an acid, the term for the water concentration is included as part of the ionization constant. For this reason, it is important to note that we haven't overlooked the concentration of water in writing our equilibrium constant but have included the constant value C^n in our value of K_A.

Our values of K_A then give a quantitative esti-

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* Because of uncertainties in the "activity" of water in aqueous solutions, we don't know the exact value of C^n, but this is unimportant as long as it is reasonably constant. The constant K_A is the measurable quantity, and because of variations in activity of both positive and negative ions, as well as HB and water, K_A shows a gradual variation as the concentration of the solution changes.

Table 11-I. **Concentration of Water in Some Common Acidic and Basic Solutions**

Acid Solution	Density (g/liter)	Acid Present (g/liter)	H_2O (g/liter)	H_2O (moles/liter)	Base Solution	Density (g/liter)	Base Present (g/liter)	H_2O (g/liter)	H_2O (moles/liter)
Pure H_2O	1000	0	1000	**55.5**	Pure H_2O	1000	0	1000	**55.5**
0.1 M HCl	1001	3.6	997	**55.5**	0.1 M NaOH	1004	4	1000	**55.5**
0.1 M H_2SO_4	1005	9.8	995	**55.4**	0.1 M $Ba(OH)_2$	1015	17	998	**55.5**
0.5 M HCl	1008	18.0	990	**55.0**	0.5 M NaOH	1021	20	1001	**55.5**
0.5 M H_2SO_4	1032	48.0	984	**54.6**	0.5 M $Ba(OH)_2$	—	—	—	—
1.0 M HCl	1018	36.5	981	**54.5**	1.0 M NaOH	1042	40	1002	**55.6**
1.0 M H_2SO_4	1061	96.0	965	**53.6**	1.0 M $Ba(OH)_2$	—	—	—	—

mate of the strength of an acid. A large value of K_A indicates a *strong* acid; a small value of K_A indicates a *weak* acid. (Remember that 10^4 is *larger* than 10^2, but 10^{-4} is *smaller* than 10^{-2}.) Acids can then be arranged in order of decreasing acid strength as shown in the Textbook (p. 191).

The special case of water as an acid is interesting because it provides the foundation for one scale for reporting $[H^+]$ in water solution—the *p*H scale. *Water is an acid.* Let us examine the implications of this statement. If water is an acid it should undergo some ionization to yield H^+ and OH^- in accordance with the equation

$$HOH + nHOH = [H^+(H_2O)_n] + OH^-(aq)$$

or

$$HOH + nHOH = H^+(aq) + OH^-(aq)$$

The earlier arguments given for the general acid H*B* indicate that we can safely write

$$HOH = H^+(aq) + OH^-(aq).$$

The equilibrium constant is

$$K' \times C^n = K_A = \frac{[H^+][OH^-]}{[HOH]} = \frac{[H^+][OH^-]}{C}$$

Thus

$$K' \times C^n \times C = K_A \times C = [H^+][OH^-] = K_w$$

which is the expression given as equation (*8*) in the Textbook (p. 181). Note that K_A differs from K_w by the factor *C*.

In discussing the *p*H scale and the conversion of $[H^+]$ values to *p*H, a review of logarithms and the material on exponents in Appendix 5 of the Laboratory Manual will be helpful. A typical problem might ask: What is the $[H^+]$ value for a solution of $pH = 5$? From the definition of *p*H we know that a solution of $pH = 5$ has an $[H^+]$ of 10^{-5}. A related question is: What is the $[H^+]$ for a solution of $pH = 4.75$? We know by inspection that the value will be close to that for the solution of $pH = 5$, so this will immediately serve as a rough check on our answer. The $[H^+] = 10^{-4.75}$ by definition of *p*H. Since we add exponents in multiplying, we can write

$$10^{-4.75} = 10^{0.25} \times 10^{-5.00}$$

or

$$[H^+] = 1.8 \times 10^{-5}$$

If we use the Brønsted-Lowry definition of a base, we must again select a common acid and a standard solvent for comparison of base strengths. If we take advantage of the fact that water can either lose or gain a proton, we can then use water as a standard acid, much as we used it as a standard base in our study of acids. The key equation becomes

$$B^- + HOH \rightleftharpoons HB + OH^-$$

(You will note that this is simply the hydrolysis equation for the ion B^- in terms of the Arrhenius definitions.) If the above equation proceeds to the right rather strongly, B^- is a strong base; if the reaction doesn't proceed to any measurable extent, B^- is a weak base. The equilibrium constant will again be useful.

Writing the equilibrium expression

$$K' = \frac{[HB][OH^-]}{[B^-][HOH]}$$

we can take advantage of our relatively constant value of [HOH], giving

$$K'[HOH] = K \times C = \frac{[HB][OH^-]}{[B^-]} = K_{hyd} \text{ or } K_B$$

We next substitute the relation

$$[OH^-] = \frac{10^{-14}}{[H^+]}$$

from the relation $[H^+][OH^-] = 10^{-14}$ and we get

$$K_B = \frac{[HB]\,10^{-14}}{[B^-][H^+]} = \frac{10^{-14}}{K_A}$$

Again, a large value of K_B indicates a strong base, and a small value indicates a weak base.

THE NATURE OF $H^+(aq)$

Because of the great practical importance of aqueous acid solutions, a vast amount of study has been devoted to the identification of the important species in them. The question has come down to clarification of the structure represented by $H^+(aq)$. There is great appeal to the proposal that the species is a unique one *and* that it is H_3O^+. One of the big advantages in using H_3O^+ is pedagogic, but it would not be fair to use this symbolism so exclusively and consistently that the student is left with a strong impression that the issue is settled beyond doubt. In fact, in view of the considerable doubt that does remain, your discussion of $H^+(aq)$ presents a desirable opportunity to stress the many important chemical problems that remain unsolved.

A wide variety of suitable methods exists for the identification of molecular species. A list of these follows, with brief comments on their application to the $H^+(aq)$ problem. References (indicated by number) are given at the end.

Nuclear Magnetic Resonance

Two research groups (1, 2) have made NMR studies of strong acid solutions. They interpret their data in terms of H_3O^+ but do not allow for hydrogen bonding, an effect expected to be as large as the effects attributed to H_3O^+.

Solid $HClO_4 \cdot H_2O$ gives a NMR pattern which has been reported (3) to show H_3O^+ in the crystal. Aside from our preference for knowing the structure in solution rather than in a solid, the data yield only average interproton distances around a central oxygen atom.

Infrared

The paper based on this technique (4) has been criticized (5) because some solutions were so concentrated there was a shortage of H_2O to form such species as $H_9O_4^+$ and H_3O^+, and in the less concentrated samples the bands attributed to H_3O^+ were absent.

Mass Spectroscopy

Acid solutions have been vaporized and the gas shown to contain relatively large amounts of $H_9O_4^+$ and H_3O^+, with smaller amounts of $H_6O_2^+$ and $H_7O_3^+$. Thus the hydrated species are shown to exist in the gaseous state.

Relaxation Methods

Data from sound adsorption, dielectric dispersion, and similar measurements have been reviewed (4) with the conclusion that $H_9O_4^+$ is the predominant species in solution (if sufficient water is present). It is not clear whether there is a pyramidal or tetrahedral arrangement of four water molecules.

This résumé indicates that the existence of H_3O^+ as the unique and predominant species in aqueous acids cannot be considered more than a working hypothesis. The 1958 review (5) concludes that the best evidence is for $H_9O_4^+$, but it is not unique.

REFERENCES

1. H. S. Gutowsky and A. Saika, Dissociation, chemical exchange, and the proton magnetic resonance in some aqueous electrolytes, *J. Chem. Phys.*, 21, 1688 (1953).
2. G. C. Hood, O. Redlich, and C. A. Reilly, Ionization of strong electrolytes III. Proton magnetic resonance in nitric, perchloric, and hydrochloric acids, *J. Chem. Phys.*, 22, 2067 (1954).
3. J. A. S. Smith and R. E. Richards, Nuclear magnetic resonance spectra of some inorganic hydrates, *Trans. Faraday Soc.*, 48, 307, 675 (1952).
4. M. Falk and P. A. Giguère, Infrared spectrum of the H_2O^+ ion in aqueous solutions, *Can. J. Chem.*, 35, 1195 (1957).
5. M. Eigen and L. De Maeyer, Self-dissociation and protonic charge transport in water and ice, *Proc. Roy. Soc.* (*London*), 247, 505 (1958).

Answers to Exercises and Problems

Ex. 11-1. Show that the addition of 0.010 mole of solid NaOH to 1.0 liter of water reduces the concentration of $H^+(aq)$ to 1.0×10^{-12} *M*.

Answer

The concentration of ions formed from the strong electrolyte NaOH will be equal to the number of moles of NaOH added divided by the volume.

$$[Na^+] = [OH^-] = \frac{0.010 \text{ mole}}{1.0 \text{ liter}} = 0.010\ M$$

Hydroxide ions are added, raising $[OH^-]$ to 0.010 *M*, and, according to (*16*) in the Textbook, the $[H^+]$ must drop.

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.010} = \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-2}}$$

$$[H^+] = 1.0 \times 10^{-12}\ M$$

Ex. 11-2. Suppose that 3.65 grams of HCl are dissolved in 10.0 liters of water. What is the value of $[H^+]$? Use expression (15) to show that $[OH^-] = 1.00 \times 10^{-12}$ *M*.

Answer

The concentrations of ions formed from the strong electrolyte HCl will be equal to the number of moles of HCl divided by the volume.

$$3.65 \text{ g HCl} = \frac{3.65 \text{ g}}{36.5 \text{ g/mole}} = 0.100 \text{ mole HCl}$$

$$[H^+] = [Cl^-] = \frac{0.100 \text{ mole}}{10.0 \text{ liters}} = 0.0100\ M$$

$$= 1.00 \times 10^{-2}\ M$$

$$[H^+] = 1.00 \times 10^{-2}\ M$$

Since $H^+(aq)$ ions are added, the concentration of OH^- drops.

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-2}} = 1.00 \times 10^{-12}$$

$$[OH^-] = 1.00 \times 10^{-12}\ M$$

Ex. 11-3. The color of a solution of potassium chromate, K_2CrO_4, changes to the color of a solution of potassium dichromate, $K_2Cr_2O_7$, when a few drops of HCl solution are added. Write the balanced equation for the reaction between $CrO_4^{-2}(aq)$ and $H^+(aq)$ to produce $Cr_2O_7^{-2}$, and explain the color change on the basis of Le Chatelier's Principle.

Answer

The balanced equation is

$$2CrO_4^{-2}(aq) + 2H^+(aq) \rightleftarrows Cr_2O_7^{-2} + H_2O$$

We see that $H^+(aq)$ is a reactant. Adding HCl changes its concentration by a very large factor, and hence changes the equilibrium concentrations to favor the product $Cr_2O_7^{-2}$.

In class discussion this can be developed in terms of the equilibrium expression to prepare the student for quantitative problems.

$$K = \frac{[Cr_2O_7^{-2}]}{[CrO_4^{-2}]^2[H^+]^2}$$

or

$$\frac{[Cr_2O_7^{-2}]}{[CrO_4^{-2}]^2} = K \times [H^+]^2$$

Thus raising $[H^+]$ requires that $[Cr_2O_7^{-2}]$ become larger and that $[CrO_4^{-2}]$ become smaller. Be sure this point is not missed; this example shows how equilibrium concentrations can be controlled by variation of $[H^+(aq)]$.

Ex. 11-4. Suppose that 0.099 mole of solid NaOH is added to 0.100 liter of 1.00 *M* HCl.

(a) How many *more* moles of HCl are present in the solution than moles of NaOH?
(b) From the excess number of moles and the volume, calculate the concentration of excess $H^+(aq)$.
(c) Calculate the excess concentration of $H^+(aq)$ from the difference between the initial concentrations of HCl and NaOH.
(d) Calculate the concentration of $OH^-(aq)$ at equilibrium (see your calculations for Ex. 11-2).

Answer

(a) There is 0.100 mole of HCl in 0.100 liter of 1.00 *M* HCl. We added 0.099 mole of NaOH. There is an excess of 0.100 − 0.099 = 0.001 mole of HCl.

(b) The concentration of excess $H^+(aq)$ is

$$\text{excess } [H^+] = \frac{\text{moles excess } H^+}{\text{volume}} = \frac{0.001 \text{ mole}}{0.100 \text{ liter}}$$

$$= 0.01\ M$$

(c) The initial concentration of $H^+(aq) = 1.00\ M$. The initial concentration of $NaOH(aq)$ is

$$\frac{\text{moles NaOH added}}{\text{volume}} = \frac{0.099}{0.100} = 0.99\ M$$

$$\begin{aligned}\text{excess }[H^+] &= \text{initial }[H^+] - \text{initial }[OH^-]\\ &= 1.00 - 0.99\\ &= 0.01\ M\end{aligned}$$

(d) We have, in Ex. 11-2, shown that at equilibrium a solution containing 0.01 M $H^+(aq)$ has a hydroxide ion concentration of $1 \times 10^{-12}\ M$. Note that this exercise warrants class discussion to ensure that students understand why it is permissible to subtract concentrations in moles/liter in calculating the excess $[H^+]$.

Ex. 11-5. Which of the following acids is the strongest acid and which the weakest?

nitrous acid, HNO_2; $K_{HNO_2} = 5.1 \times 10^{-4}$
sulfurous acid, H_2SO_3; $K_{H_2SO_3} = 1.7 \times 10^{-2}$
phosphoric acid, H_3PO_4; $K_{H_3PO_4} = 7.1 \times 10^{-3}$

Answer

The strength of the acid is revealed by K_A. The strongest acid of the three is that with the largest value of K_A. Hence sulfurous acid is strongest, and nitrous acid is weakest.

Pr. 1. What is the concentration of $H^+(aq)$ in an aqueous solution in which $[OH^-] = 1.0 \times 10^{-3}\ M$?

Answer

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-3}} = 1.00 \times 10^{-11}\ M$$

Pr. 2. 100 ml of the HCl solution described in Exercise 11-2 (p. 182) is diluted with water to 1.00 liter. What is the concentration of $H^+(aq)$? What is $[OH^-]$ in this solution?

Answer

The HCl solution in Ex. 11-2 is 0.0100 M. The dilution reduces $[H^+]$ to 0.00100 M, or $1.00 \times 10^{-3}\ M$.

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-3}} = 1.00 \times 10^{-11}$$

Pr. 3. Vinegar, lemon juice, and curdled milk all taste sour. What other properties would you expect them to have in common?

Answer

(i) They should contain hydrogen-containing compounds.
(ii) Their aqueous solutions should conduct electricity.
(iii) Their aqueous solutions should liberate hydrogen gas when zinc metal is put in them.
(iv) Their aqueous solutions should turn litmus red.

Pr. 4. Give the name and formula of three hydrogen containing compounds that are not classified as acids. State for each compound one or more properties common to acids that it does not possess.

Answer

Among the possible answers are:

Hydrogen gas, H_2	Aqueous solutions do not conduct.
Sugar, $C_{12}H_{22}O_{11}$	Lacks sourness; solutions do not conduct.
Methane, CH_4	In contact with zinc in pipes, it does not release hydrogen gas.
Sodium hydroxide, NaOH	Lacks sourness.

Pr. 5. As a solution of barium hydroxide is mixed with a solution of sulfuric acid, a white precipitate forms, and the electrical conductivity decreases markedly. Write equations for the reactions that occur, and account for the conductivity change.

Answer

$BaSO_4(s)$ precipitates, and H_2O forms. Both reactions reduce the number of ions. The electrical conductivity drops because there are fewer ions to carry the current.

Note: This question is based on the suggested demonstration on p. 344.

Pr. 6. An eyedropper is calibrated by counting the number of drops required to deliver 1.0 ml. Twenty drops are required.

(a) What is the volume of one drop?
(b) Suppose one such drop of 0.20 M HCl is added to 100 ml of water. What is $[H^+]$?
(c) By what factor did $[H^+]$ change when the one drop was added?

Answer: (c) 1000.

Answer

(a) Since twenty drops = 1.0 ml,

$$1 \text{ drop} = \frac{1.0}{20} = 0.050 \text{ ml (average)}$$

(b) $$\begin{aligned}0.050 \text{ ml} &= 5.0 \times 10^{-2} \text{ ml}\\ &= 5.0 \times 10^{-5} \text{ liter}\end{aligned}$$

$$(5.0 \times 10^{-5}\ \text{liter})\left(0.20\ \frac{\text{mole}}{\text{liter}}\right) = 1.0 \times 10^{-5}\ \text{mole HCl}$$

$$[\text{H}^+] = \frac{1.0 \times 10^{-5}\ \text{mole}}{0.100\ \text{liter}} = 1.0 \times 10^{-4}\ M$$

(c) $[\text{H}^+]$ changed from $1.0 \times 10^{-7}\ M$ to $1.0 \times 10^{-4}\ M$. The factor of change is

$$\frac{1.0 \times 10^{-4}}{1.0 \times 10^{-7}} = 1000$$

Pr. 7. Suppose drops (from the same eyedropper) of 0.10 *M* NaOH are added, one at a time, to the 100 ml of HCl in Problem 6b.

(a) What will be $[\text{H}^+]$ after one drop is added?
(b) What will be $[\text{H}^+]$ after two drops are added?
(c) What will be $[\text{H}^+]$ after three drops are added?

Answer

The solution initially contains 1.0×10^{-5} mole of HCl, and as base is added, the reaction $\text{H}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}$ occurs. Each drop of base solution adds 0.050 ml, or 5.0×10^{-5} liter, of solution, or

$$(5.0 \times 10^{-5})\left(0.10\ \frac{\text{mole}}{\text{liter}}\right) = 5.0 \times 10^{-6}\ \text{mole NaOH}$$

(a) After one drop of NaOH is added, the solution contains an excess of $\text{H}^+(aq)$, found to be 1.0×10^{-5} mole HCl $-$ 0.50×10^{-5} mole NaOH. Reaction consumes most of the OH^- added, leaving the excess 0.50×10^{-5} moles $\text{H}^+(aq)$ in the 100 ml.

$$[\text{H}^+] = \frac{0.50 \times 10^{-5}\ \text{mole}}{0.100\ \text{liter}} = 5.0 \times 10^{-5}\ M$$

(b) After two drops of NaOH are added, there is excess of neither $\text{H}^+(aq)$ nor $\text{OH}^-(aq)$. Since $[\text{H}^+] = [\text{OH}^-]$, we then have

$$[\text{H}^+] = \sqrt{K_w} = 1.0 \times 10^{-7}\ M$$

(c) With three drops of NaOH solution, there is an excess of $\text{OH}^-(aq)$, since 1.5×10^{-5} mole NaOH was added to the original 1.0×10^{-5} mole HCl. The excess, 0.5×10^{-5} mole $\text{OH}^-(aq)$, is present in 100 ml, thus the hydroxide ion concentration is

$$[\text{OH}^-] = \frac{0.5 \times 10^{-5}}{0.100} = 5 \times 10^{-5}\ M$$

Hence

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10}\ M$$

Pr. 8. Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ in a solution made by mixing 50.0 ml 0.200 *M* HCl and 49.0 ml 0.200 *M* NaOH.

Answer: $[\text{OH}^-] = 5 \times 10^{-12}\ M$.

Answer

$$\text{Moles HCl} = \left(\frac{50.0}{1000}\ \text{liter}\right) \times \left(0.200\ \frac{\text{mole}}{\text{liter}}\right) = 1.00 \times 10^{-2}$$

$$\text{Moles NaOH} = \left(\frac{49.0}{1000}\ \text{liter}\right) \times \left(0.200\ \frac{\text{mole}}{\text{liter}}\right) = 0.980 \times 10^{-2}$$

$$\text{Excess moles HCl} = (1.00 \times 10^{-2} - 0.98 \times 10^{-2}) = 0.02 \times 10^{-2}$$

$$[\text{H}^+] = \frac{0.02 \times 10^{-2}}{0.099} = 0.002\ M$$

$$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{0.002} = 5 \times 10^{-12}\ M$$

Pr. 9. Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ in a solution made by mixing 50.0 ml 0.200 *M* HCl and 49.9 ml 0.200 *M* NaOH.

Answer

$$\text{Moles HCl} = \left(\frac{50.0}{1000}\ \text{liter}\right) \times \left(0.200\ \frac{\text{mole}}{\text{liter}}\right) = 1.00 \times 10^{-2}$$

$$\text{Moles NaOH} = \left(\frac{49.9}{1000}\ \text{liter}\right) \times \left(0.200\ \frac{\text{mole}}{\text{liter}}\right) = 0.998 \times 10^{-2}$$

$$\text{Excess moles HCl} = (1.00 \times 10^{-2} - 0.998 \times 10^{-2}) = 0.002 \times 10^{-2}$$

$$[\text{H}^+] = \frac{2 \times 10^{-5}}{0.0999} = 2 \times 10^{-4}\ M$$

$$[\text{OH}^-] = \frac{1.00 \times 10^{-14}}{2 \times 10^{-4}} = 5 \times 10^{-11}\ M$$

Pr. 10. How much more 0.200 *M* NaOH solution need be added to the solution in Problem 9 to change $[\text{H}^+]$ to $10^{-7}\ M$?

Answer

Enough to make the number of moles of HCl and NaOH exactly equal. This is $50.0 - 49.9 = 0.1$ ml NaOH.

Pr. 11. An acid is a substance H*B* that can form $\text{H}^+(aq)$ in the equilibrium

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$$

(a) Does equilibrium favor reactants or products for a strong acid?

(b) Does equilibrium favor reactants or products for a very weak acid?

(c) If acid HB_1 is a stronger acid than acid HB_2, is K_1 a larger or smaller number than K_2?

$$K_1 = \frac{[H^+][B_1^-]}{[HB_1]} \qquad K_2 = \frac{[H^+][B_2^-]}{[HB_2]}$$

Answer

(a) Products.

(b) Reactants.

(c) K_1 is a larger number than K_2.

Pr. 12

(a) Which of the following acids is the strongest, and which is the weakest?
Ammonium ion, NH_4^+ (in an NH_4Cl solution);
Bisulfate ion, HSO_4^- (in a $KHSO_4$ solution);
Hydrogen sulfide, H_2S.

(b) If 0.1 M solutions are made of NH_4Cl, $KHSO_4$, and H_2S, in which will $[H^+]$ be highest, and in which will it be lowest?

Answer

(a) From Textbook Table 11-IV, we find

$K_{HSO_4^-} = 1.3 \times 10^{-2}$
(strongest of the three);
$K_{H_2S} = 1.0 \times 10^{-7}$;
$K_{NH_4^+} = 5.7 \times 10^{-10}$
(weakest of the three).

(b) $[H^+]$ is largest in the HSO_4^- solution.
$[H^+]$ is smallest in the NH_4^+ solution.

Pr. 13

(a) Nitric acid is a very strong acid. What is $[H^+]$ in a 0.050 M HNO_3 solution?

(b) Hydrogen peroxide, H_2O_2, is a very weak acid. What is $[H_2O_2]$ in a 0.050 M H_2O_2 solution?

Answer

(a) Since HNO_3 is a very strong acid, products are much favored, and practically all of the acid is in the form of ions, $H^+(aq)$ and $NO_3^-(aq)$. Therefore $[H^+] = 0.050\ M$.

(b) Since H_2O_2 is a very weak acid, reactants are much favored, and practically all of the acid is in the form of undissociated acid, $H_2O_2(aq)$. Therefore $[H_2O_2] = 0.050\ M$.

Pr. 14. From a study of Appendix 2, what generalization can you make concerning acids which contain more than one atom of hydrogen in their molecules or ions?

Answer

The acid donating the first proton is much stronger than the second, which is in turn stronger than the third. Pauling quotes about 10^5 for the ratio of succeeding steps; i.e.,

$$\frac{K_A\text{ (1st H)}}{K_A\text{ (2nd H)}} \text{ is about } 10^5$$

$$\frac{K_A\text{ (2nd H)}}{K_A\text{ (3rd H)}} \text{ is about } 10^5$$

Pr. 15. A 0.25 M solution of benzoic acid (symbolize it HB) is found to have a hydrogen ion concentration $[H^+] = 4 \times 10^{-3}\ M$.

(a) Assuming the simple reaction $HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$, calculate K_A for benzoic acid.

(b) Compare the values of $[HB]$, $[H^+]$, $[B^-]$, and K_A used in this problem to the corresponding quantities in the benzoic acid calculation presented in the text, Section 11-3.2.

Answer

(a) Since the only source of $H^+(aq)$ gives an equal amount of $B^-(aq)$, we can write $[H^+] = [B^-]$. Furthermore, the amount of $H^+(aq)$ formed is negligible compared to 0.25 M. Hence

$$K_A = \frac{[H^+][B^-]}{[HB]} = \frac{[H^+]^2}{[HB]} = \frac{(4 \times 10^{-3})^2}{(0.25)}$$

$$= \frac{16 \times 10^{-6}}{0.25} = 6.4 \times 10^{-5}$$

(b) Used in this problem,
$[HB] = 0.25\ M$
$[H^+] = [B^-] = 4 \times 10^{-3}\ M$
$K_A = 6.4 \times 10^{-5}$
Used in Sec. 11-3.2,
$[HB] = 0.010\ M$
$[H^+] = [B^-] = 8 \times 10^{-4}\ M$
$K_A = 6.4 \times 10^{-5}$

Pr. 16. If 23 grams of formic acid, HCOOH, are dissolved in 10.0 liters of water at 20°C, the $[H^+]$ is found to be $3.0 \times 10^{-3}\ M$. Calculate K_A.

Answer

If the concentrations are known, we can determine K_A in the following manner:

$$HCOOH \longrightarrow H^+ + HCOO^-$$

$$K_A = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

We know that $[H^+] = 3.0 \times 10^{-3}\ M$.
We also know that $[HCOO^-] = [H^+]$.
We can find [HCOOH] as follows:

$$\frac{23\text{ g}}{10\text{ liter}} \times \frac{1\text{ mole}}{46\text{ g}} = 0.50\ \frac{\text{mole}}{10\text{ liter}} = 0.050\ \frac{\text{mole}}{\text{liter}}$$

Since $[H^+] = 3.0 \times 10^{-3}$, and since all this came from HCOOH, the [HCOOH] must change from 0.050 to $(0.050 - 0.0030) = 0.047\ M$. Then

$$K_A = \frac{(3.0 \times 10^{-3})^2}{4.7 \times 10^{-2}} = 1.9 \times 10^{-4}$$

Pr. 17. A chemist dissolved 25 grams of CH_3COOH in enough water to make one liter of solution. What is the concentration of this acetic acid solution? What is the concentration of $H^+(aq)$? Assume a negligible change in $[CH_3COOH]$ because of dissociation to $H^+(aq)$.

Answer

$$\frac{25\text{ g}}{\text{liter}} \times \frac{1\text{ mole}}{60\text{ g}} = 0.42\ \frac{\text{mole}}{\text{liter}}\text{ or }0.42\ M$$

$$CH_3COOH \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$K_A = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Let $y = [H^+]$. Then,
$[H^+] = [CH_3COO^-] = y$
$[CH_3COOH] = 0.42 - y$
Since we may ignore y, we may write

$$\frac{y^2}{0.42} = 1.8 \times 10^{-5}$$

$$y = \sqrt{7.56 \times 10^{-6}} = 2.75 \times 10^{-3}\ M = [H^+]$$

Pr. 18. When sodium acetate, CH_3COONa, is added to an aqueous solution of hydrogen fluoride, HF, a reaction occurs in which the weak acid HF loses H^+.

(a) Write the equation for the reaction.
(b) What weak acid is competing with HF for H^+?

Answer: (b) CH_3COOH, acetic acid.

Answer

(a) $HF(aq) + CH_3COO^-(aq) \rightleftharpoons F^-(aq) + CH_3COOH(aq)$
(b) CH_3COOH

Pr. 19.

(a) Write the equation for the reaction that shows the acid-base reaction between hydrogen sulfide, H_2S. and carbonate ion, CO_3^{-2}.
(b) What are the two acids competing for H^+?
(c) From the values of K_A for these two acids (see Table 11-IV), predict whether the equilibrium favors reactants or products.

Answer: (c) Products.

Answer

(a) $H_2S(aq) + CO_3^{-2}(aq) \rightleftharpoons HS^-(aq) + HCO_3^-(aq)$
(b) H_2S and HCO_3^-, hydrogen sulfide and bicarbonate ion.
(c) K_A for $H_2S = 1.0 \times 10^{-7}$.
K_A for $HCO_3^- = 4.7 \times 10^{-11}$.

Since H_2S releases H^+ much more readily than does HCO_3^-, the reaction favors products, $HS^-(aq)$ and $HCl_3^-(aq)$.

Pr. 20. Write the equations for the reaction between each of the following acid-base pairs. For each reaction, predict whether reactants or products are favored (using the values of K_A given in Appendix 2).

(a) $HNO_2(aq) + NH_3(aq) \rightleftharpoons$
(b) $NH_4^+(aq) + F^-(aq) \rightleftharpoons$
(c) $C_6H_5COOH(aq) + CH_3COO^-(aq) \rightleftharpoons$

Answer: (a) $HNO_2(aq) + NH_3(aq) \rightleftharpoons NO_2^-(aq) + NH_4^+(aq)$
Products, $NO_2^-(aq)$ and $NH_4^+(aq)$ favored.

Answer

(a) $HNO_2(aq) + NH_3(aq) \rightleftharpoons NO_2^-(aq) + NH_4^+(aq)$
$K_A(HNO_2) = 5.1 \times 10^{-4}$
$K_A(NH_4^+) = 5.7 \times 10^{-10}$
Products favored.
(b) $NH_4^+(aq) + F^-(aq) \rightleftharpoons HF(aq) + NH_3(aq)$
$K_A(NH_4^+) = 5.7 \times 10^{-10}$
$K_A(HF) = 6.7 \times 10^{-4}$
Reactants favored.
(c) $C_6H_5COOH(aq) + CH_3COO^-(aq) \rightleftharpoons C_6H_5COO^-(aq) + CH_3COOH(aq)$
$K_A(C_6H_5COOH) = 6.6 \times 10^{-5}$
$K_A(CH_3COOH) = 1.8 \times 10^{-5}$
The reaction favors products, but very little, since the K's are nearly the same.

Pr. 21. Write the equations for the reactions between each of the following acid–base pairs. For each reaction, predict whether reactants or products are favored.

(a) $H_2SO_3(aq) + HCO_3^-(aq) \rightleftharpoons$
(b) $H_2CO_3(aq) + SO_3^{-2}(aq) \rightleftharpoons$
(c) $H_2SO_3(aq) + SO_3^{-2}(aq) \rightleftharpoons$

Answer

(a) $H_2SO_3(aq) + HCO_3^-(aq) \rightleftharpoons HSO_3^-(aq) + H_2CO_3(aq)$
$K_A(H_2SO_3) = 1.7 \times 10^{-2}$
$K_A(H_2CO_3) = 4.4 \times 10^{-7}$
Products favored.

(b) $H_2CO_3(aq) + SO_3^{-2}(aq) \rightleftharpoons HCO_3^-(aq) + HSO_3^-(aq)$
$K_A(H_2CO_3) = 4.4 \times 10^{-7}$
$K_A(HSO_3^-) = 6.2 \times 10^{-8}$
Products favored, but very little.

(c) $H_2SO_3(aq) + SO_3^{-2}(aq) \rightleftharpoons 2HSO_3^-(aq)$
$K_A(H_2SO_3) = 1.7 \times 10^{-2}$
$K_A(HSO_3^-) = 6.2 \times 10^{-8}$
Products favored.

Pr. 22. If the pH of a solution is 5, what is $[H^+]$? Is the solution acidic or basic?

Answer

Since $pH = -\log [H^+]$ and $pH = 5$, then

$$[H^+] = 10^{-5} \frac{\text{mole}}{\text{liter}}$$

The solution is acidic, since 10^{-5} is greater than 10^{-7} M.

Pr. 23. What is $[H^+]$ in a solution of $pH = 8$? Is the solution acidic or basic? What is $[OH^-]$ in the same solution?

Answer

Since $pH = -\log [H^+]$ and $pH = 8$, then

$$[H^+] = 10^{-8} \frac{\text{mole}}{\text{liter}}$$

The solution is basic, since $[H^+]$ is less than 10^{-7} M.

Since, at 25°C,

$[H^+][OH^-] = 10^{-14}$

then

$$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-6}\ M$$

Pr. 24. Devise an operational and also a conceptual definition of a gas.

Answer

Operational definition: Gases
are easily compressed,
have low density, and
diffuse until they uniformly fill a container.
The definition can include other observed properties.

Conceptual definition: Gases consist of molecular particles which possess very little attraction for each other.

Suggested Quiz Problems

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

1. Which one of the following properties would a solution have if it is an acid?

   (1) Solution turns litmus blue.
   (2) Solution tastes bitter.
   (3) Solution has a hydrogen ion concentration of 10^{-13} *M*.
   (4) Solution is a very good conductor of electricity.
   (5) Solution feels slippery.

   Answer: (4).

2. Which one of the following would be possible for both strongly acidic and strongly basic solutions?

   (1) Solution has a hydrogen ion concentration of 10^{-7} *M*.
   (2) Solution turns litmus red.
   (3) Solution tastes sour.
   (4) Solution is a very good conductor of electricity.
   (5) Solution reacts with Mg to liberate hydrogen.

   Answer: (4).

3. If an unknown solution is known to be either dilute nitric, hydrochloric, or sulfuric acid, it can be positively identified as sulfuric acid by adding which of the following?

   (1) $NH_3(aq)$ to obtain $NH_4^+(aq)$.
   (2) An indicator to determine the $[H^+]$.
   (3) A drop of $AgNO_3$ solution to see if a precipitate forms.
   (4) CH_3COONa solution to form $CH_3COOH(aq)$.
   (5) $Ba(NO_3)_2$ solution to see if a precipitate forms.

   Answer: (5).

4. Given a 0.1 *M* HCl solution,

   (1) What is the $[H^+]$?
   (2) What is the $[OH^-]$?

   Answer

   (1) $HCl \rightleftharpoons H^+(aq) + Cl^-(aq)$
   If we assume HCl to be 100% dissociated, then
   $[H^+] = 0.1$ mole/liter
   (2) $K_w = [H^+][OH^-] = 10^{-14}$
   Thus
   $$[OH^-] = \frac{10^{-14}}{10^{-1}} = 10^{-13} \text{ mole/liter}$$

5. Given a 0.01 *M* NaOH solution,

   (1) What is the $[OH^-]$?
   (2) Calculate the $[H^+]$.

   Answer

   (1) If we assume the NaOH to be 100% dissociated, then
   $[OH^-] = 10^{-2}$ mole/liter
   (2) $[H^+][OH^-] = 10^{-14}$
   $[H^+] = 10^{-12}$ mole/liter

6. The $[H^+]$ of a 0.1 *M* solution of a weak acid, HF, is found to be 8.2×10^{-3} *M*. Let the following equation represent the reaction between the weak acid and water.

   $$HF \rightleftharpoons H^+(aq) + F^-(aq)$$

   (1) What is the concentration of the fluoride ion, $F^-(aq)$?
   (2) Write the expression for the equilibrium constant, K_A, and find its numerical value.

   Answer

   (1) $[H^+] = [F^-] = 8.2 \times 10^{-3}$ mole/liter
   (2)
   $$K_A = \frac{[H^+][F^-]}{[HF]} = \frac{(8.2 \times 10^{-3})(8.2 \times 10^{-3})}{10^{-1}} = 6.7 \times 10^{-4}$$

7. Four grams of $NaOH(s)$ are dissolved in just enough water to make 1 liter of solution.

   (1) What is the molar concentration of the solution?
   (2) What is the $[OH^-]$?
   (3) What is the $[H^+]$?

Answer

(1) $\frac{4\ \text{g/liter}}{40\ \text{g/mole}} = 0.1\ M$

(2) $[OH^-] = 0.1\ \text{mole/liter} = 0.1\ M$

(3) $[H^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13}\ M$

8. Calculate $[H^+]$ in solutions made by mixing 100 ml 1.00 M HNO_3 with
   (1) 100 ml 0.100 M KOH,
   (2) 100 ml 0.990 M KOH,
   (3) 100 ml 1.010 M KOH.

Answer

(1) In each solution the molarity will be halved.
Initial $[H^+] = 0.500$.
Initial $[OH^-] = 0.050$.
Final $[H^+] = 0.500 - 0.050 = 0.450$.

(2) Again the molarities will be halved.
Initial $[H^+] = 0.500$.
Initial $[OH^-] = 0.495$.
Final $[H^+] = 0.500 - 0.495$
$= 0.005 = 5 \times 10^{-3}$.

(3) Again the molarities will be halved.
Initial $[H^+] = 0.500$.
Initial $[OH^-] = 0.505$.
Final $[OH^-] = 0.505 - 0.500$
$= 0.005$.

$$[H^+] = \frac{10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12}\ M$$

9. Consider the reaction

$$CH_3COOH \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Using Le Chatelier's Principle decide whether $[H^+(aq)]$ will be larger or smaller if sodium acetate, $NaCH_3COO$, is dissolved in the reaction mixture. Justify your answer.

Answer

The $[H^+(aq)]$ will be smaller. When $NaCH_3COO$ dissolves, it will increase $[CH_3COO^-(aq)]$. This will disturb the equilibrium condition, and a partially nullifying action will take place to reduce $CH_3COO^-(aq)$. Such action will use up $H^+(aq)$.

10. How many milliliters of 0.02 M HCl are needed to react completely with 100 ml of of 0.01 M NaOH?

Answer

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O$$

One mole of HCl reacts with one mole of NaOH.

$$\frac{100\ \text{ml}}{1000\ \text{ml/liter}} \times \frac{0.01\ \text{mole}}{\text{liter}} = 0.001\ \text{mole NaOH}$$

The 0.001 mole of NaOH will require 0.001 mole of HCl. The required amount of HCl to contain 0.001 mole is

$$\frac{0.001\ \text{mole}}{0.02\ \text{mole/liter}} \times \frac{1000\ \text{ml}}{\text{liter}} = 50\ \text{ml HCl}$$

11. If 100 ml of 0.020 M HNO_3 are added to 100 ml of 0.110 M $Ba(OH)_2$, what is $[H^+(aq)]$ at equilibrium in the resulting solution?

Answer

The molarity of both solutions will be halved.
Initial $[H^+] = 0.010$
Initial $[OH^-] = 0.110$
Final $[OH^-] = 0.110 - 0.010 = 0.100\ M$
Since $[H^+][OH^-] = 10^{-14}$,

$$[H^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13}$$

CHAPTER

12

OXIDATION-REDUCTION REACTIONS

Intent and Approach

Chapter 12 bears a rather strong resemblance to Chapter 11 in general form. We again start from a group of relatively simple observations involving easily measured phenomena (i.e., cell potentials); we look for a means of systematizing the observations; we adopt rather arbitrary definitions such as those for oxidizing agent, acid, oxidation number, etc.; then we systematize the values (table of E° values) and use the concepts we have defined to make predictions which can be tested by experiment. As mentioned in the background section, sometimes our predictions are valid (for example, in the reaction of HI and Zn), and sometimes they are wrong, as in the reaction between HI and Ag. If our predictions are wrong, we have extended our model beyond its limit of applicability, and we must look for the new variable which has become important but which was neglected in our original treatment. (See the gas laws and the related discussion of attraction between molecules as another example of this.)

In general, the definitions of oxidation, reduction, anion, cation anode, and cathode are much more standardized than are the definitions of acid and base. We still find, however, that this chapter abounds in arbitrary conventions such as the sign of E° for a process, the rules for calculating oxidation number, etc. Fortunately the rules are quite generally accepted, but this does not render them less arbitrary. Above all, they are *very useful.*

Try to point out to the student the difference between convention, model, and experimental fact. Electric current flows from one electrode to another; this is a fact. We picture the process that generates the current in terms of half-cell reactions at each electrode; this is our model. We call the electrode at which a loss of electrons is assumed to occur the anode; this is a convention. The first point is not subject to debate or compromise; it is observed. The second point, involving the model, is consistent with the facts but is not unique. We can assume other models that will explain the observations. For example, charge distribution in chemical species may not be the same as that indicated in our half-cell reactions at all. The process of electron transfer could conceivably be quite different from those that we are writing. In the reduction of permanganate ion we say the oxidation number of Mn is +7, yet no one believes that manganese actually carries this charge. This difference is even more pronounced if one considers the reaction $NO + O_2 = NO_2$ in terms of half-cell processes. We really doubt whether the electronic oxidation process is accurately pictured by the equation

$$NO = NO^{+2} + 2e^-$$

yet it may be convenient to write the oxidation in this way. A convention, such as our definition of an anode, is the most arbitrary of all and is usually closely related to the model we have chosen.

In this chapter we balance oxidation-reduction reactions by using half-cell processes and by using oxidation numbers. We are making somewhat different arbitrary decisions in the two methods, but both sets of decisions are helpful.

Just as we cannot say there is *one* set of definitions for either acids or bases, neither can we say that there is *one* way to balance oxidation-reduction equations.

Outline

1. The process occurring in an electrochemical cell is analyzed in terms of two half-cell reactions. Loss and gain of electrons in half-reactions (12-1.1) is presented as one kind of oxidation and reduction.
2. Concepts developed for half-cells are applicable to electrochemical processes occurring in a single solution (12-1.2) and are illustrated by examples.
3. Many oxidation-reduction processes are conveniently considered in terms of competition for electrons (12-1.3). A more detailed analysis of the electrochemical cell permits us to evaluate electron competition in terms of cell voltage (12-1.4).
4. In Section 12-2.1 we learn that *the voltage of a cell measures the tendency for the cell reaction to occur;* the voltage is dependent upon concentration. Voltages for different cells are additive. This observation leads to the recognition of *half-cell potentials* which can be added to get cell potentials.
5. Half-cell potentials may be conveniently measured and tabulated if certain arbitrary experimental conventions are accepted [the H_2 half-cell is 0.00 volts, and values are reported for unit concentration (or activity)] (12-2.1).
6. The table of half-cell potentials permits us to predict reactions and cell voltages (12-2.2). Solution concentration is important in such predictions (12-2.3).
7. The factors that determine equilibrium are related to $E°$ (12-2.4).
8. Section 12-2.5 introduces oxidation numbers and stresses their arbitrary nature. Here the definition of oxidation-reduction is given in terms of oxidation numbers.
9. The balancing of oxidation-reduction reactions is discussed using the half-cell and oxidation number methods (12-3–12-3.3).
10. If a spontaneous electrochemical process is forced backward by imposing a higher voltage, the process is known as electrolysis (12-4).

New Concepts

1. The half-cell reaction, as it is applied in a description of an electrochemical cell.
2. Electron transfer, as one way to express oxidation and reduction.
3. Cell potentials and competition for electrons.
4. Tables of oxidation potentials and their use in predicting reactions.
5. Balancing oxidation-reduction equations.
6. The meaning of oxidation number.

Development

Expt. 20, AN INTRODUCTION TO OXIDATION-REDUCTION, fits here. See p. 379 for guide.

Expt. 21, ELECTROCHEMICAL CELLS, fits here. (Consider doing this as a Demonstration.) See p. 383 for guide.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
Expt. 20	1	Expt. 20,					Redox Reactions
S 12-1/12-1.4 (pp. 199–207) Expt. 21	2–3	Expt. 21* Film: ELECTROCHEMICAL CELLS	1, 2	1, 2	3–5, 7, 8	6, 9†	Cells
S 12-2/12-2.1 (pp. 207–212)	4	Discussion	3		10, 11	12, 13	Electron-losing Tendency, E°
S 12-2.2/12-2.4 (pp. 212–215)	5	Discussion Film: NITRIC ACID	4–6		14	15–17	Predicting Reactions
S 12-2.5/12-3.3 (pp. 215–220)	6–7	Discussion	7–9	18	19–22	23	Oxidation Numbers Balancing Redox Reactions
S 12-4 (pp. 220–221)	8	Discussion Problems	10			24	Electrolysis
	9	Review Test					

Note: Experiments 22 and 23 (Chapter 13) require extensive preparation of solutions.

* Can be a demonstration if voltmeters are not available.

† Boldface indicates problems whose answers are given in Textbook.

ELECTROCHEMICAL CELLS (12-1)

The Chemistry of an Electrochemical Cell (12-1.1)

The central theme of the entire chapter is systematization of experimental observations through construction of a useful but somewhat arbitrary formalism. In this section we are concerned with the development of the experiments which form the background for the entire chapter. Using the student's experience from Expt. 21, emphasize the experimental aspects strongly, and show how they lead to one definition of oxidation in terms of electron loss. You may find it helpful to point out that the word oxidation arises from processes involving combination with oxygen. The burning of Mg in O_2 is easily identified as oxidation. The elements Mg and O_2 combine to give Mg^{+2} and O^{-2} in an NaCl-type lattice. When Mg is oxidized, Mg^{+2} is formed from Mg by *loss* of electrons. We can now generalize in a rather formal sense.

Note the footnote on Textbook, p. 202 about the double numbering system used for equations. The consecutive numbers (on the right) make the proper equation easy to find. The other number ties in earlier discussion of the same reaction.

Oxidation-reduction Reactions in a Beaker (12-1.2)

Point out that the reaction between copper and silver nitrate was carried out under rather specialized conditions in 12-1.1 but that the reaction will go equally well in an ordinary beaker. Exercise 12-1 is given to remind the student of his experience in Expt. 7. We still find it *convenient* to use the ideas about half-cell reactions which we developed in 12-1.1. The names and ideas are still applicable. Our observations and formalism are thus extended somewhat beyond the original experiments of Sec. 12-1.1.

The reaction of Zn and H^+, used to characterize an acid experimentally, is easily interpreted in terms of oxidation and reduction. Our formal schemes meet on a common experimental ground. Stress the experimental aspects of this whole section; remember that we do experiments to get the facts which we will later arrange in a systematic fashion. The experiments are easy to do and to interpret. That is, it is not hard to find out what reactants will give which products under a given set of conditions.

Competition for Electrons (12-1.3)

We picture two metals competing for *electrons*, and we list the metals in order of their ability to *release* electrons. Again note that in doing this we are systematically arranging *observed* facts. The table expresses a regularity. From the table, we can make useful predictions, just as we did for acids. The list developed in this section is qualitative; our quantitative list comes later.

Operation of an Electrochemical Cell (12-1.4)

The details of cell operation are explained. This is a most important section. By carefully avoiding the convention of assigning a sign to either electrode we can sidestep a problem which frequently bothers students—namely, the positive ions move toward the "positive" electrode, and the negative ions move toward the "negative" electrode. This problem can be troublesome and yields little; avoid placing it before the student if possible. Our picture is simple; the process is *driven* by the inherent tendency of the reaction to go, as measured by voltage values.

The nomenclature used in oxidation-reduction reactions can be confusing. Here are two mnemonic devices that may help.

(1) Anions are negative ions.

A N I O N S
n e
i g
o a
n t
s i
v
e

(2) Oxidation occurs at Anode (vowels together)	Reduction occurs at Cathode (consonants together)

Emphasize that *the voltage of a cell measures the tendency for the cell reactions to occur.* We need this concept in the following subsections.

ELECTRON TRANSFER AND PREDICTING REACTIONS (12-2)

Electron Losing Tendency (12-2.1)

We construct two cells and hook them up in opposition to each other. Note that when electricity flows, only one cell can operate as an *electrochemical* cell. The other cell is now *forced* to operate as an *electrolytic* cell! The latter type is treated in Sec. 12-4.

The addition of measured potentials can be used to develop a logical *experimental* justification for the additivity of half-cell values. Some precautions are needed in adding half-cell values in special situations. Specifically, the number of electrons involved in each reaction being added must be the same. For example, see the background section relative to obtaining the value for $Cr \longrightarrow Cr^{+3} + 3e^-$ from values for $Cr \longrightarrow Cr^{+2} + 2e^-$ and $Cr^{+2} \longrightarrow Cr^{+3} + e^-$.

The question of partitioning a measured physical quantity such as a cell voltage between two components to get values for two imagined parts (half-cells in this instance) is a common and difficult one in chemistry. We face the same type of problem in measuring ionic radii, ionic heats of solution, and a number of other quantities. Various means are used to solve the problem; in this particular situation, we *arbitrarily* decide to set the value of the half-cell $H_2 \rightleftharpoons 2H^+ + 2e^-$ at 0.00 volts and compare all other values to it. This is a *convenient* and *arbitrary* convention. It has no absolute significance.

Stress the utility of Le Chatelier's Principle in considering the effects of concentration on cell voltage. Since the voltage measures the tendency of the reaction to occur (12-2.1), and since concentration changes alter the tendency of a reaction to occur, concentration changes should have a *predictable* effect upon voltage. The illustration of a flashlight dry cell might be useful. The voltage is high when concentrations are a long way removed from the run-down, or *equilibrium*, condition of the cell, but *the voltage gradually drops until it is zero when the equilibrium concentrations have been reached.* Since concentration is an important variable in determining voltage, we must arbitrarily fix the concentration values for all cell components if a realistic comparison of E values for different reactions is to be made. For this reason, $E°$ values listed later in tables are based on a cell in which the *effective concentration* of each ion at the solid electrode surface is one mole/liter. Using this convention we can compare different chemical processes under conditions arranged such that concentration is not a variable. The details of measurement come later.

Don't become confused with signs. It is generally agreed that a positive value of $E°$ indicates that the equation as written (e.g., $Zn \rightleftharpoons Zn^{+2} + 2e^-$; $E° = +0.76$) has a greater tendency to go than our reference process $H_2 \rightleftharpoons 2H^+ + 2e^-$. If the equation is turned around and written $Zn^{+2} + 2e \rightleftharpoons Zn$, then $E°$ for the process as now written is *negative*. This means the reaction has a lower tendency to proceed than does the reaction $H_2 \rightleftharpoons 2H^+ + 2e^-$. Make it well known that Textbook Table 12-II applies only to solutions in which the ionic species are 1 *M*. This convention is followed almost universally.

Use several practice questions to make sure the students can correctly calculate the net $E°$ value for a given equation. This skill is needed throughout the remainder of this chapter and is used frequently in later, descriptive chapters.

Predicting Reactions from Table 12-II (12-2.2)

Considerable drill will also be helpful in fixing the main point of this section. If $E°$ for the overall process is positive, the process is spontaneous when concentrations are reasonably close to those used in establishing the table. If E° is negative, the process is spontaneous in the reverse direction. If E° is zero, the process is at equilibrium when concentrations are those of the table. Emphasize the basic rules given on p. 213 of the Textbook.

All is not gold that glitters! Sometimes, variables such as concentration may differ significantly from those used in establishing the table. Predictions made from the table without considering other factors may therefore be wrong. The reaction of Ag and H^+ given in Sec. 12-2.2 is such an example; another is the action of HBr on copper, $2HBr + Cu \rightleftharpoons \frac{1}{2}H_2 + H^+ + CuBr_2^-$. Another is the dissolution of gold by aqua regia. The E°_{net} value for the action of HNO_3 on gold is negative. The process is not spontaneous as written (for the standard concentrations).

Reliability of Predictions (12-2.3)

This section is intended to show that equilibrium considerations are not sufficient to determine whether a reaction will take place at a useful rate. In particular, we wish to restress that K (or E°, another way to express K) does not give information about the rate of reaction.

E° and the Factors That Determine Equilibrium (12-2.4)

This short portion hints at free energy and its relation to energy and entropy. But only the descriptive expression should be used. Alert the student to the two opposing tendencies without giving the thermodynamic names or equations. The Teacher's Guide for Chapters 9, 10, and 12 contains material for you on this subject.

Film, NITRIC ACID,
fits here. See p. 387 for summary.

$$\begin{array}{rcll} Au & \rightleftharpoons & Au^{+3} + 3e^- & E^\circ = -1.50 \text{ volts} \\ 4H^+ + 2NO_3^- + 2e^- & \rightleftharpoons & N_2O_4 + 2H_2O & E^\circ = +0.80 \text{ volt} \\ \hline 12H^+ + 6NO_3^- + 2Au & \rightleftharpoons & 2Au^{+3} + 3N_2O_4 + 6H_2O & E^\circ_{net} = -0.70 \text{ volt} \end{array}$$

However, if the concentration of Au^{+3} is reduced by the formation of the complex ion $AuCl_4^-$, then the reaction becomes spontaneous.

$$2Au + \underbrace{6HNO_3 + 8HCl}_{\text{aqua regia}} = 2H^+ + 2AuCl_4^- + 3N_2O_4 + 6H_2O$$

The E° value which must be considered is that for actual processes which take place. These may differ from the obvious entries in the table. Other more complex examples appear in the background section. Systems of correlation don't replace the need for thought and experimentation.

Since we have hinted that E° is related to the tendency for a reaction to go and that K measures the state which the reaction will achieve at equilibrium, some student may expect a relation between E° and K. The background gives it without the thermodynamic derivation, which is too advanced for usefulness at this time.

Oxidation Numbers—An Electron Bookkeeping Device (12-2.5)

The title of this section and the approach used are intended to emphasize that oxidation numbers do *not* represent actual charges. Oxidation numbers are a set of numbers that make equation balancing easier. Notwithstanding their nonabsolute nature, they are quite useful.

They allow us, for example, to treat reactions like number 76, which the student sees on p. 216 of the Textbook. Here there is no reason to expect an actual transfer of electrons between SO_2 and O_2. This is why we have been careful to say that the transfer of electrons is one kind of oxidation-reduction reaction.

It is best to avoid the notation, sometimes seen, which ties the electron transfer directly to ionic species:

$$\underset{+2}{NO}\ \overset{\overset{2e^-\text{ loss}}{\curvearrowright}}{\text{goes to}}\ \underset{+4}{NO_2}$$

BALANCING OXIDATION-REDUCTION REACTIONS (12-3)

Using Half-reactions for Balancing Oxidation-reduction Reactions (12-3.1)

Balancing Oxidation-reduction Reactions (12-3.2) (reduced type)

Use of Oxidation Number in Balancing Oxidation-reduction Reactions (12-3.3)

There is *no single correct* method for balancing oxidation-reduction reactions. Two methods are outlined here in some detail. The procedures in each need no amplification; both are founded on the conservation of charge and mass in a real process. If balanced half-reaction equations are available, the half-reaction method is probably best; if half-reaction equations are not available, the use of oxidation numbers is frequently preferred. Other schemes for conserving charge and mass are available. See the *Background Discussion.*

It is important to emphasize that the oxidation numbers referred to in the discussion on balancing redox equations are *arbitrary values obtained by using arbitrary* rules. The student should be cautioned against believing that the values represent real ion charges in the molecule. We don't know where the electrons in a molecule are located precisely, but we are pretty sure that they *aren't* distributed as indicated by the oxidation numbers. Oxidation numbers are convenient. They can even be applied to organic molecules if our arbitrary defining rules are extended; they have no real significance with regard to charge distribution.

To illustrate the fictitious nature of oxidation numbers, you can balance an equation by using a different set of rules from those the student is given on p. 219. Suppose you use the reaction of permanganate and ferrous ions. Let us assume the oxidation number of manganese is constant at +2 and that oxygen changes

$$MnO_4^- + Fe^{+2} + H^+ \longrightarrow Mn^{+2} + Fe^{+3} + H_2O$$

$$\begin{array}{llll}
\text{Mn} & +2 & \xrightarrow{\quad 0 \quad} & +2 \\
\text{O} & -\frac{3}{4} & \xrightarrow{\qquad -\frac{5}{4} \qquad} & -2 \\
\text{Fe} & +2 & \xrightarrow{\quad +1 \quad} & +3
\end{array}$$

If the gain in oxidation number is to equal the loss in oxidation number, then for every four oxygen atoms that change $[4 \times (-\frac{5}{4}) = -5]$ five iron atoms must react $[5 \times (+1) = +5]$.

$$MnO_4^- + 5Fe^{+2} + H^+ \longrightarrow Mn^{+2} + 5Fe^{+3} + H_2O$$

From here on just balance the H and O atoms.

$$MnO_4^- + 5Fe^{+2} + 8H^+ = Mn^{+2} + 5Fe^{+3} + 4H_2O$$

Balance the same equation using more conventional oxidation numbers; you will get the same answer.

Take another example:

$$H_2SO_4 + H_2S \longrightarrow S_8 + H_2O$$

Now let's assume the oxidation number $O = +\frac{3}{2}$; then $H = -\frac{3}{4}$. Notice that we choose oxygen to be whatever we like, but then hydrogen is fixed, leaving H_2O without charge. We cannot pick *all* the oxidation numbers at random.

In H_2SO_4,

$$2(-\tfrac{3}{4}) + S + 4(+\tfrac{3}{2}) = 0$$
$$S = -6 + \tfrac{3}{2} = -\tfrac{9}{2}$$

in H_2S

$$S = +\tfrac{3}{2}$$

$$H_2SO_4 + H_2S \longrightarrow S_8 + H_2O$$
$$-\tfrac{9}{2} \xrightarrow{+\frac{9}{2}} 0$$
$$+\tfrac{3}{2} \xrightarrow{-\frac{3}{2}} 0$$

Hence there must be three molecules of H_2S for each one of H_2SO_4, giving

$$H_2SO_4 + 3H_2S = \tfrac{1}{2}S_8 + 4H_2O$$

This is the same answer as given by the "regular" values O^{-2} and H^+.

Electrolysis (12-3.4)

Material in this section can be related conveniently to the material about opposed cells (12-2.1). Refer back to that discussion before you consider the current section. The laws of stoichiometry for the electrode process follow logically if we picture the charge of 96,500 coulombs (amperes × seconds) as that carried by one *mole* of electrons. The stoichiometric laws (Faraday's Laws) are taken up in Chapter 14.

EXPERIMENT 20 AN INTRODUCTION TO OXIDATION-REDUCTION

PURPOSE. To establish experimentally the relative electron losing tendency of three metals and the relative electron gaining tendency of three halogens.

PRELAB DISCUSSION. Little is needed if the student has read the experiment carefully. Instruct the student to set up solutions as directed in Part I and then check them every 5 or 10 minutes while continuing with Part II.

TIMING. This experiment is intended as an introduction to Chapter 12.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

12 13 × 100-mm test tubes
2 solid rubber stoppers, size #00
  (or cork size #3)
6 metal strips (about 1 × 11 cm)
  2 of copper
  2 of lead
  2 of zinc
[Metal strips can be used over again from one period to the next (see lab hint 1) or may be saved for Expt. 21.]
steel wool or sandpaper

Solutions and reagents:

9 ml 0.1 *M* $Cu(NO_3)_2$
  (24.2 g $Cu(NO_3)_2 \cdot 3H_2O$/liter)
9 ml 0.1 *M* $Pb(NO_3)_2$ (33.1 g $Pb(NO_3)_2$/liter)
9 ml 0.1 *M* $Zn(NO_3)_2$
  (29.8 g $Zn(NO_3)_2 \cdot 6H_2O$/liter)
6 ml 0.1 *M* NaBr (10.3 g NaBr/liter)
6 ml 0.1 *M* NaI (15 g NaI/liter)
6 ml 0.1 *M* NaCl (5.8 g NaCl/liter)
5 ml chlorine water (saturated; see lab hint 2)
4 ml bromine water, 1 ml Br_2/200 ml H_2O
  (see lab hint 3)
4 ml iodine in water-ethanol solution
  (see lab hint 4)
9 ml carbon tetrachloride

TIME REQUIRED. The student will need one full 45–50 minute laboratory period.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. Two strips of each metal are sufficient if the student does not test the metal with the nitrate of the same metal. Three pieces of each metal are needed if this is done.
2. To make saturated chlorine water, slowly pass chlorine gas from a lecture bottle of compressed gas into the needed amount of water, or set up a chlorine gas generator. Use a long-stem funnel and delivery tube in a 2-hole stopper inserted in a 250 ml flask. Add about 40 ml of concentrated HCl to about 10 g of MnO_2 in the flask, and warm gently. Use a fume hood. This recipe produces enough to prepare 1 liter of chlorine water.
3. Prepare bromine water by dissolving about 1 ml of bromine in 200 ml of water. Make the bromine by heating 10 g of KBr with 2 g of MnO_2 and 15 ml of 9 *M* H_2SO_4 in a glass retort and allowing the bromine to flow into a tube of water. The solution for this experiment need be only lightly colored to be concentrated enough.

   Caution: Avoid getting liquid bromine on your skin. It produces very painful burns.
4. Dissolve about 0.25 g of $I_2(s)$ in 50 ml of ethanol, and add 350 ml of water.

EXPECTED RESULTS

PART I

No reaction is evident when a metal strip is left in a solution of its own ions, although Zn may react with H^+ in the $Zn(NO_3)_2$ solution. Shiny crystals of lead will be observable on the zinc strip placed in Pb^{+2}, and a copper coating will form on the zinc strip in Cu^{+2}. The lead strip placed in Cu^{+2} will also become copper coated. There will be no reaction with the copper or lead strips placed in Zn^{+2} or with the copper strips in Pb^{+2} solution.

PART II

Chlorine doesn't color CCl_4. Iodine in CCl_4 is a deep purple if very concentrated, although an attempt has been made to keep the solution dilute enough so that a pink-lavender shade will result. Bromine in CCl_4 is red when concentrated, and straw-colored when dilute. Unless these differences in color receive comment, many fail to identify the bromine in CCl_4 in different concentrations.

Since Cl_2 will oxidize both I^- and Br^-, the color of the CCl_4 layer will show I_2 and Br_2 for Part I. When Br_2 water is added, no reaction takes place with Cl^-, although the student will not be able to determine this for sure, since a Br_2 color in CCl_4 would mask any Cl_2 even if it were produced. You may wish to clarify this point by a later demonstration with a quantitative measure. With the concentrations recommended, all the Br_2 should be used in replacing I^-, and the resulting color in CCl_4 should be due only to I_2.

With iodine solution, no reactions occur, and only the color of I_2 in CCl_4 will be noted. A comparison of the color resulting with 5 drops of the iodine solution added to 5 ml of NaI and 1 ml CCl_4 will convince the student that none of the I_2 has reacted with the Cl^- or Br^-.

CONCLUSIONS AND QUESTIONS

1. Which of the metals tested was oxidized by both of the solutions of the other metallic ions?

   Answer: Zinc.

   Which one was oxidized by only one of the metallic ions?

   Answer: Lead.

   Which one was oxidized by neither of the other metallic ions?

   Answer: Copper.

2. Arrange the metal–metal ion half-reactions $M(s) \rightleftharpoons M^{+2}(aq) + 2e^-$ in a column in order of decreasing ease of oxidation. Since you know from Expt. 7 that $Cu(s)$ is oxidized by $Ag^+(aq)$, add the $Ag(s) \rightleftharpoons Ag^+(aq) + e^-$ half-reaction to your list in the appropriate place.

   Answer

$$\begin{aligned} Zn(s) &\rightleftharpoons Zn^{+2}(aq) + 2e^- \\ Pb(s) &\rightleftharpoons Pb^{+2}(aq) + 2e^- \\ Cu(s) &\rightleftharpoons Cu^{+2}(aq) + 2e^- \\ Ag(s) &\rightleftharpoons Ag^+(aq) + e^- \end{aligned}$$

3. Write balanced total reactions for the cases where oxidation-reduction reactions between metals and metallic ions were observed [see the example for $Cu(s)$ and $Ag^+(aq)$ in the introductory section of this experiment].

Answer

$$\begin{array}{rcll}
\text{Zn}(s) & \rightleftharpoons & \text{Zn}^{+2}(aq) + 2e^- & \text{(oxidation half-reaction)} \\
2e^- + \text{Cu}^{+2}(aq) & \rightleftharpoons & \text{Cu}(s) & \text{(reduction half-reaction)} \\
\hline
\text{Zn}(s) + \text{Cu}^{+2}(aq) & \rightleftharpoons & \text{Zn}^{+2}(aq) + \text{Cu}(s) & \text{(total reaction)}
\end{array}$$

$$\begin{array}{rcll}
\text{Zn}(s) & \rightleftharpoons & \text{Zn}^{+2}(aq) + 2e^- & \text{(oxidation half-reaction)} \\
2e^- + \text{Pb}^{+2}(aq) & \rightleftharpoons & \text{Pb}(s) & \text{(reduction half-reaction)} \\
\hline
\text{Zn}(s) + \text{Pb}^{+2}(aq) & \rightleftharpoons & \text{Zn}^{+2}(aq) + \text{Pb}(s) & \text{(total reaction)}
\end{array}$$

$$\begin{array}{rcll}
\text{Pb}(s) & \rightleftharpoons & \text{Pb}^{+2}(aq) + 2e^- & \text{(oxidation half-reaction)} \\
2e^- + \text{Cu}^{+2}(aq) & \rightleftharpoons & \text{Cu}(s) & \text{(reduction half-reaction)} \\
\hline
\text{Pb}(s) + \text{Cu}^{+2}(aq) & \rightleftharpoons & \text{Pb}^{+2}(aq) + \text{Cu}(s) & \text{(total reaction)}
\end{array}$$

4. Which of the halide ions tested was oxidized by both of the other halogen elements?

   Answer: Iodide.

   Which halide ion was oxidized by only one halogen element?

   Answer: Bromide.

   Which halide ion was not oxidized by any of the halogen elements used?

   Answer: Chloride.

5. Arrange the halide ion-halogen element half-reactions in a column in order of decreasing ease of oxidation.

   Answer

$$\begin{array}{rcl}
2\text{I}^-(aq) & \rightleftharpoons & \text{I}_2(s) + 2e^- \\
2\text{Br}^-(aq) & \rightleftharpoons & \text{Br}_2(l) + 2e^- \\
2\text{Cl}^-(aq) & \rightleftharpoons & \text{Cl}_2(g) + 2e^-
\end{array}$$

6. Write balanced total reactions for the cases where oxidation-reduction reactions occurred between halide ions and elementary halogens.

   Answer

$$\begin{array}{rcll}
2e^- + \text{Cl}_2(g) & \rightleftharpoons & 2\text{Cl}^-(aq) & \text{(reduction half-reaction)} \\
2\text{Br}^-(aq) & \rightleftharpoons & \text{Br}_2(l) + 2e^- & \text{(oxidation half-reaction)} \\
\hline
\text{Cl}_2(g) + 2\text{Br}^-(aq) & \rightleftharpoons & 2\text{Cl}^-(aq) + \text{Br}_2(l) & \text{(total reaction)}
\end{array}$$

$$\begin{array}{rcll}
2e^- + \text{Cl}_2(g) & \rightleftharpoons & 2\text{Cl}^-(aq) & \text{(reduction half-reaction)} \\
2\text{I}^-(aq) & \rightleftharpoons & \text{I}_2(s) + 2e^- & \text{(oxidation half-reaction)} \\
\hline
\text{Cl}_2(g) + 2\text{I}^-(aq) & \rightleftharpoons & 2\text{Cl}^-(aq) + \text{I}_2(s) & \text{(total reaction)}
\end{array}$$

$$\begin{array}{rcll}
2e^- + \text{Br}_2(l) & \rightleftharpoons & 2\text{Br}^-(aq) & \text{(reduction half-reaction)} \\
2\text{I}^-(aq) & \rightleftharpoons & \text{I}_2(s) + 2e^- & \text{(oxidation half-reaction)} \\
\hline
\text{Br}_2(l) + 2\text{I}^-(aq) & \rightleftharpoons & 2\text{Br}^-(aq) + \text{I}_2(s) & \text{(total reaction)}
\end{array}$$

7. Use the additional information given below to construct a series of all seven half-reactions discussed in this experiment in order of decreasing ease of oxidation.
   (a) $\text{Ag}^+(aq)$ is a stronger oxidizing agent than is $\text{I}_2(s)$ but is a weaker one than $\text{Br}_2(l)$.
   (b) $\text{I}^-(aq)$ is a weaker reducing agent than is $\text{Cu}(s)$ but is a stronger one than $\text{Ag}(s)$.

Answer

$$\begin{aligned}
&\mathrm{Zn}(s) &&\rightleftharpoons \mathrm{Zn}^{+2}(aq) + 2e^- \\
&\mathrm{Pb}(s) &&\rightleftharpoons \mathrm{Pb}^{+2}(aq) + 2e^- \\
&\mathrm{Cu}(s) &&\rightleftharpoons \mathrm{Cu}^{+2}(aq) + 2e^- \\
&2\mathrm{I}^-(aq) &&\rightleftharpoons \mathrm{I}_2(s) + 2e^- \\
&\mathrm{Ag}(s) &&\rightleftharpoons \mathrm{Ag}^+(aq) + e^- \\
&2\mathrm{Br}^-(aq) &&\rightleftharpoons \mathrm{Br}_2(l) + 2e^- \\
&2\mathrm{Cl}^-(aq) &&\rightleftharpoons \mathrm{Cl}_2(g) + 2e^-
\end{aligned}$$

8. Would it be feasible to store a solution of copper sulfate in a container made of metallic zinc? Of metallic silver? Give reasons for your answers.

Answer: A solution of copper sulfate would contain $\mathrm{Cu}^{+2}(aq)$ and would react with a container made of $\mathrm{Zn}(s)$, since $\mathrm{Zn}(s)$ is a stronger reducing agent (is oxidized more easily) than $\mathrm{Cu}(s)$. The $\mathrm{CuSO_4}$ solution would not react with $\mathrm{Ag}(s)$, because $\mathrm{Ag}(s)$ is a weaker reducing agent (is oxidized less easily) than $\mathrm{Cu}(s)$.

9. Would you expect jewelry made of an alloy of silver and copper to tarnish (oxidize) in a laboratory where fumes of bromine are present? Explain.

Answer: One should expect such jewelry to tarnish, since both $\mathrm{Ag}(s)$ and $\mathrm{Cu}(s)$ are more easily oxidized than $\mathrm{Br}_2(g)$. Thus $\mathrm{Br}_2(l)$ or $\mathrm{Br}_2(g)$ would oxidize these elements. Of course, a laboratory with any appreciable concentration of bromine fumes would be uninhabitable.

POSTLAB DISCUSSION. See expected results for Part II. You may wish to demonstrate some of the halogen-halide interactions in a more quantitative way. The experiment leads quite naturally into a discussion of 12-1.2 and 12-1.3 and Table 12-I in the Textbook.

EXPERIMENT 21 ELECTROCHEMICAL CELLS

PURPOSE. To provide experimental background for the E° table and to provide additional experience with oxidation-reduction reactions.

PRELAB DISCUSSION. The introduction for Sec. 12-2 leads easily into this experiment. Recall the value of the table developed in Expt. 20 for making qualitative predictions and of the desirability of having a quantitative measure of electron-losing tendency. If porous cups are being used demonstrate a reaction with a salt bridge (see lab hint 1).

TIMING. This experiment should be done before Sec. 12-2.1, which has examples that will help with the questions, and prior to Sec. 12-2.2, on predicting reactions from E°.

EQUIPMENT NEEDED (PER GROUP OF FOUR STUDENTS)

3 250 ml beakers
1 porous cup (or substitute a U-tube salt bridge; lab hint 2)
1 voltmeter (D.C.), 20,000 ohm/volt, 0–5 volt range
2 wires with alligator clamps
1 copper strip (1 × 11 cm; see Expt. 20)
1 zinc strip (1 × 11 cm; see Expt. 20)
1 silver strip (1 × 11 cm)
1 lead strip (1 × 11 cm; see Expt. 20)
100 ml 0.5 *M* zinc nitrate (146.7 g $Zn(NO_3)_2 \cdot 6H_2O$/liter)
100 ml 0.5 *M* cupric nitrate (120.8 g $Cu(NO_3)_2 \cdot 3H_2O$/liter)
100 ml 0.5 *M* lead nitrate (165.5 g $Pb(NO_3)_2$/liter)
100 ml 0.5 *M* silver nitrate (85.0 g $AgNO_3$/liter)
50 ml 2 *M* sodium sulfide (480 g $Na_2S \cdot 9H_2O$/liter, for teacher's demonstration)
50 ml 0.5 *M* ammonium nitrate (40 g NH_4NO_3/liter)

TIME REQUIRED. Allow about one 45–50 minute laboratory period, or about half a period if the entire experiment is demonstrated. (See lab hint 1.)

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINTS

1. The diagram in the Laboratory Manual (Figure 21-1) shows a porous cup. Although the use of a porous cup is certainly convenient, it is extremely important for the student to understand that two *half*-reactions are involved. This concept will be easier for him to grasp if each takes place in a separate beaker. When the porous cup is placed in a beaker the occurrence of two separate half-reactions is not as evident. A demonstration with a salt bridge, as shown in Figure 21-2, will emphasize this point sufficiently. If the students use a salt bridge, no demonstration is needed.
2. A salt bridge may be constructed by bending a 10 mm piece of glass tubing into a U shape. Avoid constrictions at the bend. Fill the tube with 0.5 *M* NH_4NO_3 solution, and insert a loose piece of cotton in each end. Then invert the U-tube, and use it to connect the two solutions.

   A piece of tygon tubing may be used instead of glass. It is best to bend the tygon in hot water and then cool it while curved. Rolls of cotton available from dental supply houses (6 inches long and $\frac{3}{8}$ inch in diameter) may be soaked in NH_4NO_3 solution. These are convenient to use, but three or four are needed to give a good connection. The voltage readings for cells connected with a salt bridge will nearly always be lower than readings for cells joined by a porous cup.

3. To save time in later classes keep the half-cells from the first period intact.
4. If porous cups are used, fill the pores by soaking them in 0.5 *M* NH_4NO_3 solution ahead of time. After use they may be cleaned by soaking them overnight in 6 *M* HNO_3.
5. This experiment provides an excellent opportunity to demonstrate that voltage is independent of amount of solid. Use large and then small electrodes. Remove most of one electrode from the solution. Constant voltage demonstrates that $E°$ does not depend on amount, hence it is not doubled when a half-reaction is doubled.

EXPECTED RESULTS

PART I

(c) No reading. (d) The maximum reading is 1.10 volts. It will probably be somewhat below this, and will drop as polarization occurs. Students should be instructed to read the voltage as soon as the circuit is completed. Polarization results from accumulation of reaction products at the electrode. This changes the concentration and, hence, the voltage. High current flow usually increases polarization.

PART II

Attach the copper electrode to the negative terminal of the meter. The maximum reading is 0.46 volts but will be somewhat lower in practice.

PART III

Attach the lead electrode to the negative terminal of the meter. The maximum reading is 0.47 volt but is found to be somewhat lower in practice.

PART IV

Other possible combinations are lead with zinc solution, lead with silver, and zinc with silver.

PART V

Adding the sodium sulfide solution causes a black precipitate to form, and the voltage drops.

CONCLUSIONS AND QUESTIONS

1. (a) Will the cell operate when arranged as in Figure 21-1? Explain why.
   (b) What is the purpose of the porous cup (or salt bridge)?

   Answer: (a) No, because there is no path available along which the electrons may flow from the anode (where oxidation occurs) to the cathode (where reduction occurs).
   (b) The pores in the cup permit the movement of ions, which are the charge carriers in the solution. There would not be a complete circuit without this porous cup (or the salt bridge, which serves the same purpose).

2. (a) What is the spontaneous half-reaction taking place in the
      (i) $Zn(s)$–Zn^{+2} (0.5 *M*) half-cell?
      (ii) $Cu(s)$–Cu^{+2} (0.5 *M*) half-cell?
   (b) Write the total reaction.

   Answer: (a) $Zn(s) \rightleftharpoons Zn^{+2}(aq) + 2e^-$
   $2e^- + Cu^{+2}(aq) \rightleftharpoons Cu(s)$
   (b) $Zn(s) + Cu^{+2}(aq) \rightleftharpoons Zn^{+2}(aq) + Cu(s)$

3. (a) What is the direction of the electron flow in the wire connecting the zinc and copper electrodes?
   (b) What is the direction of the flow of negative ions through the porous cup (or salt bridge)?

Answer: (a) The electrons are released by the zinc atoms and then flow along the wire to the copper electrode, where they reduce copper ions.
(b) The negative ions migrate toward the zinc electrode (anode).

4. Predict the E° for the cell using the half-cells $Zn(s)$–Zn^{+2} (0.5 M) and $Cu(s)$–Cu^{+2} (0.5 M). Use the oxidation potentials in Appendix 8.

Answer

$$\begin{array}{ll} Zn(s) \rightleftharpoons Zn^{+2}(aq) + 2e^- & +0.76 \text{ volt} \\ Cu(s) \rightleftharpoons Cu^{+2}(aq) + 2e^- & -0.34 \text{ volt} \end{array}$$

Subtracting the second half-cell reaction from the first gives:

$$\begin{array}{ll} Zn(s) \rightleftharpoons Zn^{+2}(aq) + 2e^- & +0.76 \text{ volt} \\ Cu^{+2}(aq) + 2e^- \rightleftharpoons Cu(s) & +0.34 \text{ volt} \\ \hline Zn(s) + Cu^{+2}(aq) \rightleftharpoons Zn^{+2}(aq) + Cu(s) & +1.10 \text{ volts} \end{array}$$

How did your experimental result compare with the calculated value?

Answer: Student response. The use of 0.5 M solutions does not alter the predicted E°, since both the Cu^{+2} and the Zn^{+2} concentrations are the same, and since $K = \frac{[Zn^{+2}]}{[Cu^{+2}]}$. See the *Background Discussion.*

5. What is your explanation of the results obtained when sodium sulfide solution was added to the $Cu(s)$–Cu^{+2} (0.5 M) half-cell?

Answer: Since CuS is only very slightly soluble, the sulfide ions precipitate the cupric ions from solution. This causes a new equilibrium condition to be established, with a lower concentration of $Cu^{+2}(aq)$. This reduces the tendency for the reaction

$$Zn(s) + Cu^{+2}(aq) \rightleftharpoons Zn^{+2}(aq) + Cu(s) \qquad E = 1.10 \text{ volts}$$

to take place, hence we would expect the voltage to be lowered.

6. (a) Make a sketch of a cell which uses the half reaction $Zn(s)$–Zn^{+2} (0.5 M) as one electrode and the half reaction Br^- (0.5 M)–$Br_2(l)$ into which an inert electrode is placed. Predict the direction of electron flow through the wire connecting the zinc and inert metal electrodes. Predict the potential of the cell. Write the equation for each electrode reaction and for the total cell reaction.
   (b) Heat is evolved as zinc reacts with bromine. Would the potential of this cell be greater or smaller if the cell were heated? Explain.

Answer: (a) Electrons would flow from the zinc to the inert electrode. The potential would be 1.82 volts. At the zinc electrode,

$$Zn(s) \rightleftharpoons Zn^{+2}(aq) + 2e^- \qquad E^\circ = 0.76 \text{ volt}$$

At the other electrode,

$$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) \qquad E^\circ = 1.06 \text{ volts}$$

Adding gives

$$Zn(s) + Br_2(l) \rightleftharpoons Zn^{+2}(aq) + 2Br^-(aq) \qquad E^\circ = 1.82 \text{ volts}$$

(b) If heat is evolved the reactants would be favored by heating the cell. The potential would be smaller.

POSTLAB DISCUSSION. Since the voltages are nearly always less than those recorded in the $E°$ table, some explanation must be offered. The simplest is to point out the resistance of the salt bridge or walls of the porous cup to the flow of ions. This may be demonstrated by noting the drop in voltage when a salt bridge with smaller diameter is used. The accumulation of products at the poles (polarization) can reduce the observed voltage.

Supplementary Material

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

NITRIC ACID

A CHEM Study film
Running Time: 18 minutes

This film, made in collaboration with Dr. H. H. Sisler, uses the chemistry of nitric acid to review concepts of Chapters 8–12. The film shows the manufacture and use of HNO_3, but also illustrates the value of Le Chatelier's Principle, reaction rate considerations, and K and $E°$.

ELECTROCHEMICAL CELLS

A CHEM Study film
Running Time: 23 minutes

Equilibrium in an electrochemical cell is the central idea of this film. Experiments and animation illustrate the migration of ions and the electron flow in a silver–copper cell. The effect of changing concentrations of the reacting species is demonstrated in a silver–hydrogen cell and explained with animation. Prof. J. A. Campbell, of Harvey Mudd College, and June S. Ewing, CHEM Study Staff, collaborated on this film.

Background Discussion

OXIDATION-REDUCTION REACTIONS

The burning of Mg in O_2 (traditional oxidation) to give Mg^{+2} and O^{-2} in a lattice of the sodium chloride type (Mg^{+2} ions replace Na^+, and O^{-2} replace Cl^-) might be cited to establish a rationale for one definition of this chapter. If electrons are lost in a reaction, oxidation is said to have occurred; if electrons are gained in a reaction, reduction is said to have occurred. If our use of electrochemical cells to introduce oxidation-reduction seems strange in view of your past experience, you might consider any alternative procedures by which one could accumulate *quantitative* experimental information on this topic so easily. Remember that an electrochemical cell is simply an oxidation-reduction process carried out under special conditions. The systematization of the data so obtained is our basic objective.

THE DEFINITIONS OF OXIDATION-REDUCTION

You will notice the Textbook and Guide have been careful *not* to say flatly that "oxidation is the loss of electrons" or, more generally, that oxidation-reduction is the transfer of electrons. In addition, there is the definition, "oxidation-reduction is a change in oxidation number." We state these definitions cautiously because reactions exist that everyone will agree are examples of oxidation, but in which there is a real question whether any electrons were transferred. Examine the reaction

$$N_2(g) + O_2(g) = 2NO(g)$$

You cannot argue that nitrogen gave any electrons to oxygen, because the dipole moment of NO is so low (0.15D). To allow for this type of reaction, use both definitions given, and indicate that *each* is just one kind of description of oxidation-reduction.

THE THERMOCHEMICAL ASPECTS OF CELL OPERATION

In our earlier discussions (pp. 294 and 322), we noted that the balance between stability and randomness determines whether a reaction occurs spontaneously. We represented the balance by the equation

$$\Delta F = \Delta H - T\Delta S$$

and called ΔF the free energy. A spontaneous process at constant pressure and temperature has a negative value of ΔF.

We can use the relation between $E°$ and K to show some quantitative calculations. Use the equation

$$\log K = \frac{nE°}{0.0591}$$

which is valid at 25°C, the temperature for which we gave our $E°$ data. In this equation, n = the number of electrons involved in the net cell equation.

We will now apply this to the reaction represented by Textbook equation (*14*), which we found reached a state of equilibrium when rather large amounts of both reactants and products were present.

$$Co(s) + Ni^{+2} = Co^{+2} + Ni(s)$$

From Table 12-II we find

$$\begin{array}{ll}
Co \longrightarrow Co^{+2} + 2e^- & E° = +0.28 \text{ volt} \\
Ni \longrightarrow Ni^{+2} + 2e^- & E° = +0.25 \text{ volt} \\
\hline
Co(s) + Ni^{+2} \rightleftharpoons Co^{+2} + Ni(s) & E° = +0.03 \text{ volt}
\end{array}$$

Two electrons are involved in the net cell reaction. Application of our equation gives

$$\log K = \frac{2 \times 0.03}{0.0591} = \frac{2 \times 0.03}{0.06} = 1$$

$$K = 10^1 = 10$$

This value of K is commensurate with the observation that there is not a tremendous excess of products or of reactants at equilibrium.

By way of contrast, let us calculate K for reaction (*11*),

$$Zn(s) + Cu^{+2} = Zn^{+2} + Cu(s) \qquad (11)$$

for which we found experimentally that the state of equilibrium so favored the products that we could not detect the formation of any Cu^{+2} when we attempted to approach the equilibrium state by mixing the products. From Textbook Table 12-II we get

$$\begin{array}{rl}
\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{+2} + 2e^- & E^\circ = +0.76 \text{ volt} \\
\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{+2} + 2e^- & E^\circ = -0.34 \text{ volt} \\
\hline
\mathrm{Zn}(s) + \mathrm{Cu}^{+2} \rightleftharpoons \mathrm{Zn}^{+2} + \mathrm{Cu}(s) & E^\circ = +1.10 \text{ volt}
\end{array}$$

Substitution in the equation for K gives

$$\log K = \frac{2 \times 1.10}{0.0591} = 35.5$$

$$K = 10^{35.5}$$

or approximately 3×10^{35}. This very large value of K agrees with our experimental observations.

Since values of E° (Chapter 12) as well as values of K (Chapter 9) indicate the tendency for a reaction to go, it seems logical that they should be related to the value of ΔF. This expectation is realized if we consider a process under rather specific conditions.

Simple inspection of the equation

$$\mathrm{Cu} + 2\mathrm{Ag}^+ = 2\mathrm{Ag} + \mathrm{Cu}^{+2} + \text{heat}$$

and an application of Le Chatelier's Principle indicate that a large concentration of Ag^+ and a small concentration of Cu^{+2} should increase the tendency for the process

$$\mathrm{Cu} + 2\mathrm{Ag}^+ \longrightarrow \mathrm{Cu}^{+2} + 2\mathrm{Ag},$$

to occur. It would seem obvious, then, that ΔF could be used to compare the driving force for a series of chemical processes *only* if we reached some agreement relative to concentration in each process. Since E° was defined in terms of unit concentrations of ions, it seems logical to compare ΔF values when all effective concentration terms are also set equal to unity (1 mole/liter) and all effective gas pressures are set at one atmosphere. The value of ΔF measured under these conditions is designated ΔF°, which is related to the equilibrium constant for the system by the equation*

$$\Delta F^\circ = -RT \ln K = -(RT)(2.303 \log K)$$

where K is the value of the equilibrium constant, R is the gas constant of 2 cal mole^{-1} deg^{-1}, and T is the absolute temperature. For the process

$$\mathrm{Cu}(s) + 2\mathrm{Ag}^+(aq) \rightleftharpoons 2\mathrm{Ag}(s) + \mathrm{Cu}^{+2}(aq)$$

we can write $\Delta F^\circ = -2.303RT \log \frac{[\mathrm{Cu}^{+2}]}{[\mathrm{Ag}^+]^2}$. Free energy change, ΔF°, is related to the E° value for the above process by the expression

$$\Delta F^\circ = -nFE^\circ$$

where n = the number of moles of electrons transferred in the reaction as written and F = the value of the Faraday (96,500 coulombs, or 23,000 cal/volt × moles of electrons).

Since the expressions for both K and E° are equated to ΔF°, we can write

$$2.303RT \log K = nFE^\circ$$

$$\begin{aligned}
\log K &= nE^\circ \times \frac{F}{2.303 \times RT} \\
&= nE^\circ \times \frac{23{,}000}{2.303 \times 2 \times 298} \\
\log K &= \frac{nE^\circ}{0.059}
\end{aligned}$$

The above relationship is interesting and provides a direct connection between K and E°, but it is not of as much importance for the subject matter of this chapter as is the basic relationship between ΔF° and E°:

$$\Delta F^\circ = -nFE^\circ$$

Let us explore the nature of ΔF° by reviewing information we have about ΔH. The value of ΔH depends upon the quantity of materials taken. It depends also upon the initial and final states of the system; it varies with temperature; and it can be added when we add the equations for the processes (see p. 227). As might have been guessed from the similarity between ΔF and ΔH in the equation for ΔF, it is clear that ΔF also has all the characteristics shown by ΔH.

The property of additivity is especially important. By way of illustration, let us consider some processes considered in the Textbook.

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* It is probably apparent that some connections should exist between ΔF°, the equilibrium constant, K, and the standard potential for a cell, E°. The quantitative forms for such relationships are not so obvious, but they can be derived in a logical manner from basic definitions by using a routine which is somewhat too lengthy to reproduce here. You can find the derivation in any standard physical chemistry text. We have simply quoted the end results.

$$\begin{array}{ll}
(1)\ \mathrm{Zn}(s) + \mathrm{Ni}^{+2}(aq) \rightleftharpoons \mathrm{Zn}^{+2}(aq) + \mathrm{Ni}(s) & \\
\quad \Delta F^\circ = -nFE^\circ = -2 \times 23{,}000 \times 0.5 & = -23{,}000 \\
(2)\ \mathrm{Zn}^{+2}(aq) + 2\mathrm{Ag}(s) \rightleftharpoons \mathrm{Zn}(s) + 2\mathrm{Ag}^{+}(aq) & \\
\quad \Delta F^\circ = -nFE^\circ = -2 \times 23{,}000 \times (-1.6) & = \underline{+74{,}000} \\
\hfill \Delta F^\circ & = +51{,}000 \\
(3)\ \mathrm{Ni}^{+2}(aq) + 2\mathrm{Ag}(s) \rightleftharpoons 2\mathrm{Ag}^{+}(aq) + \mathrm{Ni}(s) &
\end{array}$$

$$-E^\circ = \frac{+51{,}000}{2 \times 23{,}000}$$

$$E^\circ = -1.1 \text{ volt}$$

Note two things about these equations. First, because the value for ΔF° is positive and the value for E° is negative, we know that the process is not spontaneous. The conclusion checks with all of our experience. Second, we have multiplied the E_1° and E_2° values by nF, added these ΔF° values, and then divided the sum again by nF to get E_3° of the overall process

$$\Delta F_3^\circ = \Delta F_1^\circ + \Delta F_2^\circ$$
$$-nFE_3^\circ = -nFE_1^\circ - nFE_2^\circ$$

As the above relation shows, we could have canceled the nF factor and simply added E_1° and E_2° values to get E_3°. *The addition of E° values is legitimate whenever the values of nF will cancel out.* This is true either in adding half-cell potentials to get overall cell potentials or in adding two overall cell potentials. *There are several circumstances, however, in which nF values don't cancel out and in which we must add ΔF values, not E° values.* Consider the following example. We have E° values for the two half-reactions, labeled 1 and 2 below, and we want the E° value for the reaction labeled 3.

$$\begin{array}{ll}
(1)\ \mathrm{Cr}(s) \rightleftharpoons \mathrm{Cr}^{+2} + 2e^-; & \Delta F_1^\circ = -nFE_1^\circ = -2 \times 23{,}000 \times 0.91 = -42{,}000 \text{ cal} \\
\underline{(2)\ \mathrm{Cr}^{+2} \rightleftharpoons \mathrm{Cr}^{+3} + e^-;} & \underline{\Delta F_2^\circ = -nFE_2^\circ = -1 \times 23{,}000 \times 0.41 = \quad -9{,}400 \text{ cal}} \\
(3)\ \mathrm{Cr}(s) \rightleftharpoons \mathrm{Cr}^{+3} + 3e^-; & \Delta F_3^\circ = -nFE_3^\circ = -3 \times 23{,}000 \times E^\circ \quad = -51{,}400 \text{ cal} \\
 & \qquad\qquad\qquad\qquad E_3^\circ = 0.74 \text{ volt}
\end{array}$$

$$\Delta F_1 + \Delta F_2 = \Delta F_3$$
$$-2 \times 23{,}000 \times 0.91 - (1 \times 23{,}000 \times 0.41) = -3 \times 23{,}000 \times E_3^\circ$$

The value n in processes 1, 2, and 3 is different. It is thus necessary for us to convert E° values to ΔF° values before addition, *since only ΔF° values are truly additive.*

For purposes of this course, all of our equations are of a type such that nF cancels and E° values are additive.

Reflection on the equation

$$\Delta F^\circ = -nFE^\circ$$

provides us with an answer to another question which frequently troubles students. Suppose we are considering the half-cell reaction $\mathrm{Ag}^{+}(aq) + e^- \rightleftharpoons \mathrm{Ag}(s)$, with an E° value of 0.80 volt. Suppose we double this equation in order to balance an overall equation [i.e., $2\mathrm{Ag}^{+}(aq) + 2e^- \rightleftharpoons 2\mathrm{Ag}(s)$]—why don't we double the value of E°? It is apparent that we double our value of ΔF° when we take two moles of Ag^+ instead of one, but note that, in doing this, we also double the number of electrons being transferred, hence E° remains unchanged. That is,

$$E^\circ = \frac{-\Delta F^\circ}{nF} = \frac{-1 \times \Delta F}{1 \times F} = -\frac{2 \times \Delta F^\circ}{2 \times F}$$
$$= -\frac{3 \times \Delta F^\circ}{3 \times F}$$

and so forth. Thus we see that E° is a measure of the reaction tendency not a measure of the total energy content of the system. In many ways E° is comparable to temperature in thermal systems. If we have 100 g of water at 100°C and we add to this another 100 g of water at 100°C, the temperature of the system remains at 100°C. We don't alter the intensity factor by changing the quantity of water, but we do change the *quantity* of heat (energy) stored in the system. Neither is E° changed by doubling the size of the cell, but we do double the *quantity* of energy stored in the system. Small cells have the same voltage as big cells, but they can't produce current for as long.

THE EFFECTS OF CONCENTRATION ON E VALUES FOR A PROCESS

We have been careful to define $E°$ as the voltage for a given cell when all effective concentrations are one mole/liter and all effective gas pressures are one atmosphere. We have also noticed that if we change the concentrations or gas pressures, the E value for the cell changes from that of $E°$. It would be convenient if we could simply add to or subtract from $E°$ a correction term to compensate for changes of concentration. Fortunately such a calculation is possible. By methods we prefer not to give here, we can derive a relationship which has the form

$$E = E° - \frac{0.059}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

the quantity subtracted being the correction term for the concentration effect. The expression involving products and reactants has the same form as the equilibrium constant.

Again consider, as an example, the equation

$$Zn + Cu^{+2} \rightleftharpoons Cu + Zn^{+2} \qquad E° = 1.10$$

The value of E at some concentration other than the standard 1 M becomes

$$E = E° - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

If we reduce the concentration of Zn^{+2}, the size of the second term gets smaller; we subtract a smaller number from $E°$, hence E is larger, as we would expect from Le Chatelier's Principle. If $[Zn^{+2}]$ and $[Cu^{+2}]$ are both 1, the second term goes to zero, and $E = E°$, as our definition of $E°$ demands. Finally, if Zn^{+2} and Cu^{+2} are at their equilibrium concentrations then $\frac{[Zn^{+2}]}{[Cu^{+2}]} = K$ for the process, and our equation becomes

$$E = E° - \frac{0.059}{2} \log K = 0$$

as we noted earlier in the development section (p. 375). The voltage is zero when the cell system reaches equilibrium.

The value of E is not particularly sensitive to small changes in concentration. Suppose we keep the concentration of Cu^{+2} constant at unit strength and cut the concentration of Zn^{+2} to one-tenth of its original value. We find that E then becomes

$$E = E° - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]} = 1.10 - \frac{0.059}{2} \log \frac{0.1}{1}$$

$$E = 1.10 - \frac{0.059}{2} \times -1 = 1.10 + 0.030$$

$$= 1.13 \text{ volts}$$

A ten-fold change in the concentration of Zn^{+2} gives a change of only 0.03 volt in the value of E.

FACTORS DETERMINING THE SIZE OF $E°$ VALUES

Your students are undoubtedly curious at this point about the factors that make $E°$ values large or small. The quantity $E°$ is a measure of free energy change, and ΔF is the combination of stability change (ΔH) and randomness change ($T\Delta S$).

$$\Delta F = \Delta H - T\Delta S$$

Thus $E°$ is fixed by the factors which determine relative stability (ΔH) (such as bond strengths, ionization energies, hydration energies) and by the factors which determine randomness (ΔS) (about which we have said rather little). More will be said about the factors influencing ΔH (hence, ΔF) in the Teacher's Guide for Chapter 17.

BALANCING OXIDATION-REDUCTION EQUATIONS

Two methods have been given for balancing oxidation-reduction equations, and we emphasized in the development section that the mechanics of both methods are very arbitrary. That the methods work is no evidence in support of the validity of half-cell processes or of oxidation numbers. The methods simply demand that, in the end, we conserve mass and charge. As further proof of this point, it is interesting to note that we can set up a completely algebraic process for balancing redox equations—a process based solely upon our conservation laws.

Using coefficients *a*, *b*, *c*, *d*, etc. for each item in the equation, we can write algebraic equations demanding conservation of each of the elements in the equation. If we then solve all of the resulting equations simultaneously, numerical values for *a*, *b*, *c*, *d*, etc. follow. Because this method represents an algebraic formalism, it will work on any equation. We should emphasize, then, that our use of oxidation numbers or half-reactions in balancing an equation does not imply that we really believe electronic charges are truly described by the formalism of these schemes.

Answers to Exercises and Problems

Ex. 12-1. Compare the mole ratio Ag/Cu derived from your own data for Experiment 7 to the electrochemical data given in Sec. 12-1.1.

Answer

Student Response. The sample data given on p. 69 show:

$$\begin{aligned} \text{moles Cu} &= 0.0120 \pm 2.6\% \\ \text{moles Ag} &= 0.0237 \pm 0.8\% \end{aligned}$$

which give a ratio Ag/Cu = 1.99 ± 3.4%.

Ex. 12-2. From the statement in the text that nickel metal reacts with H^+ to give $H_2(g)$ and the additional information that zinc metal reacts readily with nickel sulfate solution, decide where to add the half-reaction Ni–Ni^{+2} in our list.

Answer

The Ni–Ni^{+2} half-reaction will appear above hydrogen but below zinc. Thus

$$\begin{array}{lcl} Zn(s) & \longrightarrow & Zn^{+2} + 2e^- \\ Ni(s) & \longrightarrow & Ni^{+2} + 2e^- \\ H_2(g) & \longrightarrow & 2H^+ + 2e^- \\ Cu\ s) & \longrightarrow & Cu^{+2} + 2e^- \\ Ag(s) & \longrightarrow & Ag^+ + e^- \end{array}$$

Ex. 12-3. In Exercise 12-2 you placed the Ni–Ni^{+2} half-reaction into Table 12-I. Check your placement by examining the half-cell potential of this half-reaction in Table 12-II.

Answer

The nickel half-reaction was placed between the zinc and hydrogen half-reactions. The nickel half-cell potential, +0.25 volt, is between the zinc half-cell potential, +0.76 volt, and the hydrogen half-cell potential, 0.00 volt.

Ex. 12-4. Use the values of E° to predict whether cobalt metal will tend to dissolve in a 1 M solution of acid, H^+. Now predict whether cobalt metal will tend to dissolve in a 1 M solution of zinc sulfate (reacting with Zn^{+2}).

Answer

$$\begin{array}{llr} Co(s) + 2H^+ \xrightarrow{?} Co^{+2} + H_2(g) & & \\ Co(s) \longrightarrow Co^{+2} + 2e^- & & +0.28\ \text{volt} \\ H_2(g) \longrightarrow 2H^+ + 2e^- & & 0.00\ \text{volt} \\ \hline & \text{Net } E^\circ = & 0.28\ \text{volt} \end{array}$$

Since net E° is positive, the equilibrium reaction favors the products. *Cobalt will dissolve in H^+.*

$$\begin{array}{llr} Co(s) + Zn^{+2} \xrightarrow{?} Co^{+2} + Zn(s) & & \\ Co(s) \longrightarrow Co^{+2} + 2e^- & & +0.28\ \text{volt} \\ Zn(s) \longrightarrow Zn^{+2} + 2e^- & & +0.76\ \text{volt} \\ \hline & \text{Net } E^\circ = & (+0.28) - (+0.76) \\ & = & -0.48\ \text{volt} \end{array}$$

Since the net value of E° is negative, the equilibrium reaction forms the reactants. *Cobalt metal will not dissolve in a Zn^{+2} solution to a significant extent.*

Ex. 12-5. Use Table 12-II to decide which substances in the following list tend to oxidize bromide ion, Br^-: $Cl_2(g)$, H^+, Ni^{+2}, MnO_4^-.

Answer

To oxidize bromide ion, it is necessary to use a half-reaction in which electrons are lost less readily than in the reaction $2Br^- \rightleftharpoons Br_2(l) + 2e^-$. This is the same as saying that, to oxidize Br^-, electrons must be removed by another half-reaction. To accomplish this, we need a half-reaction whose E° is less than −1.06 volts. In the list of choices, only MnO_4^- and Cl_2 half-reactions have an E° less than −1.06 volts.

$$\begin{array}{llr} 2Br^- \longrightarrow Br_2(l) + 2e^- & & -1.06\ \text{volts} \\ Mn^{+2} + 4H_2O \longrightarrow MnO_4^- + 8H^+ & & \\ \qquad + 4H_2O & & -1.52\ \text{volts} \\ \hline & \text{Net } E^\circ = & (-1.06) - (-1.52)\ \text{volts} \\ & = & +0.46\ \text{volt} \end{array}$$

$$\begin{array}{llr} 2Br^- \longrightarrow Br_2(l) + 2e^- & & -1.06\ \text{volts} \\ 2Cl^- \longrightarrow Cl_2(g) + 2e^- & & -1.36\ \text{volts} \\ \hline & \text{Net } E^\circ = & (-1.06) - (-1.36)\ \text{volts} \\ & = & +0.30\ \text{volt} \end{array}$$

Ex. 12-6. Use Table 12-II to decide which substances in the following list tend to reduce $Br_2(l)$: Cl^-, $H_2(g)$, $Ni(s)$, Mn^{+2}.

Answer

To reduce $Br_2(l)$ it is necessary to use a half-reaction in which electrons are lost more readily than in the reaction $2Br^- \rightleftharpoons Br_2(l) + 2e^-$. To do this, we need a half-reaction whose E° is greater (more positive) than −1.06 volts. In the list of choices, only $H_2(g)$ and $Ni(s)$ half-reactions satisfy the requirement.

$$\begin{array}{lll} H_2(g) \longrightarrow 2H^+ + 2e^- & & 0.00 \text{ volt} \\ 2Br^- \longrightarrow Br_2(l) + 2e^- & & -1.06 \text{ volts} \\ \hline & \text{Net } E^\circ = (0.00) - (-1.06) \text{ volts} & \\ & \quad = +1.06 \text{ volts} & \end{array}$$

$$\begin{array}{lll} Ni(s) \longrightarrow Ni^{+2} + 2e^- & & +0.25 \text{ volt} \\ 2Br^- \longrightarrow Br_2(l) + 2e^- & & -1.06 \text{ volts} \\ \hline & \text{Net } E^\circ = (+0.25) - (-1.06) \text{ volts} & \\ & \quad = +1.31 \text{ volts} & \end{array}$$

Ex. 12-7. The reactions by which SO_2 and SO_3 dissolve in water are not considered to be oxidation-reduction reactions:

$$SO_2(g) + H_2O \longrightarrow HSO_3^-(aq) + H^+(aq) \quad (79)$$
$$SO_3(g) + H_2O \longrightarrow HSO_4^-(aq) + H^+(aq) \quad (80)$$

Convince yourself that none of the atoms in either (*79*) or (*80*) changes oxidation number.

Answer

By assumption, the oxidation number of oxygen is -2 in every one of the compounds SO_2, H_2O, HSO_3^-, SO_3, and HSO_4^-. Hence its oxidation number does not change. The same is true for hydrogen, again by assumption. We must investigate whether the oxidation number of sulfur changes in either of the two reactions.

Reaction (*79*):

$$\begin{array}{lll} SO_2: & (\text{oxid. no. sulfur}) & = (\text{charge on } SO_2) - 2(\text{oxid. no. oxygen}) \\ & & = \quad 0 \quad - \quad 2(-2) \\ & & = -(-4) = +4 \\ HSO_3^-: & (\text{oxid. no. sulfur}) & = (\text{charge on } HSO_3^-) - (\text{oxid. no. H}) - 3(\text{oxid. no. oxygen}) \\ & & = \quad (-1) \quad - \quad (+1) \quad - \quad 3(-2) \\ & & = -1 - 1 + 6 = +4 \end{array}$$

Thus, in a reaction that changes SO_2 into HSO_3^-, the oxidation number of sulfur is constant at $+4$.

Reaction (*80*):

$$\begin{array}{lll} SO_3: & (\text{oxid. no. sulfur}) & = (\text{charge on } SO_3) - 3(\text{oxid. no. oxygen}) \\ & & = \quad 0 \quad - \quad 3(-2) \quad = +6 \\ HSO_4^-: & (\text{oxid. no. sulfur}) & = (\text{charge on } HSO_4^-) - (\text{oxid. no. H}) - 4(\text{oxid. no. oxygen}) \\ & & = \quad (-1) \quad - \quad (+1) \quad - \quad 4(-2) \\ & & = -1 - 1 + 8 = +6 \end{array}$$

Thus, in the change of SO_3 into HSO_4^-, the oxidation number of sulfur is constant at $+6$.

Ex. 12-8. In reaction (*76*), the oxidation number of sulfur changes from $+4$ to $+6$. According to this, two electrons are released by each sulfur atom oxidized. Show that these electrons are gained by oxygen if we assume oxygen has oxidation number equal to zero in O_2.

Answer

If we assume the oxidation number of oxygen to be zero for O_2, then the fictitious charge of oxygen changes from zero to -2, consuming two electrons per oxygen atom. This is just the number of electrons released by each sulfur atom as its fictitious charge changes from $+4$ to $+6$. Hence, with these assumed charges, electrons are neither produced nor consumed in the balanced equation.

Ex. 12-9. Show that the oxidation number of nitrogen is $+5$ in each of the two species, NO_3^- and N_2O_5.

Answer

NO_3^- ion: By rule 4, each atom of oxygen is given oxidation number -2. Therefore, the total oxidation number of the three oxygen atoms is $3(-2) = -6$. Since the ion NO_3^- has a minus one charge, the oxidation number $+5$ must be assigned to nitrogen.

Algebraically, let y = oxid. no. of nitrogen. We have

$$y + 3(-2) = -1$$
$$y = -1 + 6 = +5$$

N_2O_5: Again letting y = oxid. no. of nitrogen,

$$2y + 5(-2) = 0$$
$$y = \frac{0 + 10}{2} = +5$$

Ex. 12-10. From Appendix 3, estimate the minimum voltage required to cause electrolysis of 1 *M* HCl, forming $H_2(g)$ and $O_2(g)$, each at one atmosphere pressure. Show that at this voltage, electrolysis to produce $H_2(g)$ and $Cl_2(g)$ will not occur.

Answer

(i) $2H^+ + 2e^- \longrightarrow H_2(g)$ 0.00 volts

(ii) $H_2O \longrightarrow 2e^- + \frac{1}{2}O_2 + 2H^+$ −1.23 volts

(iii) $2Cl^- \longrightarrow 2e^- + Cl_2(g)$ −1.36 volts

The relevant half-reactions are shown above. Combining (i) and (ii) we see that −1.23 volts is the minimum voltage required to electrolyze 1 *M* $H^+(aq)$, producing $H_2(g)$ and $O_2(g)$. The production of $H_2(g)$ and $Cl_2(g)$ requires a minimum voltage of −1.36 volts, thus they are not formed at the voltage needed for the production of $H_2(g)$ and $O_2(g)$.

Pr. 1. One method of obtaining copper metal is to let a solution containing Cu^{+2} ions trickle over scrap iron. Write the equations for the two half-reactions involved. Assume the iron becomes Fe^{+2}. Indicate in which half-reaction oxidation is taking place.

Answer

$Cu^{+2} + 2e^- \longrightarrow Cu(s)$ (reduction)

$Fe(s) \longrightarrow Fe^{+2} + 2e^-$ (oxidation)

Pr. 2

(a) If a neutral atom becomes positively charged, has it been oxidized or reduced? Write a general equation using *M* for the neutral atom.

(b) If an ion X^{-1} acquires a −2 charge, has it been oxidized or reduced? Write a general equation.

Answer

(a) Oxidized; $M \longrightarrow M^+ + e^-$

The atom M has lost an electron; thus it has undergone one type of oxidation.

(b) Reduced; $X^- + e^- \longrightarrow X^{-2}$

The ion X^- gained an electron the loss of which constitutes one type of reduction.

These are said to be types of oxidation and reduction, for there are others. Those above are clear-cut cases of electron loss or gain. Later, cases will be considered in which it is not clear whether there has been an electron transfer (e.g., when NO changes to NO_2). A change in oxidation number of N has occurred.

Pr. 3. Aluminum metal reacts with aqueous acidic solutions to liberate hydrogen gas. Write the two half-reactions and the net ionic reaction.

Answer

(a) $Al \longrightarrow Al^{+3} + 3e^-$

(b) $2H^+ + 2e^- \longrightarrow H_2(g)$

2(a) + 3(b) gives $2Al + 6H^+ \longrightarrow 2Al^{+3} + 3H_2(g)$

Pr. 4. When copper is placed in concentrated nitric acid, vigorous bubbling takes place as a brown gas is evolved. The copper disappears, and the solution changes from colorless to a greenish-blue. The brown gas is nitrogen dioxide, NO_2, and the solution's color is due to the formation of cupric ion, Cu^{+2}. Using half-reactions from Appendix 3, write the net ionic equation for this reaction.

Answer

$$Cu \longrightarrow Cu^{+2} + 2e^-$$

$$\underline{2[NO_3^- + 2H^+ + e^- \longrightarrow NO_2(g) + H_2O]}$$

Net ionic: $Cu + 2NO_3^- + 4H^+ \longrightarrow Cu^{+2} + 2NO_2(g) + 2H_2O$

Pr. 5. Nickel metal reacts with cupric ions, Cu^{+2}, but not with zinc ions, Zn^{+2}; magnesium metal does react with Zn^{+2}. In each case of reaction, ions of +2 charge are formed. Use these data to expand the table of reactions on p. 206.

Answer

The expanded table will be

$$Mg \longrightarrow Mg^{+2} + 2e^-$$
$$Zn \longrightarrow Zn^{+2} + 2e^-$$
$$Ni \longrightarrow Ni^{+2} + 2e^-$$
$$Cu \longrightarrow Cu^{+2} + 2e^-$$
$$Ag \longrightarrow Ag^+ + e^-$$

Pr. 6. In acid solution the following are true: H_2S will react with oxygen to give H_2O and sulfur. H_2S will not react in the corresponding reaction with selenium or tellurium. H_2Se will react with sulfur giving H_2S and selenium, but it will not react with tellurium. Arrange the hydrides of column VI, H_2O, H_2S, H_2Se, and H_2Te, in order of their tendency to lose electrons to form the elements, O_2, S, Se, and Te.

Answer

$H_2Te \longrightarrow 2H^+ + Te + 2e^-$

(greatest tendency to lose electrons)

$H_2Se \longrightarrow 2H^+ + Se + 2e^-$

$H_2S \longrightarrow 2H^+ + S + 2e^-$

$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

(least tendency to lose electrons)

For instance,

$H_2S \longrightarrow S + 2H^+ + 2e^-$ (a loss of electrons)

$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$ (a gain of electrons)

$H_2S + \frac{1}{2}O_2 \longrightarrow S + H_2O$

Thus the reactions given above show H_2S has a greater tendency to lose electrons than does H_2O. Similar reasoning places H_2Se above H_2S, and H_2Te above H_2Se.

Pr. 7. If you wish to replate a silver spoon, would you make it the anode or cathode in a cell? Use half-reactions in your explanation. How many moles of electrons are needed to plate out 1.0 gram of Ag?

Answer

To plate out any metal, positive metallic ions must be changed to neutral atoms:

$$M^{+n} + ne^- \longrightarrow M(s)$$

Such a reaction involves reduction. Since reduction takes place at the cathode, the spoon to be plated should be made the cathode.

For this case, the cathode reaction (reduction) would be

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

To determine moles of electrons needed to plate out 1.0 gram of Ag(*s*):

g Ag/mol wt Ag

$1.0\text{ g }(108\text{ g/mole}) = \frac{1.0}{108}$ mole of Ag

mole Ag $\times \frac{\text{mole } e^-}{\text{mole Ag}}$

$\frac{1.0}{108} \times \frac{1}{1} = 0.0093$ mole of electrons

Pr. 8. Figure 12-5 shows electrons leaving the Cu(*s*) and going to the Ag(*s*). Experimentally, both half-cells are found to be electrically neutral before current flows and to remain so as the cell operates. Explain this.

Answer

The half-cells remain electrically neutral (equal number of positive and negative charges) by movement of ions. As more Cu^{+2} ions are made, nitrate ions move into the copper half-cell. At the same time, Ag^+ ions are being removed, hence there is no excess positive charge left in the silver half-cell.

Pr. 9. In the electrolysis of aqueous cupric bromide, $CuBr_2$, 0.500 gram of copper is deposited at one electrode. How many grams of bromine are formed at the other electrode? Write the anode and cathode half-reactions.

Answer: 1.26 grams of $Br_2(l)$.

Answer

$Cu^{+2} + 2e^- \longrightarrow Cu(s)$

$2Br^- \longrightarrow Br_2(l) + 2e^-$

STEP I: $0.500\text{ g Cu} = \frac{0.500\text{ g}}{63.5\text{ g/mole}} = 7.87 \times 10^{-3}$ mole/Cu

STEP II: One mole of Br_2 is formed for every mole of Cu. Therefore 7.87×10^{-3} mole of Br_2 is formed with 7.87×10^{-3} mole of Cu.

STEP III: 7.87×10^{-3} mole gives 7.87×10^{-3} mole $\times$ 159.8 g/mole = 1.26 g $Br_2(l)$

Pr. 10. Complete the following equations. Determine the net potential of such a cell, and decide whether reaction can occur.

(a) $Zn + Ag^+ \longrightarrow$
(b) $Cu + Ag^+ \longrightarrow$
(c) $Sn + Fe^{+2} \longrightarrow$
(d) $Hg + H^+ \longrightarrow$

Answer

	$E°$
(a) $Zn \longrightarrow Zn^{+2} + 2e^-$	0.76 volt
$2(Ag^+ + e^- \longrightarrow Ag)$	+0.80 volt
$Zn + 2Ag^+ \longrightarrow Zn^{+2} + 2Ag$ E_{net} =	1.56 volts
Reaction can occur.	
(b) $Cu \longrightarrow Cu^{+2} + 2e^-$	−0.34 volt
$2(Ag^+ + e^- \longrightarrow Ag)$	+0.80 volt
$Cu + 2Ag^+ \longrightarrow Cu^{+2} + 2Ag$ E_{net} =	0.46 volt
Reaction can occur.	
(c) $Sn \longrightarrow Sn^{+2} + 2e^-$	0.14 volt
$Fe^{+2} + 2e^- \longrightarrow Fe$	−0.44 volt
E_{net} =	−0.30 volt
Practically no reaction can occur.	
(d) $Hg \longrightarrow Hg^{+2} + 2e^-$	−0.78 volt
$H^+ + e^- \longrightarrow H$	0.00 volt
E_{net} =	−0.78 volt
Practically no reaction can occur.	

Pr. 11. For each of the following,

(i) write the half-reactions;
(ii) determine the net reaction;
(iii) predict whether the reaction can occur giving the basis for your prediction:

(a) $Mg(s) + Sn^{+2} \longrightarrow$
(b) $Mn(s) + Cs^{+} \longrightarrow$
(c) $Cu(s) + Cl_2 \longrightarrow$
(d) $Zn(s) + Fe^{+2} \longrightarrow$
(e) $Fe(s) + Fe^{+3} \longrightarrow$

Answer

(a)
$$\begin{array}{lr} Mg \longrightarrow Mg^{+2} + 2e^- & 2.37 \text{ volts} \\ \underline{Sn^{+2} + 2e^- \longrightarrow Sn} & \underline{-0.14 \text{ volt}} \\ Mg + Sn^{+2} \longrightarrow & \\ \qquad Mg^{+2} + Sn \quad E_{net} = & 2.23 \text{ volts} \end{array}$$

Reaction can occur.

(b)
$$\begin{array}{lr} Mn \longrightarrow Mn^{+2} + 2e^- & 1.18 \text{ volts} \\ \underline{2Cs^+ + 2e^- \longrightarrow 2Cs} & \underline{-2.92 \text{ volts}} \\ \qquad E_{net} = & -1.74 \text{ volts} \end{array}$$

Practically no reaction can occur.

(c)
$$\begin{array}{lr} Cu = Cu^{+2} + 2e^- & -0.34 \text{ volt} \\ \underline{Cl_2 + 2e^- = 2Cl^-} & \underline{+1.36 \text{ volts}} \\ Cu + Cl_2 & \\ \qquad = Cu^{+2} + 2Cl^- \quad E_{net} = & 1.02 \text{ volts} \end{array}$$

Reaction can occur.

(d)
$$\begin{array}{lr} Zn = Zn^{+2} + 2e^- & 0.76 \text{ volt} \\ \underline{Fe^{+2} + 2e^- = Fe} & \underline{-0.44 \text{ volt}} \\ Zn + Fe^{+2} & \\ \qquad = Zn^{+2} + Fe \quad E_{net} = & 0.32 \text{ volt} \end{array}$$

Reaction can occur.

(e)
$$\begin{array}{lr} Fe = Fe^{+2} + 2e^- & 0.44 \text{ volt} \\ \underline{2Fe^{+3} + 2e^- = 2Fe^{+2}} & \underline{+0.77 \text{ volt}} \\ Fe + 2Fe^{+3} = 3Fe^{+2} \quad E_{net} = & 1.21 \text{ volts} \end{array}$$

Reaction can occur.

Pr. 12. A half-cell consisting of a palladium rod dipping into a 1 M $Pd(NO_3)_2$ solution is connected with a standard hydrogen half-cell. The cell voltage is 0.99 volt, and the platinum electrode in the hydrogen half-cell is the anode. Determine $E°$ for the reaction

$$Pd \longrightarrow Pd^{+2} + 2e^-$$

Answer

Oxidation occurs at the anode, which is given as the hydrogen electrode. The anode reaction must be

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$$

These liberated electrons must be used at the cathode by the reaction

$$Pd^{+2}(aq) + 2e^- \longrightarrow Pd(s)$$

Since the cell voltage is given as 0.99 volts, we have

$$Pd(s) \longrightarrow Pd^{+2}(aq) + 2e^- \qquad E° = -0.99 \text{ volt}$$

Pr. 13. Suppose chemists had chosen to call the $2I^- \longrightarrow I_2 + 2e^-$ half-cell potential zero.

(a) What would be $E°$ for $Na \longrightarrow Na^+ + e^-$?
(b) How much would the net potential for the reaction $2Na + I_2 \longrightarrow 2Na^+ + 2I^-$ change?

Answer

(a) $Na \longrightarrow Na^+ + e^-$ would be 0.53 volts more positive, or $E° = 2.71 + 0.53 = 3.24$ volts. All other half-cells would also be 0.53 volts more positive.

(b) No change.

With hydrogen potential = 0 volt:
$$\begin{array}{lr} 2Na \longrightarrow 2Na^+ + 2e^- & 2.71 \text{ volts} \\ I_2 + 2e^- \longrightarrow 2I^- & \underline{0.53 \text{ volt}} \\ & 3.24 \text{ volts} \end{array}$$

With iodine potential = 0 volt:
$$\begin{array}{lr} 2Na \longrightarrow 2Na^+ + 2e^- & 3.24 \text{ volts} \\ I_2 + 2e^- \longrightarrow 2I^- & \underline{0.00 \text{ volt}} \\ & 3.24 \text{ volts} \end{array}$$

Pr. 14. If a piece of copper metal is dipped into a solution containing Cr^{+3} ions, what will happen? Explain, using $E°$s.

Answer: Nothing happens.

$$\begin{array}{lr} 3Cu = 3Cu^{+2} + 6e^- & -0.34 \text{ volt} \\ \underline{2Cr^{+3} + 6e^- = 2Cr} & \underline{-0.74 \text{ volt}} \\ \qquad E_{net} = & -1.08 \text{ volts} \end{array}$$

Practically no reaction occurs spontaneously. We might use $Cu = Cu^+ + e^-$, but this is even more negative (−0.52 volts), and E_{net} is then −1.26 volts.

Pr. 15. What would happen if an aluminum spoon were used to stir an $Fe(NO_3)_2$ solution? What would happen if an iron spoon were used to stir an $AlCl_3$ solution?

Answer

The aluminum spoon would dissolve.

$$\begin{array}{lr} 2(Al \longrightarrow Al^{+3} + 3e^-) & E° = 1.66 \text{ volts} \\ \underline{3(Fe^{+2} + 2e^- \longrightarrow Fe)} & \underline{E° = -0.44 \text{ volt}} \\ 2Al + 3Fe^{+2} \longrightarrow & \\ \qquad 2Al^{+3} + 3Fe & E_{net} = 1.22 \text{ volts} \end{array}$$

Nothing would happen to the iron spoon. The reverse reaction does not occur to a significant extent.

Pr. 16. Can 1 *M* $Fe_2 SO_4)_3$ solution be stored in a container made of nickel metal? Explain your answer.

Answer

No. The container would dissolve.

$$\begin{array}{ll}
Ni \longrightarrow Ni^{+2} + 2e^- & E^\circ = 0.25 \text{ volt} \\
2Fe^{+3} + 2e^- \longrightarrow 2Fe^{+2} & E^\circ = 0.77 \text{ volt} \\
\hline
Ni + 2Fe^{+3} \longrightarrow Ni^{+2} + 2Fe^{+2} & E_{\text{net}} = 1.02 \text{ volts}
\end{array}$$

Since E_{net} is positive, the reaction dissolving nickel occurs spontaneously.

Pr. 17. Suppose water is added to each of the beakers containing copper sulfate in the two electrochemical cells shown in Figure 12-4 (p. 204). What change will occur in the voltage in each cell? Explain.

Answer

In the cell shown on the left, the reaction that occurs spontaneously is

$$2Ag^+ + Cu(s) \longrightarrow 2Ag(s) + Cu^{+2}$$

Dilution of the copper sulfate solution increases the tendency for Cu(*s*) to release electrons and dissolve. The voltage will become larger.

In the cell shown on the right, the reaction that occurs spontaneously is

$$Zn(s) + Cu^{+2} \longrightarrow Zn^{+2} + Cu(s)$$

Dilution of the copper sulfate solution decreases the tendency for Cu^{+2} to accept electrons and for copper metal to form. The voltage will become smaller.

Pr. 18. Determine the oxidation number of carbon in the compounds carbon monoxide, CO, carbon dioxide, CO_2, and in diamond.

Answer

CO	O = −2	C = +2
CO_2	O = −2	C = +4
diamond		C = 0

Pr. 19. Determine the oxidation number of uranium in each of the known compounds: UO_3, U_3O_8, U_2O_5, UO_2, UO, K_2UO_4, $Mg_2U_2O_7$.

Answer

UO_3	3O = −6	U = +6
U_3O_8	8O = −16	$U = +\left(\frac{16}{3}\right)$
U_2O_5	5O = −10	U = +5
UO_2	2O = −4	U = +4
UO	O = −2	U = +2
K_2UO_4	4O = −8	
	2K = +2	U = +6
	−6	
$Mg_2U_2O_7$	7O = −14	
	2Mg = +4	U = +5
	−10	

Pr. 20. By use of half-reactions, give a balanced equation for each of the following reactions:

(a) $H_2O_2 + I^- + H^+$ gives $H_2O + I_2$
(b) $Cr_2O_7^{-2} + Fe^{+2} + H^+$ gives $Cr^{+3} + Fe^{+3} + H_2O$
(c) $Cu + NO_3^- + H^+$ gives $Cu^{+2} + NO + H_2O$
(d) $MnO_4^- + Sn^{+2} + H^+$ gives $Mn^{+2} + Sn^{+4} + H_2O$

Answer

(a)

$$\begin{array}{l}
2e^- + H_2O_2 + 2H^+ \longrightarrow 2H_2O \\
\qquad 2I^- \longrightarrow 2e^- + I_2 \\
\hline
2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O
\end{array}$$

(b)

$$\begin{array}{l}
Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O \\
\qquad 6(Fe^{+2} \longrightarrow e^- + Fe^{+3}) \\
\hline
Cr_2O_7^- + 6Fe^{+2} + 14H^+ \longrightarrow \\
\qquad 2Cr^{+3} + 6Fe^{+3} + 7H_2O
\end{array}$$

(c)

$$\begin{array}{l}
\qquad 3(Cu \longrightarrow Cu^{+2} + 2e^-) \\
2[3e^- + NO_3^- + 4H^+ \longrightarrow NO + 2H_2O] \\
\hline
3Cu + 2NO_3^- + 8H^+ \longrightarrow \\
\qquad 3Cu^{+2} + 2NO + 4H_2O
\end{array}$$

(d)

$$\begin{array}{l}
2(5e^- + MnO_4^- + 8H^+ \longrightarrow Mn^{+2} + 4H_2O) \\
\qquad 5(Sn^{+2} \longrightarrow Sn^{+4} + 2e^-) \\
\hline
2MnO_4^- + 16H^+ + 5Sn^{+2} \longrightarrow \\
\qquad 2Mn^{+2} + 8H_2O + 5Sn^{+4}
\end{array}$$

Pr. 21. By use of oxidation numbers, give a balanced equation for each of the following reactions:

(a) $HBr + H_2SO_4$ gives $SO_2 + Br_2 + H_2O$
(b) $NO_3^- + Cl^- + H^+$ gives $NO + Cl_2 + H_2O$
(c) $Zn + NO_3^- + H^+$ gives $Zn^{+2} + NO_2 + H_2O$
(d) BrO^- gives $Br^- + BrO_3^-$

Answer

(a)

$$\begin{array}{ccccccc}
HBr & + & H_2SO_4 & \longrightarrow & SO_2 & + & Br_2 + H_2O \\
-1 & & +6 & & +4 & & 0
\end{array}$$

For bromine: $-1 \xrightarrow{+1} 0$

For sulfur: $+6 \xrightarrow{-2} +4$

To equalize changes of oxidation numbers, multiply bromine by 2 and sulfur by 1. Insert these multipliers in the equation, and complete the balancing:

$$2HBr + H_2SO_4 \longrightarrow SO_2 + Br_2 + 2H_2O$$

(b) $\underset{+5}{NO_3^-} + \underset{-1}{Cl^-} + H^+ \longrightarrow \underset{+2}{NO} + \underset{0}{Cl_2} + H_2O$

For nitrogen: $+5 \xrightarrow{-3} +2$

For chlorine: $-1 \xrightarrow{+1} 0$

To equalize changes in oxidation numbers, multiply nitrogen by 1 and chlorine by 3. Insert these multipliers in the equation, and complete the balancing:

$$2NO_3^- + 6Cl^- + 8H^+ \longrightarrow 2NO + 3Cl_2 + 4H_2O$$

(c) $\underset{0}{Zn} + \underset{+5}{NO_3^-} + H^+ \longrightarrow \underset{+2}{Zn^{+2}} + \underset{+4}{NO_2} + H_2O$

For zinc: $0 \xrightarrow{+2} +2$

For nitrogen: $+5 \xrightarrow{-1} +4$

To equalize changes in oxidation numbers, multiply zinc by 1 and nitrogen by 2. Insert these multipliers in the equation, and complete the balancing:

$$Zn + 2NO_3^- + 4H^+ \longrightarrow Zn^{+2} + 2NO_2 + 2H_2O$$

(d) $\underset{+1}{BrO^-} \longrightarrow \underset{-1}{Br^-} + \underset{+5}{BrO_3^-}$

For Br^+ to Br^-: $+1 \xrightarrow{-2} -1$

For Br^+ to Br^{+5}: $+1 \xrightarrow{+4} +5$

To equalize changes in oxidation numbers, two Br^{+1} ions must go to Br^- for each one that goes to Br^{+5}:

$$3BrO^- \longrightarrow 2Br^- + BrO_3^-$$

Pr. 22. Use oxidation numbers to balance the reaction between ferrous ion, Fe^{+2}, and permanganate ion, MnO_4^-, in acid solution to produce ferric ion, Fe^{+3}, and manganous ion, Mn^{+2}.

Answer

$\underset{+2}{Fe^{+2}} + \underset{+7}{MnO_4^-} \longrightarrow \underset{+3}{Fe^{+3}} + \underset{+2}{Mn^{+2}}$

For iron: $+2 \xrightarrow{+1} +3$

For manganese: $+7 \xrightarrow{-5} +2$

To equalize changes in oxidation number multiply iron by 5, and write

$$5Fe^{+2} + MnO_4^- \longrightarrow 5Fe^{+3} + Mn^{+2}$$

Then balance oxygen;

$$5Fe^{+2} + MnO_4^- \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

balance hydrogen;

$$8H^+ + 5Fe^{+2} + MnO_4^- \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

and check on charge,

$$\begin{aligned} 8(+1) + 5(+2) + (-1) &= 5(+3) + (+2) \\ +8 + 10 - 1 &= +15 + 2 \\ +17 &= +17 \end{aligned}$$

Pr. 23. Show the arbitrariness of oxidation numbers by balancing the reaction discussed in Problem 22 with the assumption that the oxidation number of manganese in MnO_4^- is $+2$. Compare with the result obtained in Problem 22.

Answer

If manganese has an oxidation number $+2$ in MnO_4^-, we must assign an unusual oxidation number to oxygen. Let us call it y.

$$\begin{aligned} \begin{pmatrix}\text{oxid. no.}\\ \text{Mn}\end{pmatrix} + 4\begin{pmatrix}\text{oxid. no.}\\ \text{O}\end{pmatrix} &= \begin{pmatrix}\text{charge on}\\ MnO_4^-\end{pmatrix} \\ (+2) \quad + \quad 4(y) &= -1 \\ 4y &= -3 \\ y &= -\tfrac{3}{4} \end{aligned}$$

Since oxygen has an oxidation number $-\frac{3}{4}$ in MnO_4^- and -2 in H_2O, its oxidation number drops by $\frac{5}{4}$ per oxygen atom. The four oxygen atoms in MnO_4^- change oxidation number by $4 \times (\frac{5}{4}) = 5$. Thus we have for oxygen

$$-\tfrac{3}{4} \xrightarrow{-\frac{5}{4}} -2$$

For iron:

$$+2 \xrightarrow{+1} +3$$

To equalize change in oxidation number multiply oxygen by 4 and iron by 5, and write

$$5Fe^{+2} + MnO_4^- \longrightarrow 5Fe^{+3} + 4H_2O$$

balance manganese;

$$5Fe^{+2} + MnO_4^- \longrightarrow 5Fe^{+3} + 4H_2O + Mn^{+2}$$

then balance hydrogen;

$$8H^+ + 5Fe^{+2} + MnO_4^- \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

This is, of course, the same equation obtained in Problem 22. The fact that the correct equation is obtained from a given assumption of oxidation numbers gives no assurance whatsoever that the oxidation numbers have physical reality; that is, that they show where the the charge is located in a species such as MnO_4^-.

Pr. 24. In order to make Na*(s)* and Cl_2*(g)*, an electric current is passed through NaCl*(l)*. What does the energy supplied to this reaction do?

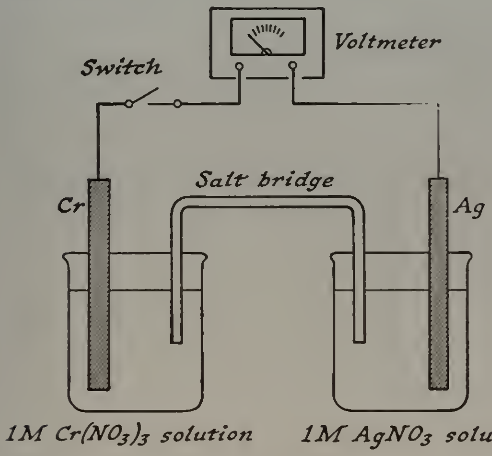
Answer

The energy is used in the process of removing electrons from Cl^- ions and adding them to Na^+ ions. More energy is required to remove an electron from Cl^- in molten NaCl than is gained when Na^+ in molten NaCl gains an electron.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1–9 apply to the following experiment: In order to make a simple cell, a student places a strip of chromium into a beaker containing 1 *M* $Cr(NO_3)_3$ solution. Into another beaker, containing 1 *M* $AgNO_3$ solution, he places a strip of silver. The electrodes are connected as shown in the circuit diagram. A salt bridge is used to connect the solutions in the two beakers.



1. When the switch is closed, oxidation will occur at the (Ag, Cr) ______ electrode.

   Answer: Cr.

2. Electrons flow in the external circuit (wires and voltmeter) from the (Ag, Cr) ______ electrode to the (Ag, Cr) ______ electrode.

   Answer: Cr to Ag electrode.

3. (a) The (Ag, Cr) ______ electrode is the cathode.
   (b) Positive ions in the solution will migrate toward the (cathode, anode) ______.

   Answer: (a) Ag.
   (b) Cathode.

4. After the cell has been operating for some time, which electrode will show an increase in mass? (Ag, Cr) ______.

   Answer: Ag.

5. If one mole of electrons is allowed to pass through the circuit, how many moles change will this produce at the Ag electrode? How many grams change will be produced at the Cr electrode (Ag, 107.9; Cr, 52.0)?

   Answer
   One mole will be added to the Ag electrode; 17.3 grams will be lost from the Cr electrode.

6. What is the maximum voltage possible for this cell?

   Answer: 1.54 volts.

7. When equilibrium is established the voltage (a) increases to maximum, (b) drops to zero, (c) does not change.

   Answer: (b) Drops to zero.

8. If the salt bridge is removed the voltage (a) increases to maximum, (b) drops to zero, (c) does not change.

   Answer: (b) Drops to zero.

9. If 50 ml of 2 *M* sodium sulfide, Na_2S, were added to the half-cell containing Ag^+ ions to precipitate Ag_2S, the voltage would (a) increase, (b) decrease, (c) remain the same.

   Answer: (b) Decrease.

Questions 10–12 refer to the following equations:

(a) $K(s) + H_2O$ (distilled water)
(b) $Cl_2(g) + Br^-(aq)$
(c) $Cu(s) + Ni^{+2}(aq)$ [remember that Cu goes to $Cu^{+2}(aq)$]
(d) $SO_2(g) + MnO_4^-(aq)$ in acid solution, H^+, to form $Mn^{+2}(aq)$ and $SO_4^{-2}(aq)$

10. Write the net reaction for (a)–(d) above.

Answer

(a) $K(s) + H_2O \rightleftarrows K^+(aq) + \frac{1}{2}H_2(g) + OH^-(aq)$

(b) $Cl_2(g) + 2Br^-(aq) \rightleftarrows 2Cl^-(aq) + Br_2(l)$

(c) $Cu(s) + Ni^{+2}(aq) \rightleftarrows Cu^{+2}(aq) + Ni(s)$

(d) $2MnO_4^-(aq) + 5SO_2(g) + 2H_2O \rightleftarrows 2Mn^{+2}(aq) + 5SO_4^{-2}(aq) + 4H^+(aq)$

11. Calculate the $E°$ for the net reactions.

Answer

(a) 2.09 volts; (b) 0.30 volt; (c) −0.59 volt; (d) 1.35 volts.

12. Which of the reactions, if any, does not occur spontaneously?

Answer: (c).

13. Write a balanced equation for this oxidation-reduction reaction, using the half-reaction method.

$$Cu(s) + NO_3^-(aq) + H^+(aq) \longrightarrow Cu^{+2}(aq) + NO(g) + H_2O$$

Answer

$3[Cu(s) \rightleftarrows Cu^{+2}(aq) + 2e^-]$

$2[NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftarrows 2H_2O + NO(g)]$

$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightleftarrows 3Cu^{+2}(aq) + 4H_2O + 2NO(g)$

14. Name the oxidizing agent in question 13.

Answer: NO_3^-.

15. Write a balanced equation, using the half-reaction method.

$$Al(s) + I_2(s) \text{ gives } Al^{+3}(aq) + I^-(aq)$$

Answer

$Al(s) \longrightarrow Al^{+3}(aq) + 3e^-$

$\frac{1}{2}I_2(s) + e^- \longrightarrow I^-(aq)$

Three iodide ions must be formed for each aluminum atom:

$Al(s) + \frac{3}{2}I_2(s) \rightleftarrows Al^{+3} + 3I^-(aq)$

or

$2Al(s) + 3I_2(s) \rightleftarrows 2Al^{+3} + 6I^-(aq)$

16. Write a balanced equation, using the oxidation number method.

$$Fe^{+3}(aq) + Sn^{+2}(aq) \text{ gives } Fe^{+2}(aq) + Sn^{+4}(aq)$$

Answer

$Fe^{+3} \longrightarrow Fe^{+2}$ (oxidation number change = −1)

$Sn^{+2} \longrightarrow Sn^{+4}$ (oxidation number change = +2)

Thus two Fe^{+3} must be reduced for each Sn^{+2} that is oxidized:

$2Fe^{+3}(aq) + Sn^{+2}(aq) \rightleftarrows 2Fe^{+2}(aq) + Sn^{+4}(aq)$

17. Write a balanced equation, using the oxidation number method.

$$Fe^{+2}(aq) + Cr_2O_7^{-2}(aq) + H^+(aq) \text{ gives } Fe^{+3}(aq) + Cr^{+3}(aq) + H_2O$$

Answer

$Fe^{+2}(aq) \longrightarrow Fe^{+3}(aq)$ (change in oxid. no. = +1)

$Cr^{+6} \longrightarrow Cr^{+3}$ (change in oxid. no. = −3)

Thus three Fe^{+2} must be oxidized for each Cr^{+6} that is reduced. Note there are two Cr^{+6} in $Cr_2O_7^{-2}$.

$6Fe^{+2}(aq) + Cr_2O_7^{-2}(aq) + H^+(aq)$ gives $6Fe^{+3}(aq) + 2Cr^{+3}(aq) + H_2O$

Adjusting hydrogen and oxygen gives the balanced form:

$6Fe^{+2}(aq) + Cr_2O_7^{-2}(aq) + 14H^+(aq) \rightleftarrows 6Fe^{+3}(aq) + 2Cr^{+3}(aq) + 7H_2O$

18. Select the compound in which chlorine is assigned the oxidation number +5?

(1) $HClO_4$
(2) $HClO_3$
(3) $HClO_2$
(4) $HClO$
(5) HCl

Answer: (2).

19. Four hypothetical elements *A*, *B*, *C*, and *D* form the aqueous ions A^{+2}, B^{+2}, C^{+2}, and D^{+2}. The following statements indicate some reactions which can, or cannot, occur. Use these data to arrange the metal-ion couples into a short oxidation-reduction potential series, putting at the top

the oxidation half-reaction which has the greatest tendency to release electrons.

$B^{+2} + D \longrightarrow D^{+2} + B$ (reacts appreciably)
$B^{+2} + A$ (will not react appreciably)
$D^{+2} + C \longrightarrow C^{+2} + D$ (reacts appreciably)

Answer: $C \longrightarrow C^{+2} + 2e^-$
$D \longrightarrow D^{+2} + 2e^-$
$B \longrightarrow B^{+2} + 2e^-$
$A \longrightarrow A^{+2} + 2e^-$

20. Which of the following will oxidize I^- to I_2 but not Br^- to Br_2?

(1) Fe^{+3} to Fe^{+2}
(2) Fe^{+2} to Fe
(3) Sn^{+2} to Sn
(4) MnO_4^- to Mn^{+2}
(5) Na^+ to Na

Answer: (1).

21. Using "T" and "F" indicate whether the following statements are true or false.

(a) Iron metal can reduce Fe^{+3} to Fe^{+2}.
(b) Copper metal can dissolve in nitric acid, liberating H_2 gas.
(c) Oxygen in moist air can oxidize Fe^{+2} to Fe^{+3}.
(d) Nickel can reduce Sn^{+2} to Sn, but cannot reduce Co^{+2} to Co.

Answer: (a) T.
(b) F.
(c) T.
(d) T.

CHAPTER

13

CHEMICAL CALCULATIONS

This chapter can be used to summarize much of the previous work involving chemical problems. Many of the problems can be related to the experimental work which the student has done in the laboratory. Such a procedure will emphasize the CHEM Study philosophy of chemistry, which stresses the experimental aspect of science.

Intent and Approach

This chapter considers the more quantitative aspects of chemistry. It can be used to emphasize the utility of the mole as a fundamental chemical quantity. A helpful point to make is that the mole is as important to the chemist as the dozen is to the poultry farmer. Routine mechanical procedures for solving problems can be devised, and may appeal to the less ambitious students, but such procedures add little real understanding of chemistry and should be *avoided.*

The specific goals of the chapter are:

1. To illustrate in a more quantitative sense the precise meaning of a chemical equation.
2. To illustrate the application of the mole concept as a unifying principle for the solution of many different types of problems involving stoichiometry.
3. To illustrate the manipulation of units in chemical problems (i.e., dimensional analysis).

Outline

1. A simple, three-step pattern of attack on problems is given (13-1). It is the mole method.
2. The manufacture of sulfuric acid and some of its reactions are taken as the "story line" in this chapter. Section 13-2 gives the basic equations for the production of H_2SO_4.
3. In each of the following sections a specific problem (related to H_2SO_4) is presented and worked out according to the three steps shown in Sec. 13-1.

   Weight-Weight Calculations (13-2.1)
   Weight-Gas Volume Calculations (13-2.2)
   Gas Volume-Gas Volume Calculations (13-2.3)
   Weight-Liquid Volume Calculations (13-2.4)
   Liquid Volume-Volume Calculations (13-2.5)

New Concepts

No really new concepts are presented, but heavy stress is laid on:

1. The utility of the mole in the solution of many different kinds of quantitative chemical problems.
2. The manipulation of units in solving problems.
3. Balancing equations.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
S 13-1/13-2.1 (p. 225–226)	1	Mole method	1	1, 2, **3**[*]	**4**, 5	**6**	Mole method, weight problems
Expt. 22[†] (Part I)	2	Expt. 22 (Part I)					Predicting reaction behavior
S 13-2.2/13-2.5 (p. 226–230)	3	Problems	2, 3	7–**9**, 13, **14**	10–12, **15**–18, 21	**19**, 20, 22, **23**	Gas volume, solution problems
Expt. 23	4	Expt. 23					Titration
	5	Expt. 23					
Review	6	Problems					
	7	Test on Ch. 11–13					

[*] Boldface indicates problems whose answers are given in the Textbook.

[†] Part II is optional. It requires another period. Experiments 22 and 23 both require extensive solution preparation.

Development

Students frequently consider stoichiometry difficult and may complain that they have trouble with mathematics. In such cases you should determine whether the trouble arises from real deficiencies in arithmetic or from a lack of familiarity with chemical units. Usually the students can handle the arithmetical problems when the units are familiar. If such is the case, an illustration of the close analogy between the mole and the dozen may be helpful. The dozen has 12 units, and the mole has 6.02×10^{23} units. The numbers involved differ widely, but the ideas underlying their use are the same.

The value of this chapter will be increased if you relate the problems to appropriate experiments from the student's background. Some specific relationships are:

Problem	Related Experiment
1	7
3	14a
10	14a
12	9
21	10

You will notice that we do not mention the "proportion method." The method is not to be used. The mole method used in the Textbook is consistent with what the student already knows about equations, requires no new terminology, and works for a broader range of problem types. It is not that "proportions" do not give the correct answer, but they bypass the understanding that is the real goal of stoichiometry.

Significant figures can be troublesome in this chapter. You should suggest a review of Appendix 4 in the Laboratory Manual. Also remember that the number of moles reacting (taken from an equation) is an *exact* number. This kind of number has as many significant figures as you need and certainly should not limit the precision of the final answer.

Should you take problems from other sources watch out for statements like "one liter of · · ·" or "Will 100 grams · · · ." Strictly speaking, these have only one significant figure. We have tried to avoid such constructions.

Supplementary Material

None.

EXPERIMENT 22 REACTIONS BETWEEN IONS IN SOLUTION

PURPOSE. To serve as a summary of ideas covered in the Chapters on solubility equilibria, oxidation-reduction reactions, and, to a limited extent, the chapter on acid-base reactions. It also gives practice in predicting results of reactions, checking these results, and interpreting them.

PRELAB DISCUSSION. Emphasize the element of *prediction.* See that students come to the laboratory with the equations written. If they seem uncertain about predicting, suggest that they list the species present in the solution and then check the table of E° values for possible oxidation-reduction reactions and the solubility charts for possible formation of precipitates. Try to get the students to work these out entirely on their own. (See lab hint 4.)

TIMING. Assign this experiment after Sec. 12-2.2 of Chapter 12, between Chapters 12 and 13, or during Chapter 13.

EQUIPMENT NEEDED (PER STUDENT OR PAIR). Solutions should be supplied in dropper bottles. Be sure there are enough sets for convenience.

Solutions: Volumes are given for 30 students; see lab hints 1 and 2.

PART I

200 ml 0.1 *M* magnesium nitrate
  [25.6 g $Mg(NO_3)_2 \cdot 6H_2O$/liter]
100 ml 0.1 *M* sodium hydroxide (4 g/liter)
100 ml 0.1 *M* sodium sulfate
  (14.2 g anhydrous/liter)
200 ml 0.1 *M* (saturated) barium hydroxide
  [19 g $Ba(OH)_2 \cdot H_2O$/liter or
  32 g $Ba(OH)_2 \cdot 8H_2O$/liter]
100 ml 0.1 *M* sulfuric acid
  (5.6 ml conc. reagent/liter)
2 ml 6 *M* sulfuric acid
  (334 ml conc. reagent/liter)
100 ml 0.1 *M* potassium dichromate
  (29.4 g/liter)
100 ml 0.1 *M* sodium sulfite (*fresh*)
  (12.6 g anhydrous/liter)
100 ml 0.05 *M* potassium permanganate
  (8 g/liter)
100 ml 0.01 *M* potassium permanganate
  (1.6 g/liter)
100 ml 1.0 *M* hydrochloric acid
  (85.5 ml conc. reagent/liter)
100 ml 0.1 *M* potassium iodide (16.6 g/liter)
200 ml 0.1 *M* ferric chloride
  (27 g $FeCl_3 \cdot 6H_2O$/liter)
100 ml 0.1 *M* potassium bromide (12 g/liter)
100 ml 0.1 *M* ferrous sulfate, acidified
  (27.8 g $FeSO_4 \cdot 7H_2O$/liter 0.01 *M* H_2SO_4)
200 ml 0.1 *M* zinc sulfate
  (29 g $ZnSO_4 \cdot 7H_2O$/liter)
100 ml 0.1 *M* ammonium carbonate
  (10 g/liter)
60 ml carbon tetrachloride
2 or more 13 × 100 mm test tubes
2 solid stoppers
  (rubber size #00 or cork size #3)

PART II (Optional)

200 ml 0.1 *M* chromium sulfate
  (60 g commercial $Cr_2(SO_4)_3 \cdot nH_2O$/liter)
10 ml 6 *M* sulfuric acid (334 ml conc.
  reagent/liter), also used in Part I
400 ml 3% hydrogen peroxide (see lab hint 3)
10 ml 6 *M* sodium hydroxide (240 g/liter)
200 ml 0.1 *M* potassium dichromate
  (29.4 g/liter), also used in Part I
100 ml 0.1 *M* lead nitrate (33 g/liter)
100 ml 1.0 *M* sodium chloride (5.9 g/liter)
100 ml 0.1 *M* potassium iodide
  (16.6 g/liter), also used in Part I
100 ml 0.1 *M* sodium sulfide
  (7.8 g/liter or 24 g $Na_2S \cdot 9H_2O$/liter)

TIME REQUIRED. Part I may be completed in one 45–50 minute period. It is assumed predictions will be made prior to class time. Part II is optional and requires an additional period. You will find stopping points after each lettered section. (See lab hint 2.)

PRECAUTIONS. Observe the usual laboratory precautions. Avoid fumes when disposing of CCl_4.

LABORATORY HINTS

1. It is essential that solutions be readily available. It will help to have on hand small trays, such as inexpensive aluminum pans or boxes (approximately 6 × 10 inches) in which reagents for a group of parts (for example, a, b, and c) may be placed. To save time, you might direct students to start at different points in the experiment. There are natural groupings: a, b, and c; d, e, and f; g and h; and i and j.
2. Another possible way to organize for this experiment is to have the students work on some of the predictions, discuss these in class, and then try them during a 15–20 minute period on each of several days. In this way all of the reagents will not have to be out at the same time. This possibility will work well if the experiment is being done while Chapter 13 is under consideration, because it will allow you to devote time to students who may need extra help with calculations.
3. Stabilized 30% hydrogen peroxide keeps well in the stock room and may be conveniently diluted, providing all glassware is scrupulously clean (detergent, H_2O rinse, dilute acid rinse, several H_2O rinses). See the precautions given near the top of p. 64.
4. The $E°$ tables used for predictions are strictly true only for 1 *M* solutions. But since the effect of concentration is not great for these reactions, the tables provide a good *approximation.*
5. Indicate that $H_2SO_3 \rightleftharpoons H_2O + SO_2$.

RESULTS AND DISCUSSION

PART I

(a) Precipitate predicted:

$$Mg^{+2}(aq) + 2OH^-(aq) = Mg(OH)_2(s) \qquad K_{sp}\ Mg(OH)_2(s) = 8.9 \times 10^{-12}$$

(b) No precipitate is predicted. Both $MgSO_4$ and NaCl are quite soluble. The student may remember the low solubility of $BaSO_4$ and $SrSO_4$ if these were used in Expt. 11, but the solubility of $MgSO_4$ is much greater.

(c) Precipitate predicted:

$$Ba^{+2}(aq) + SO_4^{-2}(aq) = BaSO_4(s) \qquad K_{sp}\ BaSO_4(s) = 1.5 \times 10^{-9}$$

The student should recognize that the equilibrium $H^+(aq) + OH^-(aq) = H_2O$ also favors the products of this reaction.

(d) Oxidation-reduction is predicted. The student may need to be reminded of reaction II c in Expt. 12 in which $H^+(aq) + SO_3^{-2}(aq)$ produced $SO_2(g)$.

$$\begin{aligned} 3[SO_2(g) + 2H_2O &= 2e^- + SO_4^{-2} + 4H^+] & E° &= -0.17 \text{ volt} \\ Cr_2O_7^{-2} + 14H^+ + 6e^- &= 2Cr^{+3} + 7H_2O & E° &= +1.33 \text{ volts} \end{aligned}$$

or

$$3SO_2(g) + Cr_2O_7^{-2} + 2H^+ = 2Cr^{+3} + 3SO_4^{-2} + H_2O \qquad E° = \ 1.16 \text{ volts}$$

The color will change from orange to green.

(e) Oxidation-reduction predicted:

$$5[2Cl^- = 2e^- + Cl_2(g)] \qquad E^\circ = -1.36 \text{ volts}$$
$$2(MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O) \qquad E^\circ = +1.52 \text{ volts}$$

or

$$2MnO_4^- + 16H^+ + 10Cl^- = 2Mn^{+2} + 8H_2O + 5Cl_2(g) \qquad E^\circ = 0.16 \text{ volt}$$

In the introduction, the student has been reminded that E° tables do not predict the rate of the reaction and has been told to make observations later if no reaction is apparent immediately. This reaction will appear inactive at first, but after 5 or 10 minutes there will be no doubt that the odor of $Cl_2(g)$ is present, and the pink color of the MnO_4^- should disappear.

(f) Oxidation-reduction predicted:

$$2I^- = I_2 + 2e^- \qquad E^\circ = -0.53 \text{ volt}$$
$$2(Fe^{+3} + e^- = Fe^{+2}) \qquad E^\circ = +0.77 \text{ volt}$$

or

$$2I^- + 2Fe^{+3} = I_2 + 2Fe^{+2} \qquad E^\circ = +0.24 \text{ volt}$$

Iodine is yellow-brown and is thus not very different in color from the Fe^{+3}. But when CCl_4 is added it extracts I_2 and becomes lavender-pink (the student is familiar with this from Expt. 20).

(g) No oxidation-reduction reaction predicted:

$$2Br^- = Br_2 + 2e^- \qquad E^\circ = -1.06 \text{ volts}$$
$$2(Fe^{+3} + e^- = Fe^{+2}) \qquad E^\circ = +0.77 \text{ volt}$$

Since the reactants are favored, the student will see no change in the color of the CCl_4 layer.

(h) Oxidation-reduction predicted:

$$5(Fe^{+2} = Fe^{+3} + e^-) \qquad E^\circ = -0.77 \text{ volt}$$
$$MnO_4^- + 8H^+ + 5e^- = Mn^{+2} + 4H_2O \qquad E^\circ = +1.52 \text{ volts}$$

or

$$5Fe^{+2} + MnO_4^- + 8H^+ = 5Fe^{+3} + Mn^{+2} + 4H_2O \qquad E^\circ = +0.75 \text{ volt}$$

The solution will change from the purple-pink of MnO_4^- to the brown-yellow of Fe^{+3}.

(i) Precipitate predicted:

$$Zn^{+2}(aq) + CO_3^{-2}(aq) = ZnCO_3(s) \qquad K_{sp}\ ZnCO_3(s) = 3 \times 10^{-8}$$

This K_{sp} is not given in the Textbook, but the solubility tables would lead one to this prediction.

(j) Precipitates predicted:

$$Ba^{+2}(aq) + SO_4^{-2}(aq) = BaSO_4(s) \qquad K_{sp}\ BaSO_4(s) = 1.5 \times 10^{-9}$$
$$Zn^{+2}(aq) + 2OH^-(aq) = Zn(OH)_2(s) \qquad K_{sp}\ Zn(OH)_2(s) = 4.5 \times 10^{-17}$$

The student who is familiar with the first of these from (c) may fail to predict the second. It may be difficult to be sure whether there are two precipitates here, but most students will see a difference from the reaction in (c).

PART II (OPTIONAL)

These reactions are more involved than those of Part I and are presented with the direction that the student try them first and then seek an explanation. For several reactions the first guess (we assume the expected familiarity with the solubility and oxidation-reduction tables) will be incorrect, and a more careful consideration will be necessary. The less-talented students will not be able to reason through some of these, and even the better students may need helpful hints.

There is ample opportunity for commenting that the first prediction is not always correct and that the final answer must be obtained from the laboratory.

(k) No color change occurs.

(l) The color changes from green to yellow.

$$2[\mathrm{Cr(OH)_4^-} + 4\mathrm{OH^-} = \mathrm{CrO_4^{-2}} + 4\mathrm{H_2O} + 3e^-] \qquad E^\circ = +0.13 \text{ volt}$$
$$3[\mathrm{HO_2^-} + \mathrm{H_2O} + 2e^- = 3\mathrm{OH^-}] \qquad E^\circ = +0.88 \text{ volt}$$

or

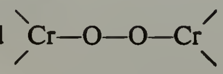
$$2\mathrm{Cr(OH)_4^-} + 3\mathrm{HO_2^-} = 2\mathrm{CrO_4^{-2}} + 5\mathrm{H_2O} + \mathrm{OH^-} \qquad E^\circ = +1.01 \text{ volts}$$

(m) The color changes from orange to green, and bubbling occurs.

$$3[\mathrm{H_2O_2} = \mathrm{O_2}(g) + 2\mathrm{H^+} + 2e^-] \qquad E^\circ = -0.68 \text{ volt}$$
$$\mathrm{Cr_2O_7^{-2}} + 14\mathrm{H^+} + 6e^- = 2\mathrm{Cr^{+3}} + 7\mathrm{H_2O} \qquad E^\circ = +1.33 \text{ volts}$$

or

$$3\mathrm{H_2O_2} + \mathrm{Cr_2O_7^{-2}} + 8\mathrm{H^+} = 3\mathrm{O_2} + 2\mathrm{Cr^{+3}} + 7\mathrm{H_2O} \qquad E^\circ = +0.65 \text{ volt}$$

A deep blue color can form due to a peroxy-chromium(III) compound  which is transitory, changing to green $\mathrm{Cr^{+3}}(aq)$.

(n) No color change takes place except the orange-to-yellow change indicated in the directions. From his experience with Expt. 19 the student should remember the equilibrium reaction

$$2\mathrm{OH^-} + \mathrm{Cr_2O_7^{-2}} = 2\mathrm{CrO_4^{-2}} + \mathrm{H_2O}$$

The $\mathrm{Cr^{+6}}$ is not reduced in a basic solution.

(o) A white precipitate appears:

$$\mathrm{Pb^{+2}} + 2\mathrm{Cl^-} = \mathrm{PbCl_2}(s) \qquad K_{sp}\ \mathrm{PbCl_2}(s) = 1.6 \times 10^{-5}$$

Since an excess of $\mathrm{Cl^-}$ was added, the $\mathrm{Pb^{+2}}$ remaining in solution is about 4×10^{-6} *M*.

(p) A yellow precipitate appears.

$$\mathrm{Pb^{+2}} + 2\mathrm{I^-} = \mathrm{PbI_2}(s) \qquad K_{sp}\ \mathrm{PbI_2}(s) = 8.3 \times 10^{-9}$$

The remaining $\mathrm{Pb^{+2}}$ from (e) was sufficient to give a visible amount of $\mathrm{PbI_2}(s)$, since the K_{sp} for $\mathrm{PbI_2}(s)$ is smaller than that of $\mathrm{PbCl_2}(s)$.

(q) A small amount of black precipitate appears.

$$\mathrm{Pb^{+2}} + \mathrm{S^{-2}} = \mathrm{PbS}(s) \qquad K_{sp}\ \mathrm{PbS}(s) = 7 \times 10^{-29}$$

There were still enough $\mathrm{Pb^{+2}}$ ions left to produce a small amount of $\mathrm{PbS}(s)$, since the K_{sp} for this salt is smaller than that for $\mathrm{PbI_2}(s)$.

Questions are not included, but it is expected that each student will write all equations. The extent of the *Postlab Discussion* will depend upon the number of students who complete Part II. If many do, some class discussion of these reactions should be profitable.

EXPERIMENT 23 QUANTITATIVE TITRATION

PURPOSE. To give the student some experience in acid–base titration, as well as additional experience in quantitative analysis.

PRELAB DISCUSSION. The introduction makes clear that titration is not limited to acid–base reactions, but you should emphasize this. Mention also that this is an important technique and is frequently used in industry as well as in research. It is an example of a quantitative technique.

Demonstrate how to rinse a buret, and show why it is necessary to flush the tip. One way to emphasize the effectiveness of several rinses each made with a small volume, compared to a single rinse made with a large volume, is to pose the following problem. Assume that one milliliter is left behind after each rinse. What volume, in a single rinse, is needed to be as effective as three rinses of 9 ml each? During the *Postlab Discussion* you can give the answer—999 ml, or 1 liter. Each 9 ml solution gives a 10/1 dilution, therefore three give a 1000/1 dilution.

Be sure that students become familiar with the section on *Care of Burets* and are reminded to look back at Figure 9-3 (of the Laboratory Manual), which shows how to read the buret correctly. Demonstrate a titration, and explain what is meant by getting volume ratios of acid to base that are within 1–2%. This is described in the Laboratory Manual (p. 63). (If 25 ml burets are used, quantities may be cut in half.)

TIMING. Assign this experiment after Sec. 13-2.5.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

2 burets or 1 buret and a 10 ml pipet
1 ring stand
2 single, or 1 double, buret or utility clamp
2 250 ml beakers (or a 400 ml beaker plus a 250 ml beaker)
1 250 ml Erlenmeyer flask
1 wash bottle with distilled water (see lab hint 3)
detergent and buret brushes
75–100 ml standard acid (recommend 0.1 *M* HCl) (see lab hint 1)
100–150 ml unknown base (recommend between 0.1 *M* and 0.2 *M*) (see lab hint 2)
few drops phenolphthalein solution (1 g/100 ml 50% ethanol)
1–2 g unknown solid acids (see lab hint 4)

TIME REQUIRED. The student will probably need two full 45–50 minute laboratory periods. A convenient stopping point is available after Part I.

PRECAUTIONS. Burets break easily. Use care in washing, and be sure clamps are adjusted securely

LABORATORY HINTS

1. The standard 0.1 *M* acid should be made up in a large batch to insure uniformity. Measure carefully 85.5 ml of concentrated (11.7 *M*) HCl (*fresh* bottle). Place in a 1 liter volumetric flask, and fill to 1 liter mark with distilled H_2O. Empty this into a large container, and add 9 more liters of distilled water. Acid diluted in this manner need not be standardized. Five-gallon water jugs are convenient for mixing and storing this large volume.
2. The NaOH solution for standardizing should be made up in several different concentrations so that each student will not have the same concentration. Make up 8 liters of 0.2 *M* NaOH (64 grams/8 liters). Save 2 liters to be used directly, and dilute the rest as follows:

   To 1800 ml 0.2 *M* NaOH, add 200 ml distilled water to give 0.18 *M*.
   To 1600 ml 0.2 *M* NaOH, add 400 ml distilled water to give 0.16 *M*.

To 1400 ml 0.2 *M* NaOH, add 600 ml distilled water to give 0.14 *M*.
To 1200 ml 0.2 *M* NaOH, add 800 ml distilled water to give 0.12 *M*.

These dilutions yield five different 2 liter solutions of base from 0.12 *M* to 0.2 *M*. Most standard acids are purchased in 2 liter bottles, which are convenient for storing and dispensing these NaOH solutions. Make sure the NaOH solutions are thoroughly mixed.

3. If the distilled water is very acidic, dissolved CO_2 may be the cause. Boil the water to eliminate the dissolved CO_2.
4. Suitable solid acids for use as unknowns are:

Acidic Substance	Grams Acid Needed for 50 ml of 0.12 *M* NaOH
potassium hydrogen sulfate ($KHSO_4$, mol wt = 136.2)	0.8
potassium acid tartrate ($KHC_4H_4O_6$, mol wt = 188.2)	1.1
potassium acid phthalate ($KHC_8H_4O_4$, mol wt = 204.2)	1.2
potassium acid oxalate (KHC_2O_4, mol wt = 128.1)	0.8

The corresponding sodium compounds can also be used. The unknown solid acids should be prepared in advance by placing 1 to 2 grams of the acid in a small plastic vial or small test tube. *The student should use a sample weight between 0.5 and 1.0 grams.* Thus with even the most dilute base, he will probably not have to use more than 50 ml in the titration. Potassium hydrogen tartrate probably won't dissolve until it is converted during titration. Warn the students of this so that they don't waste time trying to dissolve it.

5. (For *Part III—Optional Titration.*) It is difficult, if not impossible, to anticipate all of the different acidic or basic substances the students might bring from home. But phenolphthalein indicator will suffice, with relatively small error, for almost all of the substances listed. Use methyl orange as indicator when titrating $NH_3(aq)$ with HCl. Students will need help in making appropriate dilution of the substances they wish to titrate.

CALCULATIONS

1. From the concentrations given and the volume used, calculate the number of moles of hydrochloric acid involved in each titration of Part I.

Example: $10 \text{ ml} \times \frac{0.1 \text{ mole}}{1000 \text{ ml}} = 0.001 \text{ mole}$

2. From the equation for the reaction, how many moles of base are used per mole of acid in Part I?

Answer: $H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + Na^+(aq) + Cl^-(aq)$

Thus one mole of base is used per mole of acid.

3. Using the relationship in question 2, calculate the moles of base used.

Answer: 0.001 mole of base is used.

4. Calculate the molarity of the base.

Example: $\text{Molarity} = \frac{\text{moles}}{\text{liter}} = \frac{0.001 \text{ mole}}{8 \text{ ml}} \times \frac{1000 \text{ ml}}{\text{liter}} = 0.125\ M$

5. From the weight of the solid acid and the volumes involved in its titration, calculate the weight of the solid unknown acid that will react with one mole of the base.

Example: 40 ml of 0.125 M base were used to titrate 0.68 gram of unknown acid.

$$40 \text{ ml} \times \frac{0.125 \text{ mole/liter}}{1000 \text{ ml/liter}} = 0.005 \text{ mole base used}$$

Since 0.68 gram of solid acid reacted with 0.005 mole of base, then

$$\frac{0.68 \text{ gram}}{0.005 \text{ mole}} = \frac{136 \text{ grams of acid}}{\text{mole of base}}$$

6. Using the formula of the acid given you by your teacher and the equation for the reaction, calculate the theoretical value for the weight of the acid that will react with one mole of the base.

   Example: $K^+(aq) + HSO_4^-(aq) + Na^+(aq) + OH^-(aq) \rightleftharpoons$
   $H_2O(l) + Na^+(aq) + K^+(aq) + SO_4^{-2}(aq)$

   The molecular weight of $KHSO_4$ is 136.2 grams. Since one mole of base reacts with one mole of acid, 136.2 grams of the acid will react with one mole of the base.

7. Determine the percentage error, using the value calculated in question 6 as the accepted value (see Appendix 4 of the Laboratory Manual).

   Example

$$\% \text{ error} = \frac{136.2 - 136}{136.2} \times 100 = 0.15\%$$

POSTLAB DISCUSSION. Collect and post results from Question 7 to show the precision with which such titrations may be made.

Background Discussion

This chapter is to act as a summarizing review of problem types the student has already seen. It has two objects—to show the power of the mole method as a single method for all problems and to fix this method in the student's mind so that he can work stoichiometric problems easily.

SIGNIFICANCE OF QUANTITATIVE OBSERVATION

Since Chapter 13 considers certain aspects of quantitative detail, you may encounter some resistance to its acceptance by students. It may help you in your presentation of chemical stoichiometry to keep in mind that modern chemistry *originated* in the early quantitative experiments of Lavoisier. Prior to the time of Lavoisier, the oxidation of a metal was written as

$$\text{metal} \longrightarrow \text{phlogiston} + \text{ash}$$

Many postulates, long since abandoned, were needed to justify such a proposal, even in a qualitative sense. A convincing explanation of the process did not arise until Lavoisier showed *quantitatively* that the weight of metal *plus* oxygen consumed was equal to the weight of the oxide formed. He further showed that HgO could be decomposed to give gas and metal, equal in total weight to the weight of the original HgO. *Quantitative chemistry is literally the foundation of all chemistry.*

Do not conclude from the foregoing that the mole concept of stoichiometry is of historical interest only. Remind the student that the ideas of Chapter 13 provide the foundation for most of quantitative analysis. Since quantitative analysis is involved at some point in the characterization of almost all new compounds, we can properly state that concepts of the type given in this chapter form the ultimate foundation for all of modern synthetic chemistry. This chapter is a review to establish these important ideas firmly. It is appropriate to gather the problems into a single chapter, where the usefulness of the mole and of dimensional analysis can be emphasized.

THE MOLE METHOD

If you have not used the mole method you may wonder at the emphasis placed on it. Look at the various types of problems and the concepts the student must have if the mole isn't emphasized—combining weights, equivalent weights, normality equations, proportionality rules. The trial teachers were almost unanimous in their agreement that much better understanding was achieved when only the mole method was used.

For this method the student must know, at most, three things:

(a) How to balance an equation.
(b) How to get the relative number of moles from the balanced equation.
(c) How to calculate the number of moles of a specified substance.

Normally, (a) and (b) are easy, and by now should be well known to the pupil. Item (c) is more difficult, not in theory, but because the amount can be expressed in so many ways. It is in this calculation that proper handling of units can be an effective aid.

THE HANDLING OF UNITS IN PROBLEMS

One of the most common difficulties experienced by students in setting up chemical problems consists in deciding what arithmetical operations should be performed upon a given set of numerical data. Analysis of units provides one of the best possible means for obtaining a *systematic* and proper answer to this dilemma. Though you have been presenting this idea in separate problems up to now, it is convenient at this point to review the *whole concept of units and their manipulation.*

All physical measurements can ultimately be reduced to units of length, mass, time and temperature.* As a result, our different systems of units are designated by the first letter of the name of the unit used for length, mass, and time. Thus the system based on the centimeter, the gram, and the second is the c.g.s. system; the system based on the foot, the pound, and the second is the f.p.s. system, etc. In Table 13-I a number of units used in physical measurements are tabulated. It will be noticed that all entries above the heavy line can be reduced to fundamental length-mass-time units. In our discussion of the chemical units listed below the heavy line, we introduce *the particle* as a fundamental conceptual unit. The mole is defined operationally in terms of weight, but a definition in terms of particles (6.02×10^{23} of them) has a number of pedagogical advantages, and the end result is identical to that obtained in the original operational definition.

One of the major advantages to be derived from a systematic representation of units in terms of length-mass-time quantities is that the arithmetical operation needed to convert a quantity measured in one set of units to another set of units is clearly indicated by the dimensions of the quantity sought. For example, suppose we have the mass and volume of a sample from laboratory work. What arithmetical operation will convert these measured values to sample density? Since density has the units of g/cm³, it is apparent that measured mass is to be divided by the measured volume, not volume by mass. Note that units are carried along with all numbers used.

We can multiply, divide, add, subtract, and cancel units just as though they were numbers. For example, let us assume that we have a rectangular box of 2000 cm³ volume. If this box is 10 cm high, what is the area of its top? The obvious solution involving units is

$$\frac{2000\ \text{cm}^3}{10\ \text{cm}} = 200\ \text{cm}^2$$

Note that cm is divided into cm³ to give cm².

Some examples that are frequently found in working chemical problems are:

$$\frac{\text{g of reactant}}{\text{g/mole}} = \text{g} \times \frac{\text{mole}}{\text{g}}$$

$$= \text{moles reactant} \qquad \text{(wt-wt)}$$

$$(\text{moles product}) \times \left(\frac{\text{liters}}{\text{mole}}\right)$$

$$= \text{liters product} \qquad \text{(wt-gas vol)}$$

$$\text{(vol-gas vol)}$$

$$\frac{\text{ml}}{\text{ml/liter}} \times \frac{\text{moles}}{\text{liter}}$$

$$= \text{ml} \times \frac{\text{liter}}{\text{ml}} \times \frac{\text{moles}}{\text{liter}} = \text{moles} \qquad \text{(wt-liquid vol)}$$

Such simple examples can be combined and extended to somewhat more complex problems. We have had much to say about the kinetic energy of a particle in our discussion of the kinetic theory. By definition, kinetic energy is

$$\tfrac{1}{2}(\text{mass}) \times (\text{velocity})^2$$

If the mass is given in units of grams and the velocity in units of cm/sec, the kinetic energy must come out in units of *ergs*. (See Table 13-I). If we wish to convert energy in ergs to energy in calories, we must apply properly our conversion units from the table. We find 10^7 ergs/joule and 4.18 joules/cal in the table. Do we add, multiply, subtract, or divide with these factors? Subjecting our units to simple arithmetical operations provides an unequivocal answer:

$$\text{ergs} \times \frac{\text{joules}}{10^7\ \text{ergs}} \times \frac{\text{calories}}{4.18\ \text{joules}} = \text{calories}$$

Note that units are handled in division and multiplication as though they were numerical fractions. In order to divide by a fraction we invert the fraction and proceed as in multiplication. Use the above example to point out this routine to the student.

We have carefully discussed the multiplication and division of units. It is appropriate to consider briefly the problem of adding or subtracting units. Before we can perform either operation, all quantities must be expressed in the same units. For example, we know that 100 degrees centigrade plus 25 degrees centigrade gives 125 degrees centigrade, but 100 degrees centigrade

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* Through the medium of the kinetic theory and the gas laws, even temperature might be considered in terms of the units of mass, length, and time, but because of its statistical nature temperature is best defined operationally as a fundamental unit.

Table 13-I. **Some Units Used in the Study of Physical Systems**

Physical Property or Quantity	Name of Unit Used for Property	The Basic c.g.s. Units Used for Property
length	centimeter	cm
mass	gram	g
time	second	sec
volume	cubic centimeter	cm^3
density	grams per cubic centimeter	g/cm^3
velocity	centimeters per second	cm/sec
acceleration	rate of change of velocity with time	cm/sec^2
force	dyne	$g \times cm/sec^2$
energy-work	erg = dyne × cm	$g \times cm^2/sec^2$
energy	joule = 10^7 ergs	
energy	calorie = 4.18 joules	
mole	Avogadro's number of particles	6.02×10^{23} particles
gram molecular weight	grams per mole	g of 6.02×10^{23} atoms or molecules
gram molecular volume	cubic centimeters per mole	cm^3 of 6.02×10^{23} atoms or molecules

plus 25 degrees Fahrenheit gives a meaningless answer. The units of the sum, or difference, are identical to the units of the original quantities.

Students are occasionally disturbed by a problem in which, let us say, moles of H_2 are added to moles of I_2 and moles of HI to give total moles. Such concern is easily understood, since we *emphasize* that one can't add chickens and cows. It is appropriate, then, to note that our real unit here is the *mole*, or *a given number of particles*. For example, we may find that a house front consists of 10 feet of glass, 10 feet of brick and 10 feet of wood. If we add all three quantities together, we get a total width of 30 *feet* for the house. Note that we are adding feet, not glass, brick, and wood. A combination of glass, brick, and wood would give an impossible melange, but the unit is the foot. The same idea holds for the example involving moles of HI, moles of I_2, and moles of H_2. The *unit* is the *mole*, and can be handled as such.

APPLYING THE TEST OF REASON

One check that every researcher uses frequently to keep his bearings as he probes for new knowledge consists in asking, "Is this answer reasonable?" Instill this habit in your students as they work problems. It prevents many gross errors. It also aids in keeping a rough picture of nature in mind, since "reasonable" really means "compared to what you know about nature." In fact this is the answer to a question students often ask: "How do I know what is reasonable?" He should use his observations, both from experiments and otherwise.

Answers to Exercises and Problems

Ex. 13-1. If H_2SO_4 is purchased at a price of \$22.00 per ton, how many moles are obtained for a penny? (Note: One pound = 453.6 grams.)

Answer

Since 2000 pounds cost \$22.00, one pound costs

$$\frac{\$22.00}{2000} = 1.1 \text{ cents}$$

Therefore 454 grams cost 1.1 cents.
One cent will purchase

$$\frac{453}{1.1} = 412 \text{ g}$$

One cent will purchase

$$\frac{412}{\text{mol wt } H_2SO_4} \text{ moles} = \frac{412}{98.1} = 4.2 \text{ moles}$$

Ex. 13-2. Reaction (*19*) is carried out at a high temperature (about 500°C in the contact process). How does temperature affect equilibrium, according to Le Chatelier's Principle? In view of your answer, propose an explanation of why the temperature is kept high.

Answer

High temperature favors the reactants, because their formation will absorb heat and will partly relieve the change imposed. The high temperature used is probably to achieve a high reaction rate.

Ex. 13-3. Verify that reaction (*23*) is an oxidation-reduction reaction and that the oxidation number change of carbon is balanced by the oxidation number change of the sulfur.

Answer

By the conventions given, the element carbon has zero oxidation number as an element but +4 in CO_2. On the other hand sulfur is +6 in H_2SO_4 and +4 in SO_2. The change of +4 for carbon is balanced by two sulfur atoms, each changing by −2.

In the following answers we have emphasized the mole method by working each problem according to the three steps given on p. 225 of the Textbook. For each step we have given first the unit manipulation required then the numerical equation. This is a teaching aid in that you can use the unit arrangement to show how to "unravel" the problem.

Pr. 1. In Expt. 7, would the ratio between moles of copper atoms used and moles of silver atoms formed change if silver sulfate, Ag_2SO_4, had been used rather than silver nitrate, $AgNO_3$? Explain.

Answer

The ratio would not change. To change one mole of Ag^+ to $Ag(s)$ requires one mole of electrons. For copper, each mole of $Cu(s)$ that changes to Cu^{+2} liberates two moles of electrons. The behavior of atoms or ions is independent of their source.

Pr. 2. Although sodium carbonate is needed in the manufacture of glass, very little is found in nature. It is made using two very abundant chemicals, calcium carbonate (marble) and sodium chloride (salt). The process involves many steps, but the overall reaction is

$$CaCO_3 + 2NaCl \longrightarrow Na_2CO_3 + CaCl_2$$

(a) How many grams of sodium chloride react with 1.00 kg of calcium carbonate?
(b) How many grams of sodium carbonate are produced?

Answer

This problem is based on the Solvay process.

(a) STEP I

$$\frac{\text{g } CaCO_3}{\text{g/mole}}$$

$$1.00 \times 10^3/100 = 10.0 \text{ moles } CaCO_3$$

STEP II

$$(\text{moles } CaCO_3)\left(\frac{\text{moles NaCl}}{\text{mole } CaCO_3}\right)$$

$$10.0 \times \tfrac{2}{1} = 20.0 \text{ moles NaCl}$$

STEP III

$$\text{moles NaCl} \times \frac{\text{g}}{\text{mole}}$$

$$20.0 \times 58.5 = 1.17 \times 10^3 \text{ g NaCl}$$

Thus 1.17 kg NaCl react with 1.00 kg of $CaCO_3$.

(b) STEP I

moles $CaCO_3$ = 10.0 [already calculated in part (a)]

STEP II

moles Na_2CO_3

$$= (\text{moles } CaCO_3)\left(\frac{\text{moles } Na_2CO_3}{\text{mole } CaCO_3}\right)$$

$$= 10.0 \times \frac{1}{1} = 10.0$$

STEP III

$$\begin{aligned}\text{grams } Na_2CO_3 &= (\text{moles } Na_2CO_3)(\text{g/mole})\\ &= 10.0 \times 106\\ &= 1.06 \times 10^3 \text{ g } Na_2CO_3\end{aligned}$$

Thus 1.00 kg of $CaCO_3$ forms 1.06 kg Na_2CO_3.

Pr. 3. Some catalysts used in gasoline manufacture consist of finely divided platinum supported on an inert solid. Suppose that the platinum is formed by the high-temperature reaction between platinum dioxide, PtO_2, and hydrogen gas to form platinum metal and water.

(a) What is the oxidation number of platinum in platinum dioxide?
(b) Is hydrogen an oxidizing or reducing agent in this reaction?
(c) How many grams of hydrogen are needed to produce 1.0 gram of platinum metal?
(d) How many moles of water are produced along with 1.0 gram of Pt?
(e) How many grams of water are produced along with 1.0 gram of Pt?

Answer: (e) 0.18 gram of H_2O.

Answer

The balanced equation is

$$PtO_2(s) + 2H_2(g) \longrightarrow Pt(s) + 2H_2O(g)$$

(a) In PtO_2 the oxidation number of Pt is +4.

(b) Since H_2 is oxidized, it is a reducing agent.

(c) STEP I $\dfrac{\text{gram Pt}}{\text{g/mole}} = \text{moles Pt}$

$$\frac{1.0}{2.0 \times 10^{+2}} = 5 \times 10^{-3} \text{ mole Pt}$$

STEP II To produce 5.0×10^{-3} mole Pt requires $2 \times 5.0 \times 10^{-3}$ mole H_2. Hence we need 1.0×10^{-2} mole H_2.

STEP III 1.0×10^{-2} mole H_2 weighs

$$(1.0 \times 10^{-2} \text{ mole})(2.02 \text{ g/mole}) = 2.0 \times 10^{-2} \text{ g}$$

(d) In Step II of (c) we found that 1.0×10^{-2} mole H_2 was needed.

1.0×10^{-2} mole H_2 forms 1.0×10^{-2} mole H_2O.

(e) 1.0×10^{-2} mole H_2O weighs

$$(1.0 \times 10^{-2} \text{ mole})(18.0 \text{ g/mole}) = 0.18 \text{ g } H_2O$$

Pr. 4. Hydrazine, N_2H_4, and hydrogen peroxide, H_2O_2, are used together as a rocket fuel. The products are N_2 and H_2O. How many grams of hydrogen peroxide are needed per 1.00×10^3 grams of hydrazine carried by a rocket?

Answer: 2.12×10^3 grams of H_2O_2.

Answer

The equation is:

$$N_2H_4 + 2H_2O_2 = N_2 + 4H_2O$$

STEP I

g N_2H_4/mol wt N_2H_4 = moles N_2H_4
$1.00 \times 10^3/32.1 = 31.2$ moles N_2H_4

STEP II

$$(\text{moles } N_2H_4)\left(\frac{\text{moles } H_2O_2}{\text{mole } N_2H_4}\right) = \text{moles } H_2O_2$$

$$31.2 \times \frac{2}{1} = 62.4 \text{ moles } H_2O_2$$

STEP III

$(\text{moles } H_2O_2)(\text{mol wt } H_2O_2) = \text{g } H_2O_2$
$62.4 \times 34.0 = 2.12 \times 10^3 \text{ g } H_2O_2$

Pr. 5. Iodine is recovered from iodates in Chile saltpeter by the reaction

$$HSO_3^- + IO_3^- \text{ gives } I_2 + SO_4^{-2} + H^+ + H_2O$$

(a) How many grams of sodium iodate, $NaIO_3$, react with 1.00 mole of $KHSO_3$?
(b) How many grams of iodine, I_2, are produced?

Answer

The balanced equation is

$$5HSO_3^-(aq) + 2IO_3^-(aq) \longrightarrow I_2(s) + 5SO_4^{-2}(aq) + 3H^+(aq) + H_2O(l)$$

(a) STEP I Given 1.00 mole of HSO_3^-.

STEP II

$$(\text{moles } KHSO_3)\left(\frac{\text{moles } IO_3^-}{\text{mole } HSO_3^-}\right) = \text{moles } IO_3^-$$

$$1.00 \times \frac{2}{5} = 0.400 \text{ mole } IO_3^-$$

0.400 mole IO_3^- is obtained from 0.400 mole $NaIO_3$.

STEP III

$$\text{wt NaIO}_3 = (\text{mole NaIO}_3)(\text{mol wt NaIO}_3)$$
$$= 0.400 \times 198 = 79.2 \text{ g NaIO}_3$$

(b) STEP I Given 1.00 mole $KHSO_4$.

STEP II

$$(\text{moles KHSO}_3)\left(\frac{\text{moles I}_2}{\text{mole KHSO}_3}\right) = \text{moles I}_2$$

$$1.00 \times \tfrac{1}{5} = 0.200 \text{ mole I}_2$$

STEP III

$$(\text{moles I}_2)(\text{mol wt I}_2)$$
$$0.200 \times 254 = 50.8 \text{ g I}_2 \text{ produced}$$

Pr. 6. The hourly energy requirements of an astronaut can be satisfied by the energy released when 34 grams of sucrose are "burned" in his body. How many grams of oxygen would need to be carried in a space capsule to meet this requirement?

sucrose + oxygen gives carbon dioxide + water
$C_{12}H_{22}O_{11}$ + O_2 gives CO_2 + H_2O

Answer

The balanced equation is

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$$

STEP I

$$\text{g sucrose/mol wt sucrose} = \text{moles sucrose}$$
$$34/340 = 0.10 \text{ mole sucrose}$$

STEP II

$$(\text{moles sucrose})\left(\frac{\text{moles O}_2}{\text{mole sucrose}}\right) = \text{moles O}_2$$

$$0.10 \times \tfrac{12}{1} = 1.2 \text{ moles O}_2$$

STEP III

$$(\text{moles O}_2)(\text{mol wt O}_2) = \text{grams O}_2$$
$$1.2 \times 32 = 38 \text{ g O}_2$$

Pr. 7. The chlorine used to purify your drinking water was possibly made by electrolyzing molten NaCl to produce liquid sodium and gaseous chlorine.

(a) How many grams of sodium chloride are needed to produce 355 grams of chlorine gas?
(b) What volume would this gas occupy at STP?

Answer

$$2NaCl(l) \longrightarrow 2Na(l) + Cl_2(g)$$

(a) STEP I

$$\text{g Cl}_2/\text{mol wt Cl}_2 = \text{moles Cl}_2$$
$$355/71.0 = 5.00 \text{ moles Cl}_2$$

STEP II

$$(\text{moles Cl}_2)\left(\frac{\text{moles NaCl}}{\text{mole Cl}_2}\right) = \text{moles NaCl}$$

$$5.00 \times \tfrac{2}{1} = 10.0 \text{ moles NaCl}$$

STEP III

$$(\text{moles NaCl})(\text{mol wt NaCl}) = \text{grams NaCl}$$
$$10.0 \times 58.5 = 585 \text{ g NaCl needed}$$

(b) To find the volume occupied at STP:

$$(\text{moles Cl}_2)\left[\frac{\text{liters Cl}_2\text{ (STP)}}{\text{mole Cl}_2}\right] = \text{liters Cl}_2\text{ (STP)}$$

$$5.00 \times \frac{22.4}{1} = 112 = 1.12 \times 10^2 \text{ liters}$$

Pr. 8. A reaction involved in the production of iron from iron ore is:

Fe_2O_3 + CO gives Fe + CO_2
$\Delta H = -4.3$ kcal/mole Fe_2O_3

(a) How many grams of CO must react to release 13 kcal?
(b) How many liters of CO (STP) are needed to produce 1.0 kg of Fe?

Answer

The balanced equation is

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) + 4.3 \text{ kcal}$$

(a) STEP I

$$\text{moles Fe}_2\text{O}_3 \text{ needed} = \frac{(\text{heat released})}{(\text{heat/mole Fe}_2\text{O}_3)}$$
$$= \frac{13 \text{ kcal}}{4.3 \text{ kcal/mole Fe}_2\text{O}_3}$$

$$\text{moles Fe}_2\text{O}_3 \text{ needed} = 3.0$$

STEP II

$$\text{moles CO} = (\text{moles Fe}_2\text{O}_3)\left(\frac{\text{moles CO}}{\text{mole Fe}_2\text{O}_3}\right)$$
$$= 3.0 \times \tfrac{3}{1} = 9.0 \text{ moles}$$

STEP III

$$\text{Weight CO} = (\text{moles})(\text{mol wt})$$
$$= 9.0 \times 28 = 252 \text{ g}$$
$$= 2.5 \times 10^2 \text{ g}$$

(b) STEP I

moles Fe = (g Fe)/(mol wt Fe)
$1.0 \times 10^3/56 = 18$ moles Fe

STEP II

$$\text{moles CO} = (\text{moles Fe})\left(\frac{\text{moles CO}}{\text{mole Fe}}\right)$$

$$= 18 \times \tfrac{3}{2} = 27 \text{ moles}$$

STEP III

vol CO (STP) = (moles CO)(liters/mole)
$= 27 \times 22.4$
vol CO (STP) = 6.0×10^2 liters

Pr. 9. More C_8H_{18}, a hydrocarbon that is useful in gasoline, can be obtained from petroleum if this reaction takes place:

$$C_{16}H_{32}(g) + 2H_2(g) \longrightarrow 2C_8H_{18}(g)$$

(a) How many grams of C_8H_{18} can be made using 224 liters of H_2 at STP?
(b) What pressure conditions favor production of $C_8H_{18}(g)$?

Answer: (a) 1.14×10^3 g C_8H_{18}.

Answer

(a) The compound C_8H_{18} is octane.

STEP I

$$\frac{\text{liters } H_2}{(\text{liters/mole})} = \text{moles } H_2$$

$$\frac{224}{22.4} = 10.0 \text{ moles } H_2 \text{ (STP)}$$

STEP II

$$(\text{moles } H_2)\left(\frac{\text{moles } C_8H_{18}}{\text{mole } H_2}\right) = \text{moles } C_8H_{18}$$

$10.0 \times 1 = 10.0$ moles C_8H_{18}

STEP III

(moles C_8H_{18})(mol wt C_8H_{18}) = grams C_8H_{18}
$10.0 \times 114 = 1.14 \times 10^3$ g C_8H_{18}

(b) High pressure and high partial pressures (concentrations) of $C_{16}H_{32}$ and H_2 favor production of C_8H_{18}.

Pr. 10. How many liters of oxygen gas, at STP, will be released by decomposing 14.9 grams of NaOCl to produce $O_2(g) + Cl^-(aq)$ (as in Expt. 14a)?

Answer

The reaction involved is

$$2OCl^-(aq) \longrightarrow O_2(g) + 2Cl^-(aq)$$

STEP I

grams/mol wt = moles
14.9 g NaOCl = 14.9/74.5
= 0.200 mole NaOCl

STEP II

$$(\text{mole NaOCl})\left(\frac{\text{moles } O_2}{\text{mole NaOCl}}\right) = \text{moles } O_2$$

$0.200 \times \frac{1}{2} = 0.100$ mole O_2

STEP III

$$(\text{moles } O_2)\left(\frac{\text{liters at STP}}{\text{mole}}\right)$$

$0.100 \times 22.4 = 2.24$ liters O_2 produced

Pr. 11. A compound found in kerosene, a mixture of hydrocarbons, is decane, $C_{10}H_{22}$. A stove might burn 1.0 kilogram of kerosene per hour. Assume kerosene is $C_{10}H_{22}$ and answer the following:

(a) How many liters (STP) of oxygen are needed per hour?
(b) How many liters (STP) of carbon dioxide are produced per hour?

Answer

$$C_{10}H_{22}(g) + 15\tfrac{1}{2}O_2(g) \longrightarrow 10CO_2(g) + 11H_2O(g)$$

(a) STEP I

g $C_{10}H_{22}$/mol wt $C_{10}H_{22}$ = moles $C_{10}H_{22}$
$(1.0 \times 10^3)/142 = 7.0$ moles $C_{10}H_{22}$

STEP II

$$(\text{moles } C_{10}H_{22})\left(\frac{\text{moles } O_2}{\text{mole } C_{10}H_{22}}\right) = \text{moles } O_2$$

$$7.0 \times \frac{15.5}{1} = 108 \text{ moles } O_2$$

STEP III Amount of oxygen needed to burn 1.0 kg $C_{10}H_{22}$:

$$(\text{moles } O_2)\left[\frac{\text{liters (STP)}}{\text{mole}}\right]$$

$108 \times 22.4 = 2420$ liters
$= 2.4 \times 10^3$ liters

(b) STEP II

$$(\text{moles } C_{10}H_{22})\left(\frac{\text{moles } CO_2}{\text{mole } C_{10}H_{22}}\right) = \text{moles } CO_2$$

$7.0 \times \frac{10}{1} = 70$ moles CO_2

STEP III Amount of CO_2 produced from 1.0 kg $C_{10}H_{22}$:

$$(\text{moles } CO_2)\left[\frac{\text{liters (STP)}}{\text{mole } CO_2}\right]$$

$$70 \times \frac{22.4}{1} = 1570 \text{ liters}$$

$$= 1.6 \times 10^3 \text{ liters}$$

Pr. 12. How many grams of zinc metal are needed to react with hydrochloric acid to produce enough hydrogen gas to fill an 11.2 liter balloon at STP? What would be the volume of this balloon at 27°C and 680 mm Hg pressure? How many grams of zinc would be needed if sulfuric acid were used?

Answer

$$Zn(s) + 2H^+(aq) \longrightarrow H_2(g) + Zn^{+2}(aq)$$

(a) STEP I

moles H_2

$= [\text{vol } H_2 \text{ (STP)}]/[\text{liters per mole (STP)}]$

$11.2/22.4 = 0.500 \text{ mole } H_2$

STEP II

$$(\text{moles } H_2)\left(\frac{\text{moles Zn}}{\text{mole } H_2}\right) = \text{moles Zn}$$

$$0.500 \times \tfrac{1}{1} = 0.500 \text{ mole Zn}$$

STEP III

$$(\text{moles Zn})(\text{mol wt Zn}) = \text{grams Zn}$$

$$0.500 \times 65.4 = 32.7 \text{ g Zn}$$

(b) $$(11.2 \text{ liters})\left(\frac{27°\text{K} + 273°\text{K}}{273°\text{K}}\right)\left(\frac{760 \text{ mm}}{680 \text{ mm}}\right)$$

$$= 13.8 \text{ liters at new conditions}$$

(c) Same as (a). One mole of Zn gives one mole of H_2, regardless of the source of the H^+ reacting.

Pr. 13. How many liters of air (STP) are needed to burn 2.2 liters (STP) of methane, CH_4, gas in your laboratory burner? How much heat is released? The ΔH for combustion of CH_4 is -210 kcal/mole CH_4. Assume air is 20% oxygen.

Answer

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + 210 \text{ kcal}$$

STEP I

moles CH_4 = (vol CH_4)/(liters per mole)

$2.2/22.4 = 0.098 \text{ mole } CH_4$

STEP II (a)

$$(\text{moles } CH_4)\left(\frac{\text{moles } O_2}{\text{mole } CH_4}\right) = \text{moles } O_2$$

$$0.098 \times \tfrac{2}{1} = 0.196 \text{ mole}$$

or

$0.20 \text{ mole } O_2$

STEP II (b)

$$(\text{moles } O_2)\left(\frac{\text{moles air}}{\text{mole } O_2}\right) = \text{moles air}$$

$$0.20 \times \tfrac{5}{1} = 1.0 \text{ mole air}$$

STEP III

$$(\text{moles air})\left[\frac{\text{liters (STP)}}{\text{mole}}\right]$$

$$1.0 \times 22.4 = 22.4 \text{ liters}$$

or

22 liters

Or simply evoke Avogadro's Hypothesis and note from the equation that one liter of CH_4 requires 2 liters of O_2. In this problem the 4.4 liters of O_2 needed would be contained in $5 \times 4.4 = 22$ liters of air.

Pr. 14. In the reaction

$$NH_3(g) + O_2(g) \text{ gives } NO(g) + H_2O(g),$$

if 4.48 liters of ammonia gas measured at STP are used, how many liters of oxygen measured at STP will be needed to react with all the ammonia?

Answer: 5.60 liters of O_2 at STP.

Answer

$$2NH_3(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2NO(g) + 3H_2O(g)$$

When reacting gases are at the same temperature and pressure, the volume ratio is equal to the mole ratio (Avogadro's Hypothesis).

$$\left(\begin{matrix}\text{volume } O_2\\ \text{needed}\end{matrix}\right) = \left(\begin{matrix}\text{volume } NH_3\\ \text{consumed}\end{matrix}\right)\left(\frac{\text{moles } O_2}{\text{mole } NH_3}\right)$$

$$\text{vol } O_2 = 4.48 \text{ liters} \times \frac{2.5}{2} = 5.60 \text{ liters}$$

Pr. 15. The following reaction is carried out with all gas volumes measured at the same pressure and temperature:

$$C_4H_{10}(g) + O_2(g) \text{ gives } CO_2(g) + H_2O(g)$$

(a) How many liters of oxygen are required to produce 2.0 liters of CO_2?

(b) If 15 liters of oxygen are used, how many liters of butane, C_4H_{10}, will be burned?

(c) If 8.0 liters each of oxygen and butane are mixed, how many liters of CO_2 are produced (assume complete reaction)?

Answer: (a) 3.2 liters of O_2.

Answer

$$C_4H_{10}(g) + 6\tfrac{1}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g)$$

When reacting gases are at the same temperature and pressure, the volume ratio is equal to the mole ratio (Avogadro's Hypothesis).

(a) $$\begin{pmatrix}\text{volume } O_2\\ \text{consumed}\end{pmatrix} = \begin{pmatrix}\text{volume } CO_2\\ \text{produced}\end{pmatrix}\left(\frac{\text{moles } O_2}{\text{mole } CO_2}\right)$$

$$\text{vol } O_2 = 2.0 \text{ liters} \times \frac{6.5}{4.0} = 3.2 \text{ liters}$$

(b) $$\begin{pmatrix}\text{volume } C_4H_{10}\\ \text{burned}\end{pmatrix} = \begin{pmatrix}\text{volume } O_2\\ \text{consumed}\end{pmatrix}\left(\frac{\text{moles } C_4H_{10}}{\text{mole } O_2}\right)$$

$$\text{vol } C_4H_{10} = 15 \text{ liters} \times \frac{1}{6.5} = 2.3 \text{ liters}$$

(c) Since equal numbers of moles of C_4H_{10} and O_2 are present initially, and since one mole of C_4H_{10} reacts with 6.5 moles of O_2, the C_4H_{10} is present in excess. The reaction will proceed until the oxygen is consumed.

$$\begin{pmatrix}\text{volume } CO_2\\ \text{produced}\end{pmatrix} = \begin{pmatrix}\text{volume } O_2\\ \text{consumed}\end{pmatrix}\left(\frac{\text{moles } CO_2}{\text{mole } O_2}\right)$$

$$\text{vol } CO_2 = 8.0 \text{ liters} \times \frac{4}{6.5} = 4.9 \text{ liters}$$

Pr. 16. What volume of Cl_2 gas at 37°C and 753 mm could be obtained from 58.4 liters of HCl, also measured at 37°C and 753 mm, if the following reaction could be carried effectively to completion?

$$HCl(g) + O_2(g) \text{ gives } H_2O(g) + Cl_2(g)$$

Answer

$$4HCl(g) + O_2(g) \longrightarrow 2H_2O(g) + 2Cl_2(g)$$

When reacting gases are at the same temperature and pressure, the volume ratio is equal to the mole ratio (Avogadro's Hypothesis).

$$\begin{pmatrix}\text{volume } Cl_2\\ \text{produced}\end{pmatrix} = \begin{pmatrix}\text{volume HCl}\\ \text{consumed}\end{pmatrix}\left(\frac{\text{moles } Cl_2}{\text{mole HCl}}\right)$$

$$\text{vol } Cl_2 = 58.4 \text{ liters} \times \tfrac{2}{4} = 29.2 \text{ liters}$$

Pr. 17. Suppose 105 liters of NH_3 and 285 liters of O_2 are allowed to react until the reaction:

$$NH_3(g) + O_2(g) \text{ gives } H_2O(g) + NO_2(g)$$

is complete. The temperature and pressure are maintained constant at 200°C and 0.30 atmosphere during all volume measurements. What gas, and what volume of it measured at the stated conditions, remains unreacted?

Answer

$$2NH_3(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 3H_2O(g) + 2NO_2(g)$$

Since conditions are maintained at 200°C and 0.30 atmosphere, the mole ratio will equal the volume ratio (Avogadro's Hypothesis). Amount of O_2 needed to use 105 liters of NH_3:

$$(\text{liters } NH_3)\left(\frac{\text{liters } O_2}{\text{liter } NH_3}\right)$$

$$105 \times \frac{3.5}{2} = 184 \text{ liters}$$

This volume of O_2 is available, and, indeed, an excess of 285 − 184 = 101 liters of oxygen will be unreacted.

Pr. 18. A 6 volt lead storage battery contains 700 grams of pure $H_2SO_4(l)$ dissolved in water.

(a) How many grams of solid sodium carbonate, Na_2CO_3, would be needed to neutralize this acid (giving CO_2 gas and H_2O) if it were spilled?

(b) How many liters of 2.0 *M* Na_2CO_3 solution would be needed?

Answer

$$2H^+(aq) + CO_3^{-2}(aq) \longrightarrow CO_2(g) + H_2O(l)$$

(a) STEP I

$$\text{moles } H_2SO_4 = (\text{g } H_2SO_4)/(\text{mol wt } H_2SO_4)$$
$$= 700/98.1 = 7.14 \text{ moles}$$

STEP II

$$\text{moles } H^+ = (\text{moles } H_2SO_4)\left(\frac{\text{moles } H^+}{\text{mole } H_2SO_4}\right)$$
$$= 7.14 \times \tfrac{2}{1} = 14.3 \text{ moles}$$

$$\text{moles } CO_3^{-2} = (\text{moles } H^+)\left(\frac{\text{moles } CO_3^{-2}}{\text{mole } H^+}\right)$$
$$= 14.3 \times \tfrac{1}{2} = 7.14 \text{ moles}$$

STEP III

$$\text{g } Na_2CO_3 = (\text{moles } Na_2CO_3)(\text{mol wt } Na_2CO_3)$$
$$= 7.14 \times 106$$
$$= 757 \text{ g}$$

(b) STEPS I and II are the same as in (a).

STEP III

$$\begin{pmatrix}\text{vol 2.0 } M \text{ } Na_2CO_3\\ \text{solution needed}\end{pmatrix} = \left(\frac{\text{moles } Na_2CO_3 \text{ needed}}{\text{molar conc. } Na_2CO_3 \text{ solution}}\right)$$

$$\text{vol Na}_2\text{CO}_3 = \left(\frac{7.14 \text{ moles}}{2.0 \text{ moles/liter}}\right)$$

$$= 3.57 \text{ liters}$$

Pr. 19. Nitric acid, HNO_3, is made by the process

$$3NO_2(g) + H_2O(l) = 2HNO_3(l) + NO(g)$$

Commercial concentrated acid contains 68% by weight HNO_3 in water. The solution is 15 *M*. How many liters of concentrated acid are needed to react with 0.100 kg of copper metal?

$Cu(s) + H^+(aq) + NO_3^-(aq)$ gives
$Cu^{+2}(aq) + NO_2(g) + H_2O(l)$

Answer: 0.42 liter of HNO_3.

Answer

$$Cu(s) + 4H^+(aq) + 2NO_3^-(aq) = Cu^{+2}(aq) + 2NO_2(g) + 2H_2O(l)$$

STEP I

moles Cu = g Cu/mol wt Cu
100/63.5 = 1.57 moles Cu

STEP II

$$(\text{moles Cu})\left(\frac{\text{moles H}^+}{\text{mole Cu}}\right) = \text{moles H}^+$$

$$1.57 \times \tfrac{4}{1} = 6.28 \text{ moles H}^+$$

$$(\text{moles H}^+)\left(\frac{\text{moles HNO}_3}{\text{mole H}^+}\right)$$

$$6.28 \times \tfrac{1}{1} = 6.28 \text{ moles HNO}_3$$

STEP III

$$\frac{\text{moles HNO}_3}{\text{moles/liter}} = \text{liter HNO}_3$$

6.28/15 = 0.419 liter

or

0.42 liter HNO_3

Pr. 20. How many grams of silver metal will react with 2.0 liters of 6.0 *M* HNO_3? The reaction is

$Ag(s) + H^+(aq) + NO_3^-(aq)$ gives
$Ag^+(aq) + NO(g) + H_2O(l)$

Answer

$$3Ag(s) + 4H^+ + NO_3^- = 3Ag^+ + NO + 2H_2O$$

STEP I

$$\begin{aligned}\text{moles HNO}_3 &= (\text{vol HNO}_3)(\text{molar conc. HNO}_3)\\ &= (\text{liters})(\text{moles/liter})\\ &= 2.0 \times 6.0\\ &= 12 \text{ moles HNO}_3\end{aligned}$$

STEP II

$$(\text{moles HNO}_3)\left(\frac{\text{moles Ag}}{\text{mole HNO}_3}\right) = \text{moles Ag}$$

$$12 \times \tfrac{3}{4} = 9.0 \text{ moles Ag}$$

STEP III

$$\text{moles Ag} \times \frac{\text{g}}{\text{mole}} = \text{grams Ag}$$

$$9.0 \times 108 = 9.7 \times 10^2 \text{ g Ag}$$

Pr. 21. A measured volume, 10.00 liters, of the waste process water from a cotton mill requires 23.62 ml of 0.1000 *M* hydrochloric acid to produce a neutral solution. What is the hydroxide in concentration in the waste?

Answer

$$H^+ + OH^- = H_2O$$

STEP I

moles HCl = (vol HCl)(molar conc. HCl)

$$\left(\frac{23.62}{1000} \text{ liters}\right)(0.1000 \text{ moles/liter})$$

$$= 2.362 \times 10^{-3} \text{ mole HCl}$$

STEP II

$$(\text{moles HCl})\left(\frac{\text{moles OH}^-}{\text{mole HCl}}\right) = \text{moles OH}^-$$

$$2.362 \times 10^{-3} \times \tfrac{1}{1} = 2.362 \times 10^{-3} \text{ mole OH}^-$$

STEP III

$$\left(\frac{\text{moles OH}^-}{\text{liter}}\right) = (\text{molar conc. OH}^-)$$

$$\frac{2.362 \times 10^{-3}}{10.00} = 2.362 \times 10^{-4}\ M \text{ OH}^-$$

Pr. 22. What weight of silver chloride may be obtained from 1.0 liter of 1.0 *M* $AgNO_3$, if 12 ml of 0.15 *M* NaCl are added?

Answer

$$Ag^+ + Cl^- = AgCl(s)$$

STEP I

For Cl^-, we have

$$\text{moles Cl}^- = \left(\begin{matrix}\text{vol NaCl}\\ \text{solution}\end{matrix}\right)\left(\begin{matrix}\text{molar conc. NaCl}\\ \text{solution}\end{matrix}\right)$$

$$= \frac{12}{1000} \text{ liters} \times 0.15 \frac{\text{moles}}{\text{liter}}$$

$$= 1.8 \times 10^{-3} \text{ mole Cl}^-$$

For Ag^+, we have

$$\text{moles Ag}^+ = \begin{pmatrix}\text{vol AgNO}_3\\ \text{solution}\end{pmatrix}\begin{pmatrix}\text{molar conc. AgNO}_3\\ \text{solution}\end{pmatrix}$$

$$= 1.0 \text{ liter} \times 1.0\, M \text{ AgNO}_3$$

$$= 1.0 \text{ mole Ag}^+$$

Since Ag^+ is clearly in excess, the amount of Cl^- will control the amount of AgCl formed.

STEP II

$$(\text{moles Cl}^-)\left(\frac{\text{moles AgCl}}{\text{mole Cl}^-}\right) = \text{moles AgCl}$$

$$1.8 \times 10^{-3} \times \tfrac{1}{1} = 1.8 \times 10^{-3} \text{ mole AgCl}$$

STEP III

$$(\text{moles AgCl})\left(\frac{\text{g}}{\text{mole}}\right) = \text{g AgCl}$$

$$1.8 \times 10^{-3} \times 140 = 0.252$$

or

$$0.25 \text{ g AgCl formed}$$

Pr. 23. How many milliliters of a 0.050 M $KMnO_4$ solution are required to oxidize 2.00 grams of $FeSO_4$ in a dilute acid solution?

Answer: 53 ml of $KMnO_4$ solution.

Answer

$$5Fe^{+2}(aq) + MnO_4^-(aq) + 8H^+(aq) = 5Fe^{+3}(aq) + Mn^{+2}(aq) + 4H_2O$$

STEP I

$$\text{moles FeSO}_4 = \text{g FeSO}_4/\text{mol wt FeSO}_4$$

$$\frac{2.00 \text{ g}}{152 \text{ g/mole}} = 0.0132 \text{ mole FeSO}_4$$

STEP II

$$(\text{moles FeSO}_4)\left(\frac{\text{moles MnO}_4^-}{\text{mole FeSO}_4}\right) = \text{moles MnO}_4^- \text{ needed}$$

$$1.32 \times 10^{-2} \times \tfrac{1}{5} = 0.264 \times 10^{-2} \text{ mole MnO}_4^-$$

STEP III

$$\begin{pmatrix}\text{vol MnO}_4^-\\ \text{solution}\end{pmatrix} = \left(\frac{\text{moles MnO}_4^- \text{ needed}}{\text{molar conc. MnO}_4^-}\right)$$

$$= \frac{0.264 \times 10^{-2} \text{ mole}}{0.050 \text{ mole/liter}}$$

$$= 5.3 \times 10^{-2} \text{ liter}$$

$$= (5.3 \times 10^{-2} \text{ liter}) \times 1000 \text{ ml/liter}$$

$$= 53 \text{ ml}$$

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Questions 1–4 are concerned with the Haber Process. In this process ammonia is produced by passing a mixture of nitrogen and hydrogen gas through a bed of catalyst (essentially iron oxide) at about 500°C and 1000 atmospheres. The equilibrium equation is

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + 22 \text{ kcal}$$

There is about 50% conversion under these conditions. To increase the yield the ammonia is dissolved in water as it is produced.

1. If 56 kilograms of N_2 are converted to ammonia, how many kilograms of NH_3 will be produced?

   Answer

   Step I

   $$\frac{56 \times 10^3 \text{ g } N_2}{28 \text{ g } N_2/\text{mole } N_2} = 2 \times 10^3 \text{ moles } N_2$$

   Step II

   $$(2 \times 10^3 \text{ moles } N_2)\left(\frac{2 \text{ moles } NH_3}{1 \text{ mole } N_2}\right) = 4 \times 10^3 \text{ moles } NH_3$$

   Step III

   $$(4 \times 10^3 \text{ moles } NH_3)\left(\frac{17 \text{ g } NH_3}{1 \text{ mole } NH_3}\right) = 68 \times 10^3 \text{ g } NH_3 = 68 \text{ kg } NH_3$$

2. How many kilograms of H_2 would be required to produce NH_3 if 4×10^3 moles of N_2 reacted?

   Answer

   Step II

   $$(4 \times 10^3 \text{ moles } N_2)\left(\frac{3 \text{ moles } H_2}{1 \text{ mole } N_2}\right) = 12 \times 10^3 \text{ moles } H_2$$

   Step III

   $$12 \times 10^3 \text{ moles } H_2 \times \frac{2 \text{ g } H_2}{\text{mole } H_2} = 24 \times 10^3 \text{ g } H_2 = 24 \text{ kg } H_2$$

3. How much heat is liberated when 56 kilograms of N_2 react to produce ammonia?

   Answer

   Step I

   $$56 \text{ kg } N_2 = 56 \times 10^3 \text{ g } N_2$$

   $$\frac{56 \times 10^3 \text{ g } N_2}{28 \text{ g } N_2/\text{mole } N_2} = 2 \times 10^3 \text{ moles } N_2$$

   Step II

   $$(2 \times 10^3 \text{ moles } N_2)\left(\frac{22 \text{ kcal}}{\text{mole } N_2}\right) = 44 \times 10^3 \text{ kcal}$$

4. If 66×10^3 g of H_2 react to form $NH_3(g)$, what volume would the ammonia occupy at STP?

   Answer

   Step I

   $$\frac{66 \times 10^3 \text{ g } H_2}{2 \text{ g } H_2/\text{mole } H_2} = 33 \times 10^3 \text{ moles } H_2$$

   Step II

   $$(33 \times 10^3 \text{ moles } H_2)\left(\frac{2 \text{ moles } NH_3}{3 \text{ moles } H_2}\right) = 22 \times 10^3 \text{ moles } NH_3$$

   Step III

   $$(22 \times 10^3 \text{ moles } NH_3)\left[\frac{22.4 \text{ liters (STP)}}{\text{mole } NH_3}\right] = 49 \times 10^4 \text{ liters (STP)}$$

Questions 5–8 are concerned with the Ostwald Process. A large part of the ammonia produced in industry is used in the production of nitric acid by this process. The following equations represent the important steps involved:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \qquad (1)$$
$$4NO(g) + 2O_2(g) \longrightarrow 4NO_2(g) \qquad (2)$$
$$4NO_2(g) + O_2(g) + 2H_2O \longrightarrow 4HNO_3 \qquad (3)$$

In equation (*1*) a mixture of NH_3 and air is passed through platinum gauze heated to about 800°C. As the mixture cools, the product $NO(g)$ is oxidized (equation *2*) to $NO_2(g)$. The $NO_2(g)$ reacts with water and O_2 to form nitric acid, HNO_3.

5. If 68×10^3 kilograms of NH_3 are converted to HNO_3, how many moles of pure HNO_3 will be formed?

Answer

Step I

$$\frac{68 \times 10^6 \text{ g NH}_3}{17 \text{ g NH}_3\text{/mole NH}_3} = 4 \times 10^6 \text{ moles NH}_3$$

Step II

$$(4 \times 10^6 \text{ moles NH}_3)\left(\frac{4 \text{ moles HNO}_3}{4 \text{ moles NH}_3}\right) = 4 \times 10^6 \text{ moles HNO}_3$$

6. What will be the molarity of the nitric acid produced if 1.56×10^4 moles of pure HNO_3 are dissolved in sufficient water to make the volume of the acid 1.00×10^3 liters?

Answer

$$\text{Molarity} = \frac{\text{moles}}{\text{liter of solution}} = \frac{1.56 \times 10^4 \text{ moles}}{1.00 \times 10^3 \text{ liters}} = 15.6\ M$$

7. How many liters of air are needed to react with 8×10^5 liters of $NH_3(g)$ to produce $NO(g)$, as in equation (*1*)? Assume both gases to be at the same conditions of pressure and temperature. (Recall that air is about one-fifth oxygen by volume.)

Answer

Step I

$$(8 \times 10^5 \text{ liters NH}_3)\left(\frac{5 \text{ liters O}_2}{4 \text{ liters NH}_3}\right) = 10 \times 10^5 \text{ liters O}_2$$

Step II

$$(10 \times 10^5 \text{ liters O}_2)\left(\frac{5 \text{ liters air}}{1 \text{ liter O}_2}\right) = 5 \times 10^6 \text{ liters air}$$

8. How many liters of pure oxygen at STP react with sufficient ammonia to produce 95 kilograms of pure HNO_3?

Answer

Step I

$$\frac{95 \times 10^3 \text{ g HNO}_3}{63 \text{ g HNO}_3\text{/mole HNO}_3} = 1.5 \times 10^3 \text{ moles HNO}_3$$

Step II

$$(1.5 \times 10^3 \text{ moles HNO}_3)\left(\frac{8 \text{ moles O}_2}{4 \text{ moles HNO}_3}\right) = 3 \times 10^3 \text{ moles O}_2$$

Step III

$$(3 \times 10^3 \text{ moles O}_2)\left[\frac{22.4 \text{ liters O}_2 \text{ (STP)}}{\text{mole O}_2}\right] = 6.7 \times 10^4 \text{ liters O}_2 \text{ (STP)}$$

9. What volume of 10 *M* HNO_3 solution can be made from 95 kilograms of pure HNO_3?

Answer

Step I

$$\frac{95 \times 10^3 \text{ g HNO}_3}{63 \text{ g HNO}_3\text{/mole HNO}_3} = 1.5 \times 10^3 \text{ moles HNO}_3$$

Step II

$$\frac{1.5 \times 10^3 \text{ moles HNO}_3}{10 \text{ moles HNO}_3\text{/liter 10 } M \text{ HNO}_3 \text{ solution}} = 1.5 \times 10^2 \text{ liters 10 } M \text{ HNO}_3 \text{ solution}$$

10. An important fertilizer is produced according to the equation

$$2NH_3(g) + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

When 44.8 liters (STP) $NH_3(g)$ react with sufficient H_2SO_4, how many grams of ammonium sulfate are produced?

Answer

Step I

$$\frac{44.8 \text{ liters NH}_3}{22.4 \text{ liters NH}_3\text{/mole NH}_3} = 2 \text{ moles NH}_3$$

Step II

$$(2 \text{ moles NH}_3)\left[\frac{1 \text{ mole (NH}_4)_2\text{SO}_4}{2 \text{ moles NH}_3}\right] = 1 \text{ mole (NH}_4)_2\text{SO}_4$$

Step III

$$[1 \text{ mole (NH}_4)_2\text{SO}_4]\left[\frac{132 \text{ g (NH}_4)_2\text{SO}_4}{\text{mole (NH}_4)_2\text{SO}_4}\right] = 132 \text{ g (NH}_4)_2\text{SO}_4$$

For Questions 11–13 assume the reaction between kerosene and fuming HNO_3, used as a rocket fuel, to be as follows:

$$\underset{\text{kerosene}}{C_{14}H_{30}(l)} + 86HNO_3(l) \longrightarrow 14CO_2(g) + 86NO_2(g) + 58H_2O(g)$$

One liter of $C_{14}H_{30}$ weighs about 765 grams. One liter of fuming HNO_3 weighs about 1500 grams.

11. How many liters of fuming $HNO_3(l)$ are needed to react with 1 liter of $C_{14}H_{30}(l)$?

Answer

Step I

$$\frac{765 \text{ g } C_{14}H_{30}}{198 \text{ g } C_{14}H_{30}/\text{mole } C_{14}H_{30}} = 3.86 \text{ moles } C_{14}H_{30}$$

Step II

$$(3.86 \text{ moles } C_{14}H_{30})\left(\frac{86 \text{ moles } HNO_3}{1 \text{ mole } C_{14}H_{30}}\right) = 332 \text{ moles } HNO_3$$

Step III

$$(332 \text{ moles } HNO_3)\left(\frac{63 \text{ g } HNO_3}{\text{mole } HNO_3}\right) = 20{,}900 \text{ g } HNO_3$$

Step IV

$$\frac{20{,}900 \text{ g } HNO_3}{1500 \text{ g } HNO_3/\text{liter } HNO_3} = 14 \text{ liters } HNO_3$$

12. How many liters of products at STP would be formed from one mole of $C_{14}H_{30}(l)$?

Answer

Step I

One mole of $C_{14}H_{30}(l)$ produces:

14 moles CO_2
86 moles NO_2
58 moles H_2O

158 moles product gases

Step II

$$(158 \text{ moles})\left(\frac{22.4 \text{ liters}}{\text{mole}}\right) = 3540 \text{ liters of product gases}$$

13. How many liters of $C_{14}H_{30}(l)$ are there in one mole?

Answer

$$\left(\frac{198 \text{ g}}{\text{mole}}\right)\left(\frac{1 \text{ liter}}{765 \text{ g}}\right) = 0.259 \frac{\text{liter}}{\text{mole}} \; C_{14}H_{30}$$

For Questions 14–17 assume that gasoline is pure C_8H_{18}, octane, and that, in an engine, it burns with air (oxygen) to produce carbon dioxide and water vapor. The reaction is

$$C_8H_{18}(g) + O_2(g) \text{ gives } CO_2(g) + H_2O(g)$$

14. Write the balanced equation for this reaction.

Answer

$$C_8H_{18}(g) + 12\tfrac{1}{2}O_2(g) \rightleftarrows 8CO_2(g) + 9H_2O(g)$$

15. When one mole of C_8H_{18} is burned, how many grams of water are produced?

Answer

$$(1 \text{ mole octane})\left(\frac{9 \text{ moles water}}{1 \text{ mole octane}}\right) = 9 \text{ moles water}$$

$$(9 \text{ moles water})\left(\frac{18 \text{ g } H_2O}{\text{mole } H_2O}\right) = 162 \text{ g } H_2O$$

16. When 1.0 liter of liquid C_8H_{18} is vaporized and consumed, according to the reaction in 14, how many liters of gaseous products are produced at STP? (1.0 liter of C_8H_{18} weighs about 730 grams.)

Answer

$$\frac{730 \text{ g octane}}{114 \text{ g octane/mole octane}} = 6.4 \text{ moles octane}$$

$$\left(\begin{matrix}6.4 \text{ moles}\\ \text{octane}\end{matrix}\right)\left(\frac{17 \text{ moles gaseous products}}{1.0 \text{ mole octane}}\right) = 109 \text{ moles gaseous products}$$

$$\left(\begin{matrix}109 \text{ moles}\\ \text{gaseous products}\end{matrix}\right)\left[\frac{22.4 \text{ liters (STP)}}{\text{mole}}\right] = 2440 \text{ liters STP or } 2400 \text{ liters STP}$$

17. How many liters of air at STP are required to burn 1.0 liter of octane?

Answer

$$(6.4 \text{ moles octane})\left(\frac{12 \text{ moles } O_2}{1.0 \text{ mole octane}}\right) = 77 \text{ moles } O_2$$

$$(77 \text{ moles } O_2)\left[\frac{22.4 \text{ liters (STP)}}{\text{mole } O_2}\right] = 1720 \text{ liters } O_2$$

$$(1720 \text{ liters } O_2)\left(\frac{5 \text{ liters air}}{1 \text{ liter } O_2}\right) = 8600 \text{ liters air (STP)}$$

CHAPTER

14

WHY WE BELIEVE IN ATOMS

Intent and Approach

This chapter reviews many of the types of evidence that contribute to our belief in the usefulness and applicability of the atomic theory. Chemical evidence, which is one of the bulwarks of the theory, can be drawn directly from the student's experience. The other types of evidence are, generally, outside of his experience. The experiments must be described, the results cited, and the significance given in an authoritarian way. Nevertheless, this chapter is consistent with the experimental philosophy of this course, since the student is reminded that experiments provide the basis for every aspect of the atomic theory and every detail of the structure of the atom.

The totality of this evidence, together with the "garbage collector analogy," provides an excellent sample of how a scientific view, or theory, gains general acceptance. Consistency with a variety of different types of experimental evidence establishes confidence in a theory. Seldom can one behavior be singled out as *the* decisive evidence.

Outline

1. Inductive reasoning is explained; the "garbage collector" analogy and the "black box" experiment provide examples.
2. The chemical evidence for atoms is given in three parts under *The Law of Definite Composition* (*14-1.1*), *The Law of Simple Multiple Proportions* (*14-1.2*), and *The Law of Combining Volumes* (*14-1.3*).
3. Chemical evidence is given for the quantization of electric charge: Faraday's Laws (14-1.4).
4. A group of sections (in reduced type) touch on "seeing" parts of the atom.
    Mass and charge of the electron: glow discharge tubes and Millikan's oil-drop experiment (14-2.1).
    Mass of positive ions: the mass spectrograph (14-2.2).
    The nuclear atom: Rutherford's scattering experiment (14-2.3).
5. Dimensions of atoms are developed through spectroscopy: light (14-3.1), X-ray diffraction from crystals (14-3.2), microwave spectroscopy (14-3.3), and infrared spectroscopy (14-3.4).

New Concepts

1. The law of simple multiple proportions and the law of definite composition are posed as the first evidence for the atomic theory.
2. Light extends beyond the visible spectral range: gamma rays, X-rays, ultraviolet, infrared, and microwave frequencies are all part of the light spectrum.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
(pp. 233–234) Expt. 24	1	Expt. 24 and discussion Weigh electrodes Expt. 25					Garbage collector analogy and logical inference
S 14-1 (pp. 234–238)	2	Expt. 25	1, 2	2, 5, 6	1, 3, 7	4	Expt. 25
	3	Discussion of induction and atomic theory of chemistry; discussion of Ex. 14-1, 14-2					Laws of Definite Composition, Simple Multiple Proportions, Faraday's Laws, Electrical nature of matter
S 14-2 (pp. 239–245) (reduced type)	4	Discussion; Ex. 14-3, 14-4	3–5		11–13, 15	14, 16	Gas discharge tubes; electron charge, e/m, mass spectra
S 14-3/14-3.2 (pp. 245–249)	5	Discussion		8, 17	**9***	18, 19	Rutherford experiment and the nuclear atom. The nature of light
S 14-3.3/14-3.4 (pp. 249–250)	6	Film: MOLECULAR SPECTROSCOPY or CRYSTALS AND THEIR STRUCTURES Discussion		10			Mainly vibrational spectroscopy (infrared)

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* Boldface indicates problems whose answers are given in the Textbook.

3. Light is characterized by wavelength and frequency.
4. X-Rays reflected from crystal surfaces indicate atomic positions in the crystal.
5. Rotation can be excited by absorption of microwave frequencies; vibration, by absorption of infrared frequencies.

Development

INDUCTIVE REASONING AND THE "BLACK BOX"

This chapter is intended to provide a firm foundation for the belief that most students have in atoms. This belief, planted by early science courses and nurtured by outside sources, is usually rather vague and is almost always instilled through a completely authoritarian approach. The student believes there are atoms, but has no experimental basis for this tenet. In this section, set up the logical mechanism by which belief in an unseen object can have foundation. The "garbage collector" analogy gives a consistent set of familiar observations that display the general pattern. Observations concerning the unseen object are collected, and various theories are compared on the basis of consistency with the observations. Experiment 24 lets the student try this pattern via observations on a physical system which he cannot see. The "black box" experiment forces the student to form a picture of an object on the basis of indirect observations. This is exactly analogous to our attempts to form a picture of the atom.

Expt. 24, CONSTRUCTION OF A LOGICAL MODEL,
fits here. See p. 441 for guide.

CHEMICAL EVIDENCE FOR THE ATOMIC THEORY (14-1)

The Law of Definite Composition (14-1.1)

The Law of Simple Multiple Proportions (14-1.2)

The Law of Combining Volumes (14-1.3)

These sections remind the student that the success he has observed in explaining facts of chemistry through the atomic theory constitutes a basis for belief in the atomic theory. He is informed that these facts of chemistry fostered the first useful hypothesis of the atomic theory. In fact the chemical evidence—definite composition, simple multiple proportions, and combining volumes—occupies a central position in the evidence for the atomic theory that is analogous to the disappearance of the garbage in the "garbage collector" analogy. The intuitively more direct types of evidence, actual "seeing," would not lead to a garbage collector theory if the garbage merely accumulated.

Chemical Evidence for the Electrical Nature of Atoms (14-1.4)

The full significance of Faraday's Laws emerges when they are interpreted in terms of the atomic theory. If electric charge can "count" atoms (as Faraday's Laws imply), then electric charge must come in "packages." From this notion it is only a step (but it *is* another step) to that of associating the unit charge with a fundamental particle.

Experiment 25 gives the student the opportunity to verify a Faraday Law. In this experiment we cannot claim any flavor of discovery, since Chapter 12 is founded on the same reasoning used in Expt. 25.

Expt. 25, THE RELATION BETWEEN THE MOLES OF COPPER, MOLES OF SILVER, AND MOLES OF ELECTRONS INVOLVED DURING ELECTROLYSIS,
fits here. See p. 443 for guide.

"SEEING" PARTS OF ATOMS (14-2) (reduced type)

"Seeing" Electrons (14-2.1)

"Seeing" Positive Ions (14-2.2)

"Seeing" the Nucleus: Structure of the Atom (14-2.3)

Although these three sections are *not* intended for use with the average class, they may be suitable if most of your students have had physics. If your class does not meet this prerequisite you should summarize these sections, stressing the experimental basis of the deductions. It is most important that you put over the outlines of the Rutherford model—the nuclear atom. The Textbook gives a good development—the discovery of different kinds of "beams" (electrons and positive ions), the measurement of charge, the charge-to-mass ratio, and then the electron arrangement. Here the historical timing is less important than a clear flow of concepts.

The measurements of the charge-to-mass ratio for electrons and for positive ions are identical in principle. For electrons, however, there is only one value for the ratio e/m. For positive ions the ratio can have several discrete values. The existence of several e/m ratios is readily understood in terms of two effects. First, the positive ion may have different charges: a unit charge, a double charge, a triple charge, etc. Second, the positive ion may have different masses from various isotopes. In discussing these two effects, be sure the student realizes that we don't predict the different ratios *because* there are isotopes; we deduce the existence of isotopes *because* we observe the different ratios of e/m.

The significance of the Rutherford experiment escapes some students. The Thomson model of the atom provides an intuitively reasonable basis for the expectation that bombarding particles would be reflected, since there are obviously no "holes" between the atoms. What it does *not* do, however, is provide a reasonable basis for explaining why most of the bombarding particles penetrate almost undeflected and only a few reflect back toward the source. Thus the penetrating particles are as important in this experiment as the reflected particles.

Since the student already has been using the atomic theory, it will require some emphasis to make sure he recognizes that the results in these sections, which seem to *follow* from the atomic theory, actually form the basis for the theory—that is, the atomic theory follows from the experiments.

MEASURING DIMENSIONS OF ATOMS AND MOLECULES (14-3)

The student has viewed many molecular models and, no doubt, has wondered just how these bond lengths, molecular geometries, and crystal packings have been learned. The remainder of Chapter 14 describes some of the experiments used to deduce the sizes and shapes of atoms and molecules. These sections draw heavily upon arguments that, although not fully substantiated, are intuitively acceptable to the student.

Light and the Frequency Spectrum (14-3.1)

Light is called an "electromagnetic disturbance traveling through space" and is then immediately likened to a water wave. Meaning can be added to the term "electromagnetic disturbance" by considering the electric field near an electron that is moved up and down with a regular periodic motion. The resultant oscillating electric field radiates at the speed of light. Another electron at some distance from the first responds to the oscillating electric field, taking up the same periodic motion as the first electron. These two electrons furnish a useful model for demonstrating the emission of light (the first electron) and the absorption of light (the second electron).

By an extension of the water wave analogy, it is reasonable to associate different colors with different frequencies. Furthermore, the idea that the human eye is not sensitive to all frequencies is readily grasped. (Notice that the existence of light energy outside the visible range is demonstrated in the film MOLECULAR SPECTROSCOPY.)

X-Ray Diffraction Patterns (14-3.2)

The phenomenon of X-ray diffraction is treated empirically. The student is told that X-rays reflect from the surface of a crystal to give patterns that reveal the spacing and arrangement of atoms. Constructive and destructive interference are not mentioned. Figure 14-15 (Textbook) shows the type of line-pattern obtained from a finely-divided sample (a "powder" pattern).

Microwave Spectroscopy: Molecular Rotation (14-3.3) (reduced type)

Infrared Spectroscopy: Molecular Vibration (14-3.4)

More emphasis is placed on molecular vibration than on rotation. The reason is that the existence of characteristic, or "resonant," vibrational frequencies in a vibrating system is common (tuning forks, cymbals, vibrating strings, etc.). This emphasis is appropriate, since the vibrational spectroscopy is more widely applicable (solids, liquids, and gases) and is much more widely used. Each molecular species has an absorption spectrum that can be likened to a fingerprint. Hence the spectrum has obvious value for analysis, both qualitative and quantitative.

Film, MOLECULAR SPECTROSCOPY or
CRYSTALS AND THEIR STRUCTURE,
fits here. See p. 451 for summary.

EXPERIMENT 24 CONSTRUCTION OF A LOGICAL MODEL

PURPOSE. To give practice in constructing a model of an unseen object. To emphasize the inferential thinking process involved in the garbage collector analogy.

PRELAB DISCUSSION. Show a model (before you pass any out), and make a few simple observations. Try to get the class involved in the interpretation. Look for descriptions that lead to a definitive experiment, set up the hypothesis, and then test it—all the while explaining what you (and the class) are doing.

Be sure to make the connection to scientific method—observation leads to a model; the model leads to a test; the test leads to an improved model. Finally, ask the students to do the same thing with their models. The student may not think of such tests as:

holding a magnet to the side of his box;
balancing the box across a knife-edge;
building a model to duplicate the behavior of the unknown.

You can suggest such tests judiciously. Small, controlled movements usually give more useful data than wild rattling.

Insist that the student record his observations. After the first half-period of observation, give each student a homework assignment consisting of writing a description of his model and proposing one or more experiments to test his description. In the second half-period, have him make the suggested tests and modify the description if necessary.

TIMING. This experiment should follow the presentation of the introductory material—the garbage collector analogy.

EQUIPMENT NEEDED. One model system per student (see lab hint).

TIME REQUIRED. The experiment requires one period, with the first half-period used to demonstrate what is to be done (see lab hint) and to make observations on the system and the second half-period used to test descriptions.

PRECAUTIONS. Observe the usual lab precautions.

LABORATORY HINT. Shoe boxes or cigar boxes are suitable containers for the unknowns; you may wish to ask your students to bring boxes. For most students, the object in the box should be simple, as in Type I, below. It is interesting if several boxes have objects that seem the same but that are quite different upon direct examination. For example, a solid cylinder, two spheres connected by a rod, and a hollow tube are difficult to differentiate. Several similar objects of different materials are good, e.g., a rubber cube, a styrofoam cube, and a metal cube.

TYPE I (*one object per box*)
cylinders of wood, metal (e.g., from a density set), glass tubing, rubber tubing;
sphere or hemisphere of styrofoam, cork, rubber, metal, glass;
discs of rubber, metal (washers), wood, cork;
cubes or boxes: solid or hollow, open or closed.

TYPE II (*one or two objects per box;* generally smaller objects than Type I objects)

marble
dice
jacks
piece of chain
pencil
beans
nails or screws
washers
nuts
lead shot
stone
marshmallow
modeling clay
test tube
crucible
bell
rubber stopper
funnel

TYPE III (*difficult*)

balloon containing water;
stoppered tube containing water, mercury, liquid with floating object, liquid with a solid, such as a marble;
smaller box or bag containing Type I or Type II object;
tethered object;
baffles plus an object;
styrofoam sphere with off-center weight.

POSTLAB DISCUSSION. After the experiment, students will want to examine the contents of the box used for their models. This is interesting as a class demonstration. You can select several reports to read or summarize, perhaps picking some in which different conclusions have been reached for similar objects and/or similar conclusions have been made for different objects. After the demonstration, have the students open the boxes. Emphasize how much correct information was collected; minimize what could not be known.

EXPERIMENT 25 THE RELATION BETWEEN THE MOLES OF COPPER, MOLES OF SILVER, AND MOLES OF ELECTRONS INVOLVED DURING ELECTROLYSIS

PURPOSE. To demonstrate the quantitative relationships between numbers of electrons and atoms deposited during electrolysis.

PRELAB DISCUSSION. Although the actual relationship of silver to copper has been previously determined (Expt. 7) and the relationship of electrons to silver and copper ions previously studied (Chapter 12), this experiment will remain a challenge to most students because of the precision possible and the complexity of equipment. Point out that the focus of interest in this experiment has to do with the method rather than with the quantitative analysis of the data. Explain that getting a successful plate on a metal surface is dependent upon many factors—the cleanliness of the surface to be plated, the voltage, the current density (ratio of amps to surface area), the source of the ion to be deposited. In this experiment the copper anode supplies the copper ions, which are then plated on the cathode. For review define the cathode as the electrode at which reduction occurs; the anode as the electrode at which oxidation occurs (from Chapter 12).

The $Cu^{+2}(aq)$ is continually replaced, thus the concentration does not change during the process. (See lab hint 1 for your own background.) In contrast to this, the silver that is plated comes from the solution, where it is present as a complex ion. (There is no need to go into details here.)

Remind students to have all connections tight and to check the wiring carefully. Do not rub or twist the cathodes while removing or drying them. Some metal may flake off.

TIMING. Assign this experiment early in Chapter 14. It should precede p. 234.

EQUIPMENT NEEDED (PER GROUP)

200 ml copper sulfate electrolyte solution (lab hint 1)
200 ml silver thiosulfate electrolyte solution (lab hint 2)
D.C. source (lab hint 3)
D.C. ammeter (at least 1 amp; Welch 3031H is excellent)
variable resistor (lab hint 4)
5 lengths (20–30 cm) of copper wire, 4 alligator clips (lab hint 5 and diagram in Laboratory Manual)
2 pieces (6 × 16 cm) copper screen (lab hint 6)
1 strip 2 × 7 cm of sheet lead (about $\frac{1}{16}$ inch thick) with 5 cm wire attached (lab hint 7)
1 piece copper foil about 6 cm square (0.002 inch thick) with 5 cm wire attached, or 80 cm copper wire (B and S gauge #16)
2 holders for electrodes (lab hint 8)
balance (±0.01 gram)
2 250 ml beakers

In laboratory (shared by several groups)

clock (with second hand, if possible)
200 ml acetone

TIME REQUIRED. The student will need one full period (if equipment is prepared and electrodes are weighed on the preceding day).

PRECAUTIONS. The $CuSO_4$ solution contains H_2SO_4. Although it is dilute, take care to avoid dripping when electrodes are withdrawn. The silver electrolyte will cause stains on hands and clothing if not rinsed off immediately after contact.

LABORATORY HINTS

1. Preparation of copper electrolyte solution

   For 1 liter of solution:

   200 g $CuSO_4 \cdot 5H_2O$
   150 ml 6 *M* H_2SO_4 (or 50 ml conc. H_2SO_4)

   To approximately 600 ml water, add the copper sulfate, then the sulfuric acid (take care if concentrated H_2SO_4 is used). Add water to make 1 liter. (If 1 *M* copper sulfate is available, to one liter add 200 ml 6 *M* sulfuric acid.)

   If the electrolyte is to be used next year, add 15 ml 6 *M* H_2SO_4 to each liter to replace the $H^+(aq)$ discharged. If $CuSO_4 \cdot 5H_2O$ precipitates, add water to dissolve.

2. Preparation of silver electrolyte solution

   For 1 liter of solution:

   170 g $Na_2S_2O_3 \cdot 5H_2O$ or 108 g $Na_2S_2O_3$ (anhydrous)
   22 g $Na_2S_2O_5$ (sodium metabisulfite)
   50 g $Na_2SO_4 \cdot 10H_2O$ or 22 g Na_2SO_4 (anhydrous)
   25 g $NaCH_3COO$ (anhydrous) or 41 g $NaCH_3COO \cdot 3H_2O$
   40 g AgCl

   Dissolve the thiosulfate, bisulfite, sulfate, and acetate in 1 liter of water. Dissolve the AgCl in this solution. Be sure to pulverize the AgCl and warm the solution slightly (not above 35°C) to aid in dissolving. The AgCl from Expt. 7 may be used after thorough washing. Additional AgCl may be freshly precipitated as needed, using $AgNO_3$ solution and NaCl solution. The AgCl must be washed before dissolving it in the hypo solution. Try to eliminate all the NO_3^-, since these ions interfere with the firm attachment of Ag plate.

   To prepare 40 grams of AgCl:

   Dissolve 50 g $AgNO_3$ in 100 ml H_2O;
   Dissolve 30 g NaCl in 100 ml H_2O;
   Mix the two solutions, heat to boiling, decant and wash the precipitate.

   The electrolyte may be replenished after each 30 minute run by adding about 12 grams of AgCl/liter. It is wise to check the *p*H. The sodium acetate will probably keep the *p*H near 5 for four runs (with Ag^+ replenished after each use), but if the solution becomes yellow and the *p*H drops to 3, add more sodium acetate and a little hypo as well as AgCl. Sometimes a small amount of milky white precipitate forms, but the cell seems to work satisfactorily.

   At the lead electrode, O_2 is produced, and the lead itself is very little changed. The solution does become acid, however, and unless a buffer is used, the thiosulfate is reduced to sulfide, which precipitates black Ag_2S.

   The silver electrolyte solution contains the following ions in equilibrium:

$$Ag(S_2O_3)_2^{-3} \rightleftharpoons Ag^+ + 2S_2O_3^{-2}$$

   The equilibrium constant is 3.5×10^{-14}. Note the similarity between the way this electrolyte is made and the way the hypo solution was used in dissolving the unexposed AgCl from the emulsion in photographic film.

3. D.C. Source

   For use as a D.C. source, Heathkit "battery eliminators" are fine. Selenium rectifiers are often available at "surplus" stores. A combination of one of these with a Variac or Powerstat is good. Storage batteries, such as 12 volt automobile batteries, can also be used.

   Since current sources are not consistent, and since ammeters vary greatly, do not attempt

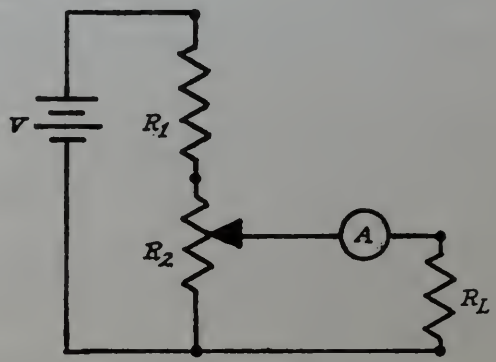

Fig. 14-1

Electrolysis circuit *for Expt. 25.*

to predict the uncertainty of measurement in this experiment, but instead collect data from as many runs as possible, and then discuss the variables.

4. Variable resistor

   The size of the variable resistor used depends upon the voltage of the battery used and upon the number of electrolytic cells placed in the circuit. If a battery is available for each experimental group, the load resistance will be two or three ohms. A suitable circuit is shown in Figure 14-1. If the sum of the resistances for the two cells in series (R_L) is 2 or 3 ohms, the variable resistance, R_2, should be 18–25 ohms. The size of the auxiliary resistance, R_1, depends upon the voltage. Table 14-I shows how large R_1 should be in order to pass 1.0 amp through the cell and draw 1.2 amps from the battery. Notice that R_1 and R_2 must be able to carry a current of 1.2 amps continuously.

Caution: If your only source of D.C. voltage is 100 or 120 volts, fuse the circuit for 2 amps, and take suitable precautions to avoid electrical shorts and shocks.

5. Copper Wire

   Copper bell wire is suitable (preferably insulated). Alligator clips should be provided for connections.

6. Cathodes

   A good grade copper window screen is satisfactory, but a finer mesh is better. Most scientific supply companies carry 20 mesh wire gauze, which has eight copper wires per centimeter. A piece 6 × 16 cm has about 185 cm² surface, which, with a current of 1 amp, gives an adequate current density for Cu, and has been found to be satisfactory for the Ag plating in this experiment.

   Prepare the cathodes beforehand. They may be used several times. Loose pieces should be removed after cutting so that they will not fall off between weighings. Make a cylinder of the screen by weaving copper wire through about 1 cm of overlap. The screens may be cut and

Table 14-I. **Values for R_1 for Various Experimental Conditions**

Battery Voltage (volts)	R_1 (ohms) Needed if R_2 = 18 ohms	R_1 (ohms) Needed if R_2 = 23 ohms
6	0	—
12	5	0
24	15	10
100	80	75
120	95	90

fashioned into cylinders at any time, but the following cleaning process should be performed just before the experiment (the day before, but not much sooner). The first time the screen is used, clean it by using "bright dip" cleaning solution made as follows:

Add slowly to 490 ml of water
435 ml conc. (18 *M*) H_2SO_4
Then add: 72 ml conc. (16 *M*) HNO_3
3 ml conc. (12 *M*) HCl

This must be used in a hood. Dip the screen briefly (up to 5 seconds), and quickly rinse with water. If the surface is not bright copper, dip again. As soon as washed, dip in acetone, and allow to dry.

The screen that is to be used for the silver plating electrode should then be placed in the silver electrolyte for about 10 minutes. Wash the silver-covered copper electrode with water, dip in acetone, and dry. Do not try to obtain a shiny surface. This electrode may be used repeatedly, but after three or four plating periods the silver tends to flake off, especially when the wire is bent.

7. Anodes
Copper sheet is available 0.008 inch thick. Cut it in 2 × $7\frac{1}{2}$ cm strips, and pinch a corner over a copper wire, or solder it to the wire. Foil or wire may be also used. The copper foil can be rolled around a pencil and a 5 cm wire attached either by soldering it or by folding it within an edge of the foil and crimping the fold. Alternately, an 80 cm piece of 16 gauge copper wire can be coiled around a pencil to make an almost solid tube, leaving 5 cm free for attachment.

   A strip of sheet lead 2 × 7 cm is suitable. This may be $\frac{1}{16}$ inch sheet or several thicknesses of lead foil, which is commonly 0.006 inch thick. Attach the 5 cm Cu wire as described for the copper electrode.
8. Holders for the electrodes
Wooden holders for the top of the beaker are easily made from thin strips of wood. To make these, glue a piece 6.4 × 2.5 cm, with rounded corners to fit inside the beaker, at right angles to a somewhat longer (about 8 cm) and narrower (1 cm) piece. Bore a hole in the center for the anode wire, or wires, and bring them up to a connecting post or hold them in place with a small peg. Bore two holes at the sides for the cathode wires, then connect the wires.
9. After several platings the silver can be reclaimed if you desire. Some silver will flake off if the screen is twisted back and forth and/or brushed with a stiff brush. Dissolve the silver flakes in nitric acid. Nitric acid may also be used directly on the screen, but considerable copper will also dissolve. Since it is difficult to preserve the screen during such treatment, we suggest you use new ones for the next year. The silver nitrate produced in this manner may be used to precipitate AgCl for next year's experiment. The $AgNO_3$ will probably contain too much copper to be suitable for Expt. 7. See lab hint 5 of Expt. 8, p. 102. Refer to *J. Chem. Education*, 36, 286–287 (1959) for additional details on separating Ag from Cu.

DISCUSSION OF OPERATION. There may be a drop in current after a few minutes, probably due to polarization. Stirring or placing the beakers on hot plates helps prevent this drop. However, the current usually becomes quite steady as the reaction proceeds and frequently needs little adjusting after the first few minutes.

The deposition of about 0.6 gram of copper and 2.0 grams of silver requires 1.0 amp for a 30 minute period. The electrodes may be weighed the day before. (Their weight will not change overnight even as much as 0.01 gram.) They may also be left overnight after the electroplating if they are washed and thoroughly dried.

An alternate procedure consists in connecting the cells for the entire class in series and running them overnight at a much lower current. The current must be stabilized with an automatic current control. Good plating is obtained because of the low current density, hence the results tend to be more consistent, but student interest is, understandably, lessened.

POSTLAB DISCUSSION. Focus the discussion of the circuit on the fact that the current is the same in all parts of the circuit. The metallic copper and silver are plated by the same current.

The ratio of Cu/Ag plated will be more reliable than the ratio of either to electrons. Collect class data, and discuss the possible errors and the uncertainty in the measurements. Be sure that your students realize the significance this experiment holds with regard to our knowledge of the composition of matter.

CALCULATIONS AND QUESTIONS

A Sample Set of Measurements

Copper Cathode in Copper Sulfate Electrolyte		*Copper Cathode in Silver-hypo Electrolyte*	
Original weight	8.26 ± 0.01 g	Original weight	8.41 ± 0.01 g
Final weight	8.86 ± 0.01 g	Final weight	10.44 ± 0.01 g
Cu deposited	0.60 ± 0.02 g	Ag deposited	2.03 ± 0.02 g
Anode (optional)			
Original weight	6.26 ± 0.01 g	Current	1.0 ± 0.05 amp (5%)
Final weight	5.63 ± 0.01 g	Time	30 ± 0.17 min (0.3%)
Cu removed	0.63 ± 0.02 g		(±10 sec)

1. Calculate the number of moles of electrons which were used. Recall that 1.04×10^{-5} mole of electrons is involved when a current of one ampere flows for one second.

Answer

$$(1.0 \text{ amp})(30 \text{ min})(60 \text{ sec/min})(1.04 \times 10^{-5} \text{ mole of electrons/amp-sec}) = 1.9 \times 10^{-2} \text{ mole of electrons}$$

(The 1.04×10^{-5} mole/amp-sec is calculated from the value of the coulomb, which has an uncertainty of about ±0.001%—so small that it can be ignored in this calculation. A coulomb is the amount of electricity needed to deposit 1.04×10^{-5} mole of silver.)

2. Calculate the number of moles of copper deposited on the cathode from the electrolyte containing copper ions.

Answer: $$\frac{(0.60 \text{ g}) \text{ Cu deposited}}{63.5 \text{ g/mole}} = 0.94 \times 10^{-2} \text{ mole Cu}$$

3. Calculate the number of moles of silver deposited on the cathode from the electrolyte containing silver ions.

Answer: $$\frac{(2.03 \text{ g}) \text{ Ag deposited}}{108 \text{ g/mole}} = 1.88 \times 10^{-2} \text{ mole Ag}$$

4. Calculate the relationship between moles of electrons and moles of copper reduced.

Answer: $\dfrac{\text{moles electrons}}{\text{moles Cu reduced}} = \dfrac{(1.9 \times 10^{-2}) \text{ mole of electrons}}{(0.94 \times 10^{-2}) \text{ mole Cu}} = 2.0 \dfrac{\text{moles } e^-}{\text{mole Cu}}$

5. Calculate the relationship between moles of electrons and moles of silver reduced.

Answer: $\dfrac{\text{moles electrons}}{\text{moles Ag reduced}} = \dfrac{(1.9 \times 10^{-2}) \text{ mole of electrons}}{(1.98 \times 10^{-2}) \text{ mole of silver}} = 1.0 \dfrac{\text{mole } e^-}{\text{mole Ag}}$

6. Write equations for the cathode reactions. Assume that the reacting species are simple copper ions or silver ions.

Answer: $Cu^{+2}(aq) + 2e^- \longrightarrow Cu(s)$
$Ag^+(aq) + 1e^- \longrightarrow Ag(s)$

7. Calculate the relationship between moles of silver reduced and moles of copper reduced.

Answer: $\dfrac{\text{moles of Ag reduced}}{\text{moles of Cu reduced}} = \dfrac{(1.88 \times 10^{-2}) \text{ mole Ag}}{(0.94 \times 10^{-2}) \text{ mole Cu}} = 2.0 \dfrac{\text{moles Ag}}{\text{mole Cu}}$

8. How does this relationship compare to the relationship you obtained in Expt. 7?

Answer: It is the same.

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{+2}(aq) + 2Ag(s)$$

9. Write the balanced equation for the oxidation reaction which occurs at the copper anode. How would you expect the loss of weight at the copper anode to compare with the gain of weight at the cathode?

Answer

$$Cu(s) \rightleftharpoons Cu^{+2}(aq) + 2e^-$$

One would expect that the two would be equal. This is the appropriate student answer. In the sample data, more weight was lost at the anode than was gained at the cathode. Such a difference, which is just barely significant, is likely to be found. It may occur because the high current density at the small-area anode causes uneven removal of the metal. Flecks of copper are often visible in the acetone when this electrode is rinsed prior to weighing. Moreover, the concentration of $CuSO_4$ tends to increase, and that of H_2SO_4 to decrease. Copper may exist as both $CuSO_4$ and Cu_2SO_4 in the sulfate solution. Copper is oxidized either to Cu^+ or Cu^{+2} at the anode. The Cu^+ is then oxidized to Cu^{+2} in solution. In addition, some Cu dissolves according to the reactions

$$Cu + CuSO_4 \longrightarrow Cu_2SO_4$$
$$Cu_2SO_4 + O_2 + 2H_2SO_4 \longrightarrow 4CuSO_4 + 2H_2O$$

These reactions account for the observed difference in weight lost at the Cu anode compared to the weight gained at the cathode.

10. What are some sources of error in your measurements and procedures? How many significant figures in the mole relationship can be justified by your data?

Answer: The largest error is in the measurement of the current. Not only is it difficult to hold constant, but it is uncertain to at least ±5%. The weight of copper, about 0.60 gram, is uncertain by about ±0.02 gram, hence introduces an uncertainty of about 3%. The uncertainty of the time measurement is negligible if measured to the nearest second. Thus the total uncertainty is between 5% and 10%, justifying two significant figures.

11. How many moles of electrons would be required to plate 52.0 grams of chromium on a cathode from a suitable cell containing an electrolyte solution in which the chromium is in oxidation state (VI)?

Answer: Chromium(VI) plus 6 electrons gives chromium metal.

$$\frac{52.0\text{ g Cr}}{52.0\text{ g/mole}} = 1.00\text{ mole Cr}$$

Since each atom of chromium deposited requires six electrons, 1.00 mole of chromium plated requires 6.00 moles of electrons. Chromium is usually plated from an acid solution of dichromate ion.

$$Cr_2O_7^{-2}(aq) + 14H^+(aq) + 12e^- \longrightarrow 2Cr(s) + 7H_2O$$

Supplementary Material

Articles

1. A. O. C. Nier, "The mass spectrometer," *Scientific American*, March 1953* (Offprint No. 256).† Suitable for the advanced student.
2. B. Crawford, Jr., "Chemical analysis by infrared," *Scientific American*, October 1953.* Useful for the teacher; suitable for the advanced student.
3. G. C. Pimentel, "Infrared spectroscopy, a chemist's tool," *J. Chem. Education*, 37, 651–657 (1960). Useful for teacher; suitable for advanced student.

Books

1. M. J. Sienko and R. A. Plane, *Chemistry*, McGraw-Hill, New York (1961). Chapter 3, pp. 33–45, is suitable for the above-average student. It covers Faraday's Laws, discharge-tube experiments, determination of e/m, nuclear atom.
2. W. J. Moore, *Physical Chemistry*, Prentice-Hall, Englewood Cliffs (1955). Chapter 8 is suitable for the advanced student and is useful for the teacher. It covers the same topics as Chapter 3 of reference 1, but in quantitative form, and adds some new topics.
3. G. M. Barrow, *Physical Chemistry*, McGraw-Hill, New York (1961). Chapter 10 provides an *excellent background in depth for the teacher*, but is too advanced for the high school student. The chapter covers rotational, vibrational, and electronic spectroscopy in quantitative detail.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

MOLECULAR SPECTROSCOPY

A CHEM Study film
Running Time: 23 minutes

This film was produced with the collaboration of Professor Bryce Crawford, Jr., of the University of Minnesota. Professor Crawford, who appears in the film, is one of the foremost molecular spectroscopists in the world. The film correlates well with the textbook discussion of the properties of light and of infrared spectroscopy. It adds more depth in microwave spectroscopy. Topics taken up include:

1. The dispersion of white light into a spectrum: color and frequency.
2. The existence of energy in wave form beyond both ends of the visible spectrum.
3. The details of constructing and operating a spectrometer.
4. Resonant vibration frequencies demonstrated with a ball-and-spring molecular model of CO_2.
5. The isotope effect observed for HCl and DCl.
6. The difference between the infrared spectra of $CHCl_3$ and CCl_4 and its use in quantitative analysis of mixtures.
7. The quantization of rotational energy levels.

This film will be a valuable aid in the difficult task of introducing spectroscopy without the background of a prior physics course.

CRYSTALS AND THEIR STRUCTURES

A CHEM Study film
Running Time: 22 minutes

Professor J. Arthur Campbell, of Harvey Mudd College, collaborated in producing this film and appears in it. He demonstrates some common crystalline properties (plane faces, sharp melting points, cleavage) and introduces diffraction of X-rays. Such properties lead to the belief that crystals are composed of regular repeating arrangements of atoms. How we discover these arrangements is illustrated by experiments done in a ripple tank, giving direct observation of the type of measurement by which actual structures are determined.

This film may be shown with Chapter 14 or Chapter 17. Note that since Bragg's law is used in the calculations, questions may be raised about the sine of an angle θ. Answer this simply, by explaining that, in a right triangle, it is the ratio of the side opposite the angle θ over the hypotenuse.

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* Included in "Supplementary Readings for Chemical Bond Approach"; reprints from *Scientific American*.

† Available from W. H. Freeman and Co., San Francisco Order by number.

Background Discussion

In Chapter 2 we presented an authoritarian view of atomic theory. This theory leads naturally to the balancing of chemical equations and the implied weight relations. After the student has gained confidence in the use of the theory, through its application to his own experimental data, we return to a survey of some of the bases for belief in the atomic theory.

This presentation was chosen after prolonged deliberation by an assemblage including most of the coauthors listed on the title page and most of the CHEM Study Steering Committee. Among these thirty-five scientists and educators there were seven or eight individuals with international recognition in chemical research. The consensus of this group was that a mature scientist believes in the usefulness of the atomic hypothesis because he himself has felt innumerable successes in a wide variety of applications using this hypothesis. They agreed that the experimental theme of this course would not be well served by enumerating these at the beginning of the course, when the student has no corroborating experience.

It is possible to develop the atomic hypothesis from the laws of chemical composition. This can best be done only after the student has accumulated a substantial knowledge of descriptive chemistry—enough to enable him to clearly understand what is meant by such words as hydrogen, oxygen, hydrogen peroxide, chemical reaction, composition, weight ratios, elements, and compounds. Then the student must be asked to follow (at the age of 16) the inductive reasoning that took the most brilliant scientists in the world over fifty years to agree upon. Quite aside from the likelihood that many of the students will never follow the argument, this delays the initial use of the atomic hypothesis many weeks. Further, it neglects completely the advantage we enjoy in that most of the students already believe in atoms (without reason) when they enter the course.

An alternative often used in traditional courses is to present the laws of chemical composition during the first two or three weeks upon a foundation of memorized definitions of words like element, compound, physical change, chemical change, mixture, homogeneous, heterogeneous, etc. The handing down of definitions labels this alternative as a frankly authoritarian treatment.

Some attempts to circumvent the historical introduction and present an experimental basis for the atomic theory are based upon the "modern" methods of demonstrating the particulate nature of matter. To be sure, the student receives an experimental basis for the atomic theory provided he will accept, on faith, the explanation that there are invisible things called electrons that boil out of a hot filament; that are accelerated by an electrical voltage; that, when they impinge upon a gas, produce electrically charged particles (is the argument now circular?) that can, in turn, be accelerated by another voltage. Then he must accept the statement that such a moving charged particle (if it exists) would follow a known curved path in a magnetic field. Hence lines on a photographic plate (how are the lines produced?) show the existence of atoms. What an illusion it is, however, to pretend the experimental approach on the basis of such an experiment!

With these considerations in mind, we have concluded that, in order to achieve the optimum results, one should propose the atomic theory tentatively—as a working hypothesis to be tested and judged by its success. This is a legitimate scientific approach, and it permits an intuitively simple introduction to the ideas of balancing chemical equations, the existence of definite weight relations, the differentiation between elements and compounds, etc. Then here in Chapter 14, after the student has accumulated a significant background of experience, we review the evidence for the atomic theory, beginning with already familiar chemical evidence. Even now, when the student is halfway through the course, the operation of a mass spectrograph will be somewhat mysterious, but at least this complicated machine is mentioned only after an entire semester of laboratory work. Furthermore, this timely review of evidence for atoms can be presented in a useful and sophisticated manner that will show the student how a scientific theory gains general acceptance. Consistency among many kinds of data establishes confidence in a theory. Any single behavior must be interpreted within a web of premises. The credibility of the interpretation is attested by its reasonableness when viewed in the pattern of agreement with the other types of evidence.

THE NATURE OF PROOF

Scientists are aware of all of the evidence for atoms discussed in this chapter and of other evidence as well. Yet they do not claim to have *proved* the existence of atoms. The explanation of their attitude lies in the nature of proof. Proof of a proposal requires more than consistency with all the known evidence; it requires also that the proposal is and will remain the only one that can explain the facts. This guarantee cannot be given. There always remains the possibility that new experiments will produce evidence that will force us to modify or abandon current theories. Since this possibility can never be ruled out completely, scientists are unwilling to make dogmatic assertions claiming final proof. When a scientist says he believes in atoms, he means it is *useful* to believe in atoms. There is a tentativity in his attitude, however; he stands ready to stop believing in atoms if new evidence were to appear that would make it no longer useful to do so.

THE ORIGIN OF THE ATOMIC HYPOTHESIS

There are two possible motivations underlying a discussion of the origin of the atomic hypothesis: to relate the chronology of the process and to convey the logic by which chemical evidence supports the atomic theory. To a certain extent, a simple chronological discussion must reveal the logic, therefore the first motivation can be said to include the second. The reverse is not true. If one intends only to clarify the logic by which chemical evidence supports the atomic theory, there is no obligation to display the tortuous process by which this logic was recognized. There is no need to lead the student up Dalton's wrong path of incorrect atomic weights. There is no need to drag the student through the half-century of confusion that beclouded the acceptance and effective use of this theory. Indeed, if one's intent is to ensure that the student *understands* the logic, it is *undesirable* to frame the logic in the chronology, because it accents difficulty. The argument by which one proceeds from combining weights to a hypothesis of atoms is straightforward, but it is not simple. It is not made simple by telling the student that it took the world's best scientists fifty years to follow this logic and that he has three periods in which to do the same.

Why, then, do so many educators (e.g., Conant) argue for the "case history," or historical presentation? The answer is: because there is a deeper motivation in relating chronology than the mere "setting the record straight" on who discovered what and when. The chronological development reveals that the path to understanding our environment is fraught with wrong turns. It shows that views acceptable in the light of today's knowledge are likely to need modification tomorrow. It proves by example the remark made on p. 3: "It is inherent in the exploration of the unknown that not every step is an advance. Yet there is no other way to advance than by taking steps." The historically accurate account inevitably reveals the aptness of the fable of the lost child given in Chapter 1. These are useful gains, and there is no doubt that they need to be made in this course if it is to be a satisfactory introductory science course. In fact the importance we place upon conveying these aspects of scientific progress is shown by their prominence in Chapter 1 (via the lost child fable) and throughout the book (via emphasis on uncertainty and tentativity). A historical approach is deliberately used in Sec. 15-1.4 in showing the development of our understanding of the energy states of atoms. This example serves admirably the purposes mentioned above. This example was conscientiously selected in preference to a historical development of the origin of the atomic hypothesis. Freeing the development of the atomic hypothesis from chronology makes it possible to use the simplest and most easily grasped presentation of the logic by which chemical evidence supports the atomic theory.

CHEMICAL EVIDENCE FOR THE EXISTENCE OF ATOMS

The logic by which chemical evidence leads to the atomic hypothesis is direct.

1. *There are compounds and elements.* Operationally, an element is a substance that *cannot* be decomposed into two or more distinct substances, and a compound is a substance that *can* be decomposed into two or more distinct substances.
2. Compounds are found to have definite composition (in terms of the relative weights of the elements contained). That there are some exceptions to this statement (for example, $Cu_{1.8-2.0}S$) does not deny its general validity. Definite composition does not of itself prove the existence of atoms—it is consistent with their existence. Lack of definite composition does not disprove the existence of atoms—the lack is explained by assuming that some of the positions in the crystal lattice are vacant.
3. When two elements are combined in two different compounds, their relative weights are related by ratios of simple whole numbers (the law of *simple multiple proportions*).
4. Gases react in simple proportions by volume, and the volume of any gaseous product bears a whole number ratio to that of any gaseous reactant (*the law of combining volumes*).

The first evidence for the existence of elements and compounds is consistent with, but does not imply, the atomic hypothesis. This is shown by the differentiation between elements and compounds that had been made centuries before Dalton proposed the atomic hypothesis.

The second evidence raises real questions about the structure of matter. Why do elements react only in certain ratios? This fact causes one to consider models of the structure of matter—models that would "explain" the definite composition of compounds. Once again, however, the evidence is consistent with (in an intuitively satisfying way) the atomic theory, but does not suggest it by itself.

The third evidence *does* suggest the atomic hypothesis. Simple integer relationships suggest "units" or "portions." A given amount of oxygen can react with one "portion" of hydrogen, or two "portions," but not 1.8732 "portions." These simple integer relationships interweave all of chemistry, relating the compositions of compounds. Thus the composition of NH_3 is simply related to the compositions of NO and H_2O_2.

0.0625 g hydrogen reacts with 1.000 g oxygen (in H_2O_2)
0.8750 g nitrogen reacts with 1.000 g oxygen (in NO)
3(0.0625) g hydrogen reacts with 0.8750 g nitrogen (in NH_3)

Such evidence naturally leads to a model involving "portions," "particles," or, finally, atoms.

The fourth evidence again involves simple integer relationships, but in quite another way—the volumes are related simply. Two volumes of hydrogen react with one volume of oxygen and produce two volumes of water vapor (all at the same temperature and pressure). Once again these integer relationships lead to models made up, somehow, of "units" or "portions," and point the way to the atomic hypothesis.

Once the atomic model is proposed, we need only verify that it is consistent with the known facts. The student himself knows that such a theory is consistent with many experiments he has done and is, no doubt, ready to believe that the theory does pass this test.

This is the substance of the logic by which chemical evidence supports the atomic theory. Most students who take high school chemistry will understand this reasoning. The atomic theory occupies such a central position in chemistry that this logic should be presented in the sharpest possible focus.

EVIDENCE FOR THE EXISTENCE OF ATOMS FROM MOTIONS OF ATOMS AND MOLECULES

Other evidence for the existence of atoms and molecules is contained in a number of observations best explained in terms of motion. According to Newton's laws of motion, applicable to all visible bodies, momentum (mass × velocity) is conserved.

$$\Delta(mv) = 0 \qquad (1)$$

The force, f, required to accelerate bodies is equal to the product of the mass, m, and the acceleration, a;

$$f = ma \qquad (2)$$

The kinetic energy of a moving body is

$$\text{K.E.} = \tfrac{1}{2}mv^2 \qquad (3)$$

If quantitative explanations are made possible by assuming that these same relations apply to the postulated invisible particles, atoms and molecules, we can be more certain of their existence. This is true with regard to a variety of phenomena.

Gas Behavior

The kinetic theory of gases,* devised for "ideal" gases (consisting of particles with mass but negligible volume and negligible attraction for one another) predicts remarkably well the behavior of real gases. It is in accord with *PVT* behavior, Avogadro's Hypothesis, effusion rates, diffusion phenomena, and viscosities. Furthermore, the rates of effusion and diffusion of different gases are those predicted by the kinetic theory for particles with masses equal to the chemist's molecular masses.

Diffusion in Condensed Phases

The diffusion of substances in liquids, and its dependence on temperature, lends further support to the idea that particles (atoms, molecules, and ions) in liquids are in motion and that their motion increases with increasing temperature. Kinetic effects in solids are harder to observe, but it is necessary to postulate the motion of particles in solids to explain their melting, evaporation, and solution to form liquids and gases, in which kinetic effects are visible.

Gases at Low Pressures

Many of the experiments described in the chapter take place in vacuum tubes in which some new effects appear. The particle theory of gases helps us to interpret them.

A 245 ml flask holds 0.01 mole (25°C, 1 atmosphere) and about 6×10^{21} molecules of gas. If a good vacuum pump is used to lower the pressure to 10^{-8} atmosphere, 10^{-10} moles, or 6×10^{13} molecules, will remain. Although this is a large number of molecules, collisions between them will almost disappear. That is, the average distance traveled by a particle between collisions, called the *mean free path*, will be very large. If there are n particles of diameter d in each milliliter, their mean free path in centimeters will be

$$\text{mean free path} = \frac{1}{\sqrt{2}\pi n d^2} \qquad (4)$$

In a gas at atmospheric pressure and 25°C the number of molecules per milliliter is approximately 2.5×10^{19}. If the molecular diameter is 3×10^{-8} cm the mean free path is 1×10^{-5} cm. The mean free path under these conditions is 330 times the molecular diameter and approximately thirty times the average distance between molecules. If the pressure and number of molecules are reduced to one-millionth (10^{-6}) of the initial values, the mean free path increases to 10 cm. At 10^{-8} atmosphere the mean free path becomes 1000 cm. In an ordinary-sized vessel, collisions between molecules become rare at this pressure—most collisions are with the walls of the vessel.

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* In 1738, Daniel Bernoulli, a Swiss mathematical physicist, explained gas pressure in terms of the rapid motion of small particles of gas. In 1748, M. Lomonosov, a Russian scientist, suggested a kinetic theory to explain both pressure and temperature effects in gases. These brilliant, early proposals of the atomic hypothesis seem to have had slight impact in promoting the atomic view of the structure of matter. The detailed kinetic theory of gases was not developed until about one hundred years later (1860–1890), after the atomic theory had been deduced from chemical evidence.

In a gas-filled tube like that in Figure 14-4 (Textbook p. 239), any electrons sent into the gas phase will collide with gas molecules and be scattered. When the amount of gas is reduced, the mean free path of the electrons increases, with the result that, between collisions, they can be accelerated to high speeds by the electric field. Then they collide with more energy and produce gaseous ions from the gas molecules. The color comes from the excited ions. At low enough pressures most of the electrons can travel to the end of the tube without collisions. As a result few ions are produced, and the glow is lost again.

Beams of Matter

Much of the evidence for atoms and molecules comes from the behavior of beams of matter. These behave as if they are made up of individual particles having definite masses and individual speeds, and independently obeying the laws of motion [equations (*1*), (*2*) and (*3*)].

As is true of light beams, beams of matter travel in straight lines until deflected. Neither beams of light nor beams of neutral matter change speed or direction when subjected to electric or magnetic fields, but beams of charged matter are affected. Charged beams act as if they consist of charged particles, each responding to electric and magnetic fields in the same way that visible charged bodies are known to respond. The mass of the particles is found to be that of the chemist's atoms and molecules.

Charged beams, both positive and negative, can be produced in evacuated tubes. The negative beams, regardless of the nature of the electrodes, all show highly curved paths corresponding to a single value of e/m.

$$e/m = 1.77 \times 10^8 \text{ coulomb/g}$$

These particles are called electrons. Their charge (the electron charge) has been evaluated independently as 1.60×10^{-19} coulombs. Thus the electron mass (at nonrelativistic speeds) is 9×10^{-28} gram.

All positively charged beams show much smaller deflections. The most easily deflected beams (of charged hydrogen atoms) have an e/m ratio which is $\frac{1}{1840}$ that of the electron. If the particles in the hydrogen beam carry a charge equal in magnitude (but opposite in sign) to the electron charge, their masses are 1840 times the electron mass. Beams of H^+ ions are proton beams. All other positive beams show even less deflection; their masses must be correspondingly greater than the proton mass, since no charge smaller than the proton charge or the electron charge has been found.

The positive beams obtained from different gases were studied by J. J. Thomson, who found that *the masses are those predicted by the atomic theory for the atoms and molecules* and that *the masses are approximately whole numbers on the atomic mass scale, based on 16 for the oxygen atom.* Later experiments showed that substances whose atomic weights differ substantially from whole numbers give two or more e/m values in which each mass has approximately an integral value. Such substances are mixtures of isotopes. The atoms of each isotope have the same mass number.

The mass spectrograph is an instrument designed especially to give very precise values for e/m, and hence for atomic masses. It can separate atoms of two elements having the same mass number but slightly different exact masses. The hydrogen isotope ^3H has the mass 3.017029, whereas the helium isotope ^3He has the mass 3.017016.

All negative beams other than electron beams undergo small deflections similar to those of positive beams. These beams may be explained in terms of negatively charged atoms and molecules, just as positive beams are explained by positively charged atoms and molecules.

SIZES OF ATOMS: THE DIMENSIONS AND SHAPES OF MOLECULES

The size of an object means the dimensions of the boundary surfaces that define the object. Quantum mechanics tells us that the probability of finding an electron approaches zero as the distance from the nucleus becomes infinitely large; the atom has no boundary surfaces. Nevertheless chemists are very concerned about what is called the "size" of an atom. They have an operational meaning in mind. Despite the fact that atoms have infinite volume, they pack close together at definite distances in solids, liquids, and molecules. These packing and bonding distances constitute a basis for defining "effective sizes." Because atomic packing is important in explaining chemistry, these "effective sizes" are important to chemists.

Collision experiments, in a certain sense, are quite ambiguous as a means of defining atomic size. The scattering caused by collision depends upon the energy of the colliding particles. Nevertheless, the scattering of neutral atoms by other neutral, gaseous atoms has given valuable information about effective atomic size. The velocities are in the range for which the electrons exert significant forces. Thus the scattering pattern is interpreted in terms of a simplified model; all collisions are assumed to be of the billiard ball type. The effective sizes obtained are in reasonable accord with internuclear distances found in solids and liquids by other techniques. Nevertheless careful analyses of such scattering patterns show small discrepancies between the expected scattering (based upon the hard-sphere atomic model) and the experimental pattern. These discrepancies can be considered to be direct experimental evidence that the atom does not have a boundary surface.

All the other methods we shall consider are "spectroscopic" methods—methods involving the interaction of matter with light.*

X-Ray Diffraction

X-Ray diffraction methods for determining the spacing of atoms in crystals arose from Max von Laue's prediction, made in 1912, that crystals would give a diffraction pattern if the wave length of the light used was as small as the distance between the atoms in the crystal. Two English scientists, W. H. Bragg and his son W. L. Bragg, found that the scattering of X-rays can be explained as a reflection of the rays by successive layers of atoms in the crystal. At a definite angle θ, between the beam of wave length λ and the atomic layers in the crystal, the reflections of the different layers reinforce one another. The equation is

$$n\lambda = 2d \sin \theta$$

where n is an integer and d is the distance between the reflecting layers.

The experimental data are compared with calculated diffraction patterns based upon reasonable models. Different packing arrangements imply different interlayer spacings (differing values of d), and hence different diffraction patterns. The packing arrangement and the assumed atomic radius are varied until a model is found that reproduces the observed pattern. For simple packing arrangements (as in metals and simple ionic solids), it is not too difficult to find the appropriate parameters. For molecular crystals, however, analysis is much more difficult.

X-Ray methods are applicable to solids over a wide temperature range. The methods are not applicable to the gas phase, and in X-ray studies of liquids the scattering patterns are difficult to interpret because of the disordered packing of the molecules. In none of the phases are hydrogen atoms located precisely.

Microwave Spectroscopy

A method for deriving the distances between atoms in a molecule in the gas phase is based on the rotation of molecules. The rotational frequencies are determined by the molecular moment of inertia. Since the atomic masses are known, the data lead to a measure of the equilibrium internuclear distances. The microwave spectrum consists of a series of lines, each line representing a frequency absorbed by the molecule. For a diatomic molecule, the lines are equally spaced at frequencies ν given by (5):

$$\nu \text{ (cycles/sec)} = J(J+1)\left(\frac{h}{8\pi^2 I}\right) \qquad J = 0, 1, 2, 3, \cdots \quad (5)$$

where h = Planck's constant = 6.624×10^{-27}

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* The term "light" means the entire spectral range. This term should not be identified with "visible light," the spectral range detected by the human eye.

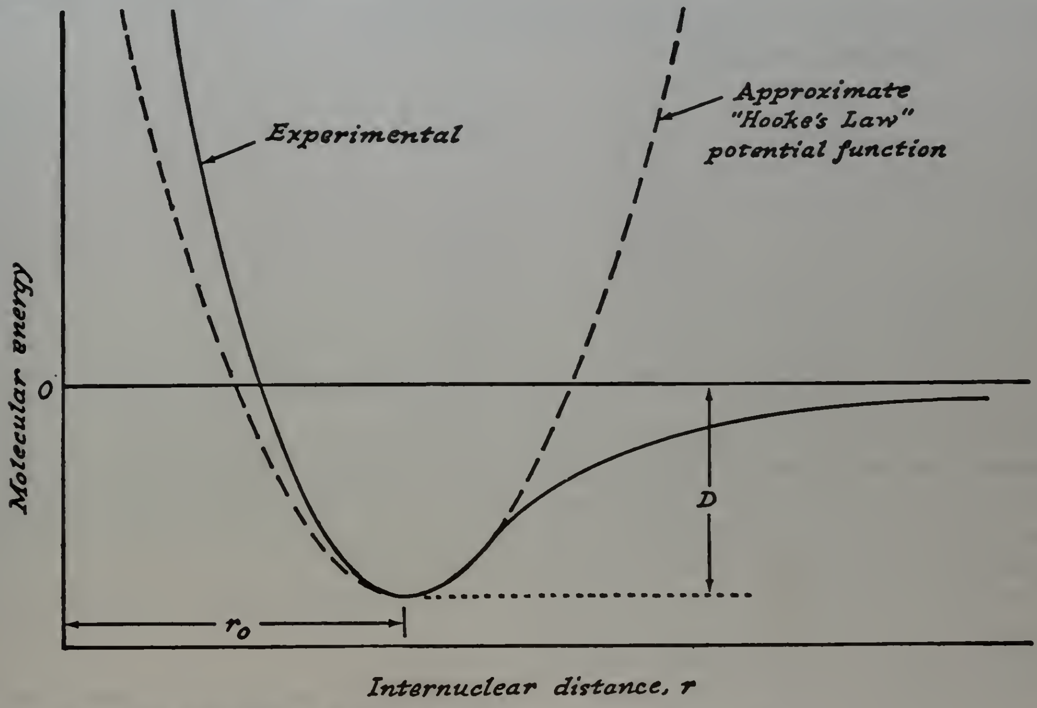

Fig. 14-2. **Molecular energy versus internuclear distance** *for a diatomic molecule.*

erg-sec, I = moment of inertia in gram-cm^2, and J = an integer.

Microwave spectroscopy has great accuracy but limited applicability. It can be carried out only with gaseous samples of substances having a nonzero dipole moment. Except for the most symmetrical molecules, it is difficult to analyze rotational spectra. Yet, when the spectra can be interpreted, internuclear distances can be measured to about ±0.001 Å.

Infrared Spectroscopy

The absorption of energy in the infrared spectral region is connected with vibrational motions within the molecule. The frequencies are fixed by the molecular geometry and by the strengths of the chemical bonds. Since the spectra are readily obtained for the solid, liquid, and gas phases, the infrared technique is probably the most important and most used by the chemist. Infrared spectra are recorded as a routine part of the laboratory work in undergraduate chemistry courses at the university level. In organic chemistry, the infrared spectrum has assumed as important a role as the melting point.

Interpretations of infrared spectra are based upon an analysis of how the molecular energy depends upon the internuclear distance.* Since a plot of molecular energy as a function of internuclear distance relates energy to position, it is appropriate to call this a potential energy plot, or in common usage, a "potential function." The solid line in Figure 14-2 shows a typical plot of molecular energy versus internuclear distance for a diatomic molecule.

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* Such a potential energy function can be used because the motions of the nuclei are so slow compared to the motions of the electrons. As the nuclei vibrate about their equilibrium positions, the electron distribution readjusts continuously. Thus the molecular energy changes to the new energy required by the less-than-optimum internuclear distance. This separation of electron motion and nuclear motion is called the Born-Oppenheimer approximation.

Table 14-II. **Correlations Among Bond Order, Bond Length, and Force Constant**

Bond Between	As in	Bond Multiplicity	Bond Length (A)	Force Constant dynes/cm)
C—C	ethane	single	1.54	5×10^5
C=C	ethylene	double	1.34	10×10^5
C≡C	acetylene	triple	1.21	16×10^5
N—N	hydrazine	single	1.47	4.5×10^5
N=N	N_2F_2	double	1.25	13×10^5
N≡N	nitrogen	triple	1.10	23×10^5

Figure 14-2 shows that the molecular energy is lowest when the internuclear distance is r_0. This fixes the equilibrium bond length. If there is any change of bond length, the energy rises, establishing a restoring force. Thus the molecular energy acts like a spring insofar as the slow movements of the nuclei are concerned. The molecular energy fixes the potential function for the vibrational movement of the atoms.

To treat the problem quantitatively, the potential function is approximated by the parabola of closest fit, as shown by the broken line in Figure 14-2. This curve has the simple mathematical form

$$V(r) = \tfrac{1}{2}k(r - r_0)^2 = \tfrac{1}{2}kx^2 \qquad (6)$$

where $x = r - r_0$ = displacement from equilibrium distance. The restoring force implied by (6) is

$$F = kx \qquad (7)$$

which is just Hooke's Law of force, commonly applied in the vibrations of objects connected by springs. Equation (7) is called the "harmonic approximation." The restoring-force constant, k, is determined mathematically by the curvature of the potential function, $V(r)$, at the equilibrium distance. In practice k comes from the frequency of absorption and the masses of the vibrating atoms.

The value of learning k is that it is a measure of the strength of the chemical bond. In fact there are generally linear relationships for a given pair of atoms among the following: the energy needed to break a bond (D in Figure 14-2), the length of bond (r_0), the force constant (k), and the bond multiplicity. Table 14-II shows some data applicable to carbon–carbon bonds and to nitrogen–nitrogen bonds. The stronger bonds (higher bond multiplicity) clearly have shorter bond lengths and higher force constants.

The vibrational spectra of polyatomic mole-

Table 14-III

Characteristic Absorption Frequencies for Stretching Some Common Chemical Bonds

Functional Group	Frequency Range in Which Absorption Occurs (cycles/sec)
O—H	11.0 to 10.8×10^{13}
>N—H	10.5 to 9.9×10^{13}
—C—H (paraffins)	8.9 to 8.5×10^{13}
—C≡C—	6.8 to 6.3×10^{13}
>C=O	5.5 to 5.0×10^{13}
>C=C<	5.0 to 4.9×10^{13}
—C—F	4.2 to 3.0×10^{13}
—C—Cl	2.4 to 1.8×10^{13}
—C—Br	1.8 to 1.5×10^{13}

cules are more complicated, of course, than those of diatomic molecules. Fortunately, certain functional groups have characteristic vibrational frequencies. Hence the infrared spectrum provides a valuable diagnostic tool for various bond arrangements. Table 14-III shows some characteristic absorption frequencies for various groupings. It is evident that the vibration frequency is indicative of the chemical bonding. By recording an infrared spectrum and making a careful analysis of the spectrum, a chemist can learn much about the molecular structure of an unknown compound.

Other Spectroscopic Methods

Chemists also use other methods to learn molecular structures.

1. Electron diffraction is applicable only to gases because the degree of scattering from condensed phases is too large.
2. Neutron diffraction has come into use since the advent of high flux neutron beams from nuclear piles. This technique is important because it locates hydrogen atoms quite precisely.
3. Nuclear magnetic resonance has the same potentialities discussed for infrared spectroscopy. The method depends upon nuclear magnetic properties that cause some nuclei to absorb microwave frequencies when they are subjected to a high magnetic field. The actual frequencies absorbed reveal the type of nucleus and its chemical environment.

Answers to Exercises and Problems

Ex. 14-1. Two compounds are known that contain only nitrogen and fluorine. Careful analysis shows that 23.67 grams of compound I contain 19.00 grams of fluorine, and that 26.00 grams of compound II contain 19.00 grams of fluorine.

(a) For each compound, calculate the weight of nitrogen combined with 19.00 grams of fluorine.
(b) What is the ratio of the calculated weight of nitrogen in compound II to that in I?
(c) Compound I is NF_3. This compound has one atom of nitrogen per three atoms of fluorine. How many atoms of nitrogen are there per three atoms of fluorine for each of the molecular formulas, N_2F_2 and N_2F_4? Compare these atom ratios to the weight ratio obtained in Part (b), and convince yourself that compound II could have the formula N_2F_4 but not N_2F_2.

Answer

(a) Compound I contains $23.67 - 19.00 = 4.67$ g N/19.00 g F.
Compound II contains $26.00 - 19.00 = 7.00$ g N/19.00 g F.

(b) $$\frac{\text{g N in II}}{\text{g N in I}} = \frac{7.00}{4.67} = 1.50$$

(c)

(atoms N)/(3 atoms F)	Compound
1	NF_3
3	N_2F_2
1.5	N_2F_4

Compound II has 1.5 times as much N per fixed amount of F, as does compound I. Such is also the case for N_2F_4, but not for N_2F_2.

Ex. 14-2. As current is passed through the cells shown in Figure 14-2, the oxygen produced in the first cell is collected, and its volume is compared with the volume of chlorine produced in the center cell (the volumes being compared at identical temperatures and pressures). The volume of chlorine is found to be exactly double that of oxygen. Applying Avogadro's Hypothesis, explain how this result shows that electricity can "count" atoms.

Answer

Avogadro's Hypothesis states that "Equal volumes of gas (identical temperature and pressure) contain equal numbers of molecules."

The volume of chlorine is double the volume of oxygen, hence it follows that twice as many molecules of chlorine as of oxygen were produced. Since the cells are in series, the same current passed through the two cells. This current "counted" two molecules of chlorine for every molecule of oxygen produced.

Ex. 14-3. Suppose five measurements of oil-drop charges give the values listed below.

4.83×10^{-19} coulomb
3.24×10^{-19}
9.62×10^{-19}
6.44×10^{-19}
4.80×10^{-19}

(a) Divide each charge by the smallest value to investigate the relative magnitudes of these charges.
(b) Assuming each measurement has an uncertainty of $\pm .04 \times 10^{-19}$, decide what electron charge is indicated by these experiments alone.

Answer

(a) $$\frac{4.83 \times 10^{-19}}{3.24 \times 10^{-19}} = 1.49$$
$$\frac{3.24 \times 10^{-19}}{3.24 \times 10^{-19}} = 1.00$$
$$\frac{9.62 \times 10^{-19}}{3.24 \times 10^{-19}} = 2.97$$
$$\frac{6.44 \times 10^{-19}}{3.24 \times 10^{-19}} = 1.99$$
$$\frac{4.80 \times 10^{-19}}{3.24 \times 10^{-19}} = 1.48$$

(b) We assume each measured charge is an integral number of electron charges. Hence the lowest charge, 3.24×10^{-19}, cannot be one electron charge, because the first and last measurements are not integral multiples of it. If the lowest charge, 3.24×10^{-19} coulomb, is *two* electron charges, then the electron charge is $\frac{1}{2}(3.24 \times 10^{-19}) = 1.62 \times 10^{-19}$ coulomb. With this electron charge, all of the measurements are, within experimental uncertainty, integral multiples of 1.62×10^{-19}.

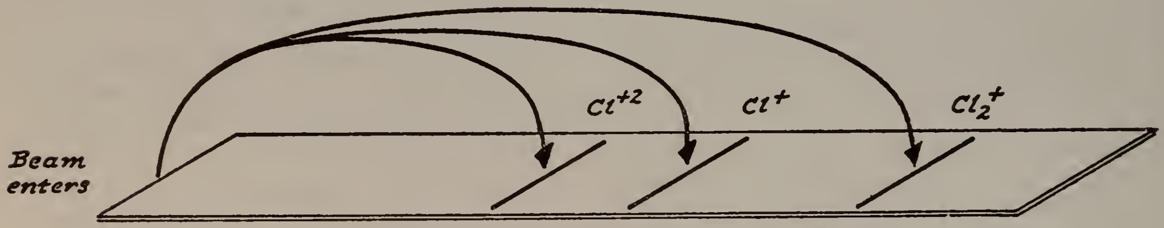
It is useful to ask the students whether the five measurements are consistent with an electron charge of $\frac{1}{3} \times 3.24 \times 10^{-19}$

(they are not) with an electron charge of $\frac{1}{4} \times 3.24 \times 10^{-19}$ (they are). Then ask how we could decide whether the electron charge is 1.62×10^{-19} or 0.81×10^{-19} coulomb. If no one thinks of the answer, perhaps it would be worthwhile letting the students think about this problem overnight. The answer is, of course, to make more measurements. If enough measurements are made, sooner or later a charge would be observed that would be compatible with 0.81×10^{-19}, and not 1.62×10^{-19}, if 0.81×10^{-19} were the correct value. If 1.62×10^{-19} is the correct value, there would *never* be a measurement that would be inconsistent with *either* value.

Ex. 14-4. When chlorine, Cl_2, is examined in a mass spectrograph, Cl_2^+, Cl^+, and Cl^{+2} ions are formed. Remembering that there are two isotopes in chlorine, 35 (75%) and 37 (25%), describe qualitatively the appearance of the mass spectrum. Which ion will produce lines at the largest radius? Which at the smallest radius? How many lines will each ion produce?

Answer

Qualitatively, the heaviest mass and lowest charge will be found at the largest radius (Cl_2^+), and the lowest mass and highest charge will be found at the smallest radius (Cl^{+2}). Hence, if there were but one isotope, there would be three lines, as follows.



Spectrum for isotopically pure chlorine, e.g., $^{35}Cl_2$

Each of these lines, however, will be influenced by the presence of two isotopes. Thus there will be a line due to $(^{35}Cl)^{+2}$ and $(^{37}Cl)^{+2}$. The heavier isotope, ^{37}Cl, will show the higher radius. Since there is three times as much ^{35}Cl as there is ^{37}Cl, the inner line will be three times as intense as the other. A similar pair will be obtained for Cl^+. The species Cl_2^+ will consist of three lines, due to $(^{37}Cl - {}^{37}Cl)^+$, $(^{37}Cl - {}^{35}Cl)^+$, and $(^{35}Cl - {}^{35}Cl)^+$. Thus the spectrum will be as shown on p. 465.

The better students may care to attempt to calculate the relative intensities of the triplet caused by Cl_2^+. The probability of both atoms being ^{37}Cl is $\frac{1}{4} \times \frac{1}{4} = \frac{1}{16}$. The probability of both atoms being ^{35}Cl is $\frac{3}{4} \times \frac{3}{4} = \frac{9}{16}$. The rest of the molecules, the fraction $\frac{16}{16} - \frac{10}{16} = \frac{6}{16}$, will contain one atom of ^{35}Cl and one atom of ^{37}Cl. Thus the intensities will be in the ratio 1:6:9.

Quantitatively, the radius depends upon charge and mass, as follows

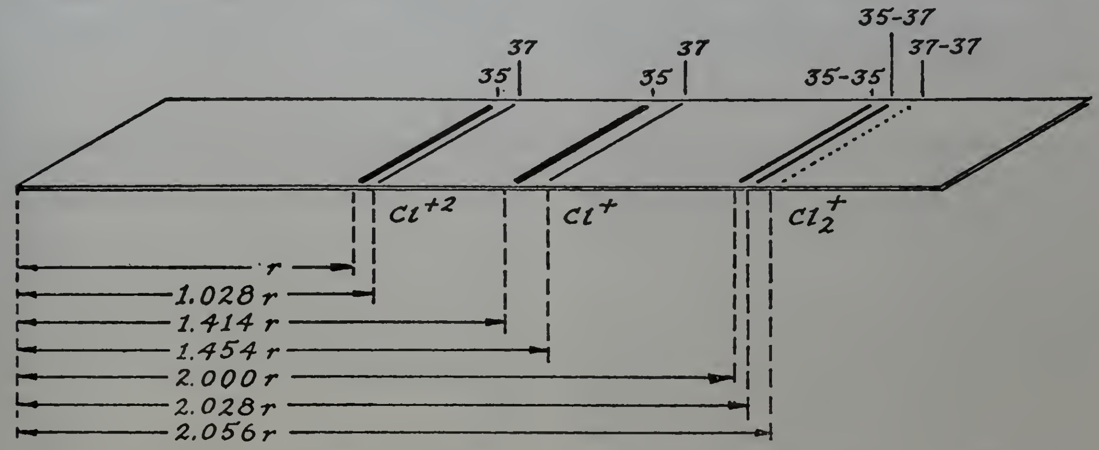
$$r = \frac{1}{B}\sqrt{\frac{2Vm}{e}}$$

With this expression, the relative radii can be calculated quantitatively. The lower figure shows these radii expressed in terms of the smallest observed radius, that of $(^{35}Cl)^{+2}$.

Ex. 14-5. Suppose a mass spectrograph is used to measure the charge/mass ratio for fluorine ions. Fluorine has only one stable isotope, and its atomic weight is 19.0 grams/mole. From the measured charge/mass ratio, 5.08×10^3 coulombs per gram, and the assumption that the ion has one electron charge, calculate the mass of one ion. Repeat the calculation assuming the ion has two electron charges. Now calculate Avogadro's number from the weight of a mole of fluorine ions, using each of your two calculations. Which assumption about ion charge do you prefer? Could the other be correct as well?

Answer

Since e/m is given as 5.08×10^3 coulombs/gram, and since $e = 1.60 \times 10^{-19}$, then $m = 1.60 \times 10^{-19}/5.08 \times 10^3 = 3.16 \times 10^{-23}$ g.



Spectrum for natural chlorine, 25% ^{37}Cl, 75% ^{35}Cl

If the measured charge/mass ratio is $2e/m$, then

$$m = \frac{2(1.60 \times 10^{-19})}{5.08 \times 10^3} = 2(3.16 \times 10^{-23})$$

$$= 6.32 \times 10^{-23} \text{ g.}$$

Using e, we find that Avogadro's number is

$$\frac{19.0 \text{ g/mole of atom}}{3.16 \times 10^{-23} \text{ g/atom}} = 6.02 \times 10^{23} \frac{\text{atoms}}{\text{mole of atoms}}$$

Using $2e$, we find Avogadro's number to be

$$\frac{19.0}{6.32 \times 10^{-23}} = 3.01 \times 10^{23} \frac{\text{atoms}}{\text{mole of atoms}}$$

The single electron charge results in a value of Avogadro's number that is consistent with a multitude of other data, thus it is an acceptable result. It is based upon the assumption that the species detected is F^+.

Yet the assumption of a double electron charge would be consistent with the accepted value of Avogadro's number, if the mass of the particle were also doubled. This means the species detected might be F_2^{+2} rather than F^+, which is not unreasonable.

Pr. 1. A compound of carbon and hydrogen is known that contains 1.0 gram of hydrogen for every 3.0 grams of carbon. What is the atomic ratio of hydrogen to carbon in this substance?

Answer

$$\frac{1.0 \text{ g H}}{1.0 \text{ g/mole}} = 1.0 \text{ mole H}$$

$$\frac{3.0 \text{ g C}}{12 \text{ g/mole}} = 0.25 \text{ mole C}$$

There are 1.0/0.25 = 4.0 hydrogen atoms for each carbon atom. The formula is CH_4.

Pr. 2. There are two known compounds containing only tungsten and carbon. One is the very hard alloy, tungsten carbide, used for the edges of cutting tools. Analysis of the two compounds gives, for one, 1.82 grams and, for the other, 3.70 grams of tungsten per 0.12 gram of carbon. Determine the empirical formula of each.

Answer

To determine the formulas, the number of each kind of atom present must be known.

For one compound:

$$\text{moles W} = \text{g W/mol wt W}$$

$$\frac{1.82 \text{ g}}{184 \text{ g/mole}} = 0.0099 \text{ mole W}$$

$$\frac{0.12 \text{ g}}{12 \text{ g/mole}} = 0.010 \text{ mole C}$$

Since 0.0099 mole of W combines with 0.010 mole C, the empirical formula for this compound is, within experimental uncertainty, WC.

For the other compound, 3.70 g/184 g/mole = 0.0205 mole W combines with 0.010 mole C. Therefore the empirical formula of this compound is W_2C.

Pr. 3. John Dalton thought the formula for water was HO (half a century passed before the present formula for water was generally accepted). What relative weights did he then obtain for the weight of oxygen and hydrogen atoms?

Answer

Experimentally it was known that 8 grams of oxygen combine with 1 gram of hydrogen to form water. If the formula is HO, then the oxygen atom must be 8 times as heavy as the hydrogen atom.

Pr. 4. Nitrogen forms five compounds with oxygen in which 1.00 gram of nitrogen is combined with 0.572, 1.14, 1.73, 2.28, 2.85 grams of oxygen, respectively. Show that the relative weights of the elements in these compounds are in the ratio of small whole numbers. Explain these data using the atomic theory.

Answer

The five weights of oxygen combined per gram of nitrogen are 0.572, 1.14, 1.73, 2.28, and 2.85. Dividing each by 0.572 gives 1, 1.99, 3.02, 3.98, and 4.98, or within experimental uncertainty, the weights of oxygen per gram of nitrogen are in the ratios 1:2:3:4:5.

Such data arise because each of the atoms in one gram of nitrogen can combine with fixed numbers of oxygen atoms. Without knowing the atomic weights, we can conclude that the formulas are N_xO_y, N_xO_{2y}, N_xO_{3y}, N_xO_{4y}, N_xO_{5y}. Given the atomic weights, the ratio of atoms can be calculated for each formula:

$N_{0.0715}$	$O_{0.0358}$	N_2O
$N_{0.0715}$	$O_{0.0714}$	N_2O_2 or NO
$N_{0.0715}$	$O_{0.1070}$	N_2O_3
$N_{0.0715}$	$O_{0.1425}$	N_2O_4 or NO_2
$N_{0.0715}$	$O_{0.1781}$	N_2O_5

Pr. 5. Using Appendix 3 list two metals that could have given the same number of moles as aluminum did in the experiment shown in Figure 14-2.

Answer

Any metal showing a three-electron change is a possible answer. The student should search for half-reactions of the form

$$M = M^{+3} + 3e^-$$

In Appendix 3, the student will find Cr^{+3}, Fe^{+3}, and Au^{+3}. Some others not included in Appendix 3 are Sc, Y, the rare earths, Ga, and In. Discussion might bring some of these out with the aid of a more extended list of $E°$ values. If so, observe the placement of these in the periodic table.

Pr. 6. If *n* coulombs will deposit 0.119 gram of tin from a solution of $SnSO_4$, how many coulombs are needed to deposit 0.119 gram of tin from a solution of $Sn(SO_4)_2$?

Answer

$2n$. Since sulfate ion has a double negative charge, SO_4^{-2}, the oxidation numbers of Sn in the two compounds are +2 in $SnSO_4$ and +4 in $Sn(SO_4)_2$. Hence the electrode reactions are

from $SnSO_4$ solution	$Sn^{+2} + 2e^- = Sn(s)$
from $Sn(SO_4)_2$ solution	$Sn^{+4} + 4e^- = Sn(s)$

Pr. 7. Suppose two more cells were attached to the three in Figure 14-2. In one cell, at one of the electrodes copper is being plated from $CuSO_4$ solution, and at one of the electrodes in the other cell bromine, $Br_2(g)$, is being converted to bromide ion, Br^-. How many grams of Cu and Br^- would be formed during the same operation discussed in the figure?

Answer

The plating reaction, $Cu^{+2} + 2e^- = Cu$, requires the same number of electrons per mole as the reaction $Hg^{+2} + 2e^- = Hg$, hence there would be 0.0300 mole Cu. The reaction $Br_2 + 2e^- = 2Br^-$ requires one electron per mole of Br^- produced, as does the reaction $Na^+ + e^- = Na$, therefore 0.0600 mole Br^- will be formed.

$$(0.0300\text{ mole Cu})\left(\frac{63.5\text{ g}}{\text{mole}}\right) = 1.91\text{ g Cu}$$

$$(0.0600\text{ mole Br}^-)\left(\frac{79.9\text{ g}}{\text{mole}}\right) = 4.79\text{ g Br}^-$$

Pr. 8. Carbon monoxide absorbs light at frequencies near 1.2×10^{11}, near 6.4×10^{13}, and near 1.5×10^{15} cycles per second. It does not absorb at intermediate frequencies.

(a) Name the spectral regions in which it absorbs (see Figure 14-14).
(b) Explain why carbon monoxide is colorless.

Answer

(a) 1.2×10^{11} is in the microwave region.
6.4×10^{13} is in the infrared region.
1.5×10^{15} is in the ultraviolet region.
(b) Since no light is absorbed in the visible

spectral region, carbon monoxide is colorless.

Pr. 9. The wavelength and frequency of light are related by the expression $\lambda = c/\nu$, where λ = wavelength in centimeters, ν = frequency in cycles per second, and c = velocity of light = 3.0×10^{10} cm/sec. Calculate the wavelength corresponding to each of the three frequencies absorbed by CO (see Problem 8). Express each answer first in centimeters and then in Ångstroms (1 A = 10^{-8} cm).

Answer: 1.5×10^{15} cycles/sec:

$$2.0 \times 10^{-5} \frac{\text{cm}}{\text{cycle}} = 2.0 \times 10^{3} \frac{\text{Å}}{\text{cycle}}$$

Answer

1.2×10^{11} cycles/sec:

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{10}\ \text{cm/sec}}{1.2 \times 10^{11}\ \text{cycles/sec}} = 0.25\ \text{cm/cycle}$$
$$= 2.5 \times 10^{7}\ \text{Å/cycle}$$

6.4×10^{13} cycles/sec:
$$\lambda = \frac{3.0 \times 10^{10}\ \text{cm/sec}}{6.4 \times 10^{13}\ \text{cycles/sec}}$$
$$= 4.7 \times 10^{-4}\ \text{cm/cycle}$$
$$= 4.7 \times 10^{4}\ \text{Å/cycle}$$

1.5×10^{15} cycles/sec:
$$\lambda = \frac{3.0 \times 10^{10}\ \text{cm/sec}}{1.5 \times 10^{15}\ \text{cycles/sec}}$$
$$= 2.0 \times 10^{-5}\ \text{cm/cycle}$$
$$= 2.0 \times 10^{3}\ \text{Å/cycle}$$

Pr. 10. The oxygen molecule carries out molecular vibration at a frequency of 2.4×10^{13} cycles/second. If the pressure is such that an oxygen molecule has about 10^{9} collisions per second, how many times does the molecule vibrate between collisions?

Answer

The number of vibrations per collision is

$$\frac{2.4 \times 10^{13}\ \text{cycles/sec}}{10^{9}\ \text{collisions/sec}} = 2.4 \times 10^{4} \frac{\text{cycles}}{\text{collision}}$$

Pr. 11. When several oil drops enter the observation chamber of the Millikan apparatus, the voltage is turned on and adjusted. One drop may be made to remain stationary; but some of the others move up while still others continue to fall. Explain these observations.

Answer

The drops fall because of gravity, and are moved upward by the force between the charged plate and charges on the drop. Since the mass of the drops varies, and since a variable number of charges can be picked up by each drop, the upward force that suspends one charged drop may be greater than or less than the downward force on some other charged drop.

Pr. 12. Dust particles may be removed from air by passing the air through an electrical discharge and then between a pair of oppositely charged metal plates. Explain how this removes the dust.

Answer

The electric discharge produces a charge on the dust particles. It doesn't matter whether positive or negative charges are formed, because one of the metal plates will attract the particles and the other repel them. Both actions cause the particles to move toward a plate, where they lose their charge, and then the dust particles settle to the bottom of the chamber.

Pr. 13. How many electrons would be required to weigh one gram? What would be the weight of a "mole" of electrons?

Answer

$$1\ \text{electron} = 9.11 \times 10^{-28}\ \text{g}$$

$$\frac{1}{9.11 \times 10^{-28}} = 1.10 \times 10^{27}\ \text{electrons/g}$$

One mole of electrons weighs

$$(9.11 \times 10^{-28})(6.02 \times 10^{23}) = 5.48 \times 10^{-4}\ \text{g}$$

Pr. 14. About how many molecules would there be in each cubic centimeter of the tube shown in Figure 14-3 when the glow appears? When the glow disappears again because the pressure is too low?

Answer

At STP,

$$1\ \text{cm}^3 = \frac{1}{22400}\ \text{mole}$$

or

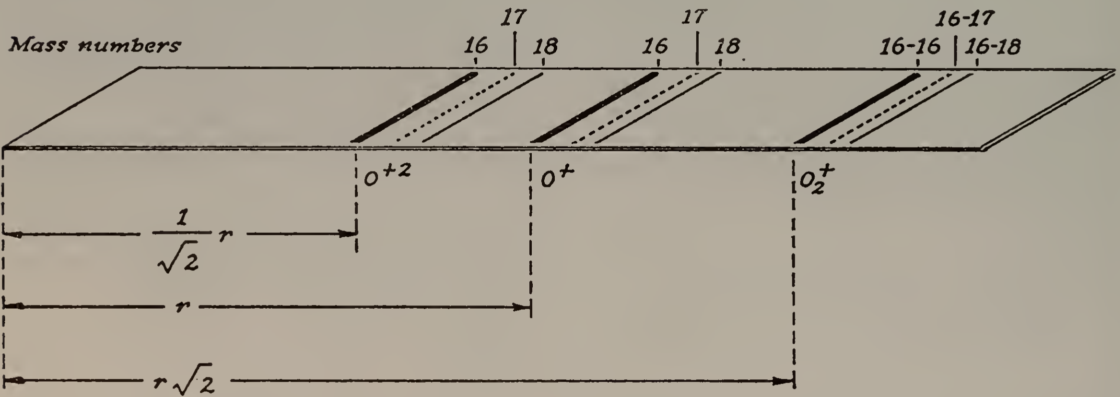
$$4.5 \times 10^{-5}\ \text{mole}$$

This 1 cm³ will contain $(4.5 \times 10^{-5})(6.02 \times 10^{23}) = 2.7 \times 10^{19}$ molecules at STP. When glow starts at 0.01 atmosphere there will be 2.7×10^{17} molecules/cm³. When glow disappears at 10^{-6} atmosphere there will be 2.7×10^{13} molecules/cm³.

Pr. 15. Describe the spectrum produced on a photographic plate in a mass spectrograph if a mixture of the isotopes of oxygen (^{16}O, ^{17}O, and ^{18}O) is analyzed. Consider only the record for +1 and +2 ions.

Answer

The relative abundance of the isotopes can be found in Table 6-II, as ^{16}O, 99.8; ^{17}O, 0.04; and ^{18}O, 0.20. The student should certainly assume a singly and a doubly charged ion for each of the three isotopes. This assumption will lead to two sets of three lines each, as in the figure below (left and center). But if he should follow the example of chlorine given on p. 243 he might also assume the existence of O_2^+ ions, including the various combinations of the isotopes. There are six possible combinations, but since ^{17}O and ^{18}O are so rare, lines formed by combinations containing only these isotopes would be too faint to be detectable. The visible lines due to O_2^+ ions would be due to these isotopic varieties: $(^{16}O^{16}O)^+$, strong; $(^{16}O^{17}O)^+$, extremely faint; and $(^{16}O^{18}O)^+$, faint. The spectrum would resemble this:



Pr. 16. Hydroxylamine, NH_2OH, is subjected to electron bombardment. The products are passed through a mass spectrograph. The two pairs of lines formed indicate charge/mass ratios of 0.0625, 0.0588 and 0.1250, 0.1176. How can this be interpreted?

Answer

It is always assumed that integral numbers of charges are involved. The dimensions used are electron charges/gram (not coulombs/gram), hence we can invert these numbers to find for each particle the number of grams per charge.

$$\frac{1}{0.0625} = 16.0 \frac{\text{grams}}{\text{electron charge}}$$

$$\frac{1}{0.0588} = 17.0 \frac{\text{grams}}{\text{electron charge}}$$

$$\frac{1}{0.1250} = 8.00 \frac{\text{grams}}{\text{electron charge}}$$

$$= 16.0 \frac{\text{grams}}{\text{2 electron charges}}$$

$$\frac{1}{0.1176} = 8.50 \frac{\text{grams}}{\text{electron charge}}$$

$$= 17.0 \frac{\text{grams}}{\text{2 electron charges}}$$

A particle with mass 16 grams per mole is NH_2, and a particle with mass 17 grams per mole is OH. Hence the spectrum can be explained in terms of the species NH_2^+, OH^+, NH_2^{+2}, and OH^{+2}.

Pr. 17. Platinum and zinc have the same number of atoms per cubic centimeter. Would thin sheets of these elements differ in the way they scatter alpha particles? Explain.

Answer

Yes. The scattering of alpha particles of moderate energy is determined by the charge on the nucleus. Platinum has the larger nuclear charge, hence will deflect more α-particles through large scattering angles. In this connection, it can be remarked that the mass of the electron is so low that they offer negligible opposition to an alpha particle, about as much as a one pound brick gives to a four ton truck.

Pr. 18. Assume that the nucleus of the fluorine atom is a sphere with a radius of 5×10^{-13} cm. Calculate the density of matter in the fluorine nucleus.

Answer

$$V = \tfrac{4}{3}\pi r^3 = \tfrac{4}{3}(3.14)(5 \times 10^{-13})^3 = 5.2 \times 10^{-37}\ \text{cm}^3$$

$$\text{weight of one atom} = \frac{19.0\ \text{g/mole}}{6.02 \times 10^{23}\ \text{atoms/mole}}$$

$$= 3.2 \times 10^{-23}\ \text{g/atom}$$

$$\text{density} = \frac{3.2 \times 10^{-23}}{5.2 \times 10^{-37}} = 6.1 \times 10^{13}\ \text{g/cm}^3$$

The weight 6.1×10^{13} grams is about that of 50 million cubic yards of dry sand. Imagine all that compressed into one cubic centimeter!

Pr. 19. An average dimension for the radius of a nucleus is 1×10^{-12} cm, and for the radius of an atom is 1×10^{-8} cm. Determine the ratio of atomic volume to nuclear volume.

Answer

$$\frac{V_{\text{atom}}}{V_{\text{nucleus}}} = \frac{\tfrac{4}{3}\pi r^3{}_{\text{atom}}}{\tfrac{4}{3}\pi r^3{}_{\text{nucleus}}} = \frac{r^3{}_{\text{atom}}}{r^3{}_{\text{nucleus}}}$$

$$= \frac{(10^{-8})^3}{(10^{-12})^3} = \left(\frac{1}{10^{-4}}\right)^3 = 10^{12}$$

The atom has 10^{12} times the volume of the nucleus.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

There are several oxides of nitrogen. Careful analysis of one of these oxides shows that 30.0 grams of the compound contains 14.0 grams of nitrogen.

1. What is the empirical formula for this oxide of nitrogen?

   Answer

   30.0 g − 14.0 g = 16.0 g oxygen

   $$\frac{14.0\text{ g nitrogen}}{14.0\text{ g nitrogen/mole}} = 1.00\text{ mole nitrogen atoms}$$

   $$\frac{16.0\text{ g oxygen}}{16.0\text{ g oxygen/mole}} = 1.00\text{ mole oxygen atoms}$$

   The ratio is 1 atom of nitrogen per 1 atom of oxygen. Therefore the empirical formula is NO.

2. A 92.0 gram sample of another oxide of nitrogen contains 28.0 grams of nitrogen. What is the empirical formula for this oxide of nitrogen?

   Answer

   92.0 g − 28.0 g = 64.0 g oxygen

   $$\frac{28.0\text{ g nitrogen}}{14.0\text{ g nitrogen/mole}} = 2.00\text{ moles nitrogen atoms}$$

   $$\frac{64.0\text{ g oxygen}}{16.0\text{ g oxygen/mole}} = 4.00\text{ moles oxygen atoms}$$

The ratio is 1 atom of nitrogen per 2 atoms of oxygen. Therefore the empirical formula is NO_2.

3. How does the atomic theory account for the oxygen to nitrogen ratios in the two oxides of nitrogen discussed in questions 1 and 2?

   Answer

   When two elements combine to form more than one compound the combining ratios will always be small whole numbers because the atoms combine as units.

4. Two compounds are known that contain only phosphorus and chlorine. Accurate analysis shows that 68.7 grams of compound I contain 15.5 grams of phosphorus, whereas 104.0 grams of compound II contain 15.5 grams of P.
   (a) Find the weight of chlorine combined with 15.5 grams of phosphorus in each compound, and calculate the ratio of chlorine in compound I to that in compound II.
   (b) Compound I is PCl_3. Decide whether compound II is P_2Cl_2, P_2Cl_4, or PCl_5.

   Answer

   (a) Compound I:
   68.7 g − 15.5 g = 53.2 g Cl
   Compound II:
   104.0 g − 15.5 g = 88.5 g Cl

   $$\frac{\text{Cl in I}}{\text{Cl in II}} = \frac{53.2}{88.5} = 0.6$$

   (b) Compound II is PCl_5. Compute the following ratios of chlorine in compound I to chlorine in compound II, and compare to 0.6 in part (a).

   $$\frac{Cl_3}{Cl_2} = \frac{3 \times 35.5}{2 \times 35.5} = \frac{3}{2} = 1.5$$

   $$\frac{Cl_3}{Cl_4} = \frac{3 \times 35.5}{4 \times 35.5} = \frac{3}{4} = 0.75$$

   $$\frac{Cl_3}{Cl_5} = \frac{3 \times 35.5}{5 \times 35.5} = \frac{3}{5} = 0.6$$

Use the following information for questions 5 and 6. During the electrolytic decomposition of acidified water, hydrogen and oxygen gas are produced.

5. How many moles of electrons are required to reduce sufficient hydrogen ions, H^+, to produce 2 moles of hydrogen gas, $H_2(g)$?

Answer

$$2e^- + 2H^+ = H_2(g)$$

Four moles of electrons required to produce 2 moles of $H_2(g)$.

6. How many moles of oxygen gas, $O_2(g)$, would be produced at the same time the 2 moles of hydrogen are produced?

Answer

$$2H_2O = 2H_2(g) + O_2(g)$$

One mole of O_2 is produced while 2 moles of H_2 are produced.

7. How many electrons are needed to reduce 1.08 grams of silver from a suitable electroplating bath containing Ag^+ ions?

Answer

$$\frac{1.08 \text{ g Ag}}{108 \text{ g Ag/mole}} = 1.00 \times 10^{-2} \text{ mole Ag}$$

$$(1.00 \times 10^{-2} \text{ mole Ag})\left(\frac{1 \text{ mole electrons}}{1 \text{ mole Ag}}\right) \times \left(\frac{6.02 \times 10^{23} \text{ electrons}}{1 \text{ mole electrons}}\right) = 6.02 \times 10^{21} \text{ electrons}$$

In an experiment, 1 mole of electrons passing through a series of solutions causes $\frac{1}{2}$ mole of one metal (X) to be deposited from a solution and $\frac{1}{3}$ mole of a different metal (Y) to be deposited from a second solution.

8. Write the formula for each of the metallic ions which were reduced to form the metals X and Y.

Answer: X^{+2} and Y^{+3}.

9. Explain, in terms of basic atomic structure, how it is possible for an electric current to "count" atoms.

Answer

According to the atomic theory, atoms are composed of protons (+), electrons (−), and neutrons. The positive metallic ions are atoms that have lost one or more electrons. If we assume an electric current to be the flow of electrons along a conductor, then the current is able to "count" atoms, since each metallic ion species can only accept an integral number of electrons to form a neutral metallic atom. For +1 ions, only one electron is needed per ion. For +2 ions, two electrons are required per ion, and so forth.

10. Refer to Textbook Figure 12-6. How many moles of electrons have passed through the cells when 2.16 grams of silver have been deposited? How many grams of nickel dissolved in the other cell during the same time?

Answer

2.16 grams of Ag is

$$\frac{2.16 \text{ g}}{108 \text{ g/mole Ag}} = 0.0200 \text{ mole Ag}$$

The silver metal is produced by the reaction $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$. The 0.0200 mole of silver will be deposited by 0.0200 mole of electrons. The nickel dissolves by the reaction

$$Ni(s) \rightleftharpoons Ni^{+2}(aq) + 2e^-$$

The 0.0200 mole of electrons will be supplied by 0.0100 mole of nickel.

$$(0.0100 \text{ mole})\left(\frac{58.7 \text{ g Ni}}{\text{mole}}\right) = 0.600 \text{ g Ni}$$

11. Chlorine monoxide gas, Cl_2O, absorbs light at frequencies near 9.9×10^{12}, 2.0×10^{13}, 2.9×10^{13} and 7×10^{14} cycles per second.
(a) Name the spectral region in which each frequency falls.
(b) Would you expect this compound to be colored? Explain.

Answer

(a) The first three frequencies are in the infrared region, the last in the visible.
(b) Yes, the compound would be colored. The light in the visible region at 7×10^{14} cycles per second would be absorbed. The student is not asked to, but he may supply the information that this light is blue. Since the blue light is absorbed, the gas would appear orange.

12. Prospecting for uranium minerals is aided by the use of "black-light" lamps. These lamps, which emit light of frequencies near 10^{15} cycles/second (to which the human eye is not sensitive), cause the minerals to glow (to become "fluorescent"). In what spectral range is this light?

    Answer

    The frequency 10^{15} cycles/sec is in the ultraviolet region.

13. Commercial heat lamps emit light of frequencies near 3×10^{14} cycles/sec. In what spectral range is this light?

    Answer

    This is the infrared region. It is so near the red end of the visible region that it is called the "near infrared," and heat lamps usually glow with a reddish color. Nevertheless their maximum emission is beyond the red sensitivity of the human eye.

14. Most of the sunlight in the spectral region 2×10^{13} to 12×10^{13} cycles/sec fails to reach the earth's surface because the atmosphere is almost opaque in much of this region. Water vapor and carbon dioxide are the chemical substances that absorb most of this light. Describe the type of excitation accompanying the absorption of this light.

    Answer

    The region described is the infrared spectral region. Water and CO_2 absorb in this region, producing excitation of vibrational motions.

The following questions cover material in reduced type.

15. Describe as briefly as possible how the use of infrared spectroscopy has contributed to our understanding of size and shape of molecules.

    Answer

    Changes in vibrational motions of molecules may be caused by the absorption of infrared frequencies. These to-and-fro motions of the atoms within molecules occur at natural frequencies. These natural frequencies are fixed by the masses of the atoms, the shapes of the molecules, and the strengths of the chemical bonds that link the atoms together. The frequency absorbed can be correlated with bond strengths and angles when one knows the atomic masses.

16. Describe as briefly as possible how the use of microwave spectroscopy has contributed to our knowledge of interatomic distances in certain molecules.

    Answer

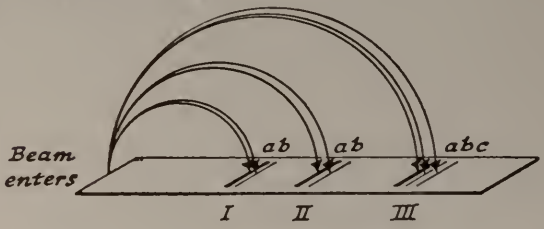
    The microwave frequencies are absorbed by molecules through excitation of the rotational degrees of freedom. The frequencies of these rotational motions depend upon the molecular moments of inertia. The moment of inertia depends upon the distance of the atoms from the molecular center of gravity and the atomic masses.

17. Describe briefly how X-ray diffraction methods help us to understand the crystal structure of sodium chloride.

    Answer

    Light waves in the X-ray frequencies, when reflected from the surface of crystals, give a pattern on a photographic plate. The pattern is fixed by the spacing and nature of the ions. The arrangement of ions in the crystal may be deduced from the pattern produced on the photographic plate.

Questions 18–20 depend upon the following information. The spectrum shown below was obtained from a mass spectrograph experiment using a sample of chlorine gas. Three positively charged gaseous ions were produced: $Cl_2^+(g)$, $Cl^{+2}(g)$, and $Cl^+(g)$.



18. Which of the three sets of spectral lines I, II, and III is most likely to be representative of the singly charged gaseous chlorine atom, $Cl^+(g)$? Why?

Answer

II. The lightest particles (Cl^+ and Cl^{+2}) will travel in a path having the smallest radius, striking the plate closest to the beam source. The particles with greatest charge (Cl^{+2}) are curved more sharply and strike the plate closest to the beam source. Thus particles with a small value of e/m are bent least; those with large e/m are bent most (see p. 243).

19. Which of the two lines, a or b, at either I or II is representative of the heavier isotope of chlorine (^{35}Cl or ^{37}Cl)?

Answer: b.

20. There are three combinations possible in forming a Cl_2 molecule from ^{35}Cl and ^{37}Cl atoms: $^{35}Cl_2$, $^{37}Cl_2$, and $^{35}Cl-^{37}Cl$. Which of the three possible molecules would form a mass spectral line between the other two, providing each of the three has the same net positive charge [$Cl_2^+(g)$]?

Answer: $^{35}Cl-^{37}Cl$.

21. In the Millikan oil drop experiment the tiny charged droplets can be made to rise, fall, or remain stationary between the charged plates. Account for the fact that, with the plate voltage set so that at least one droplet is stationary, others may be rising or falling at different rates. The upper plate is negative. Assume all droplets to be of the same mass.

Answer

Uncharged droplets would be unaffected by the charged plates and therefore would fall. Droplets having less positive charge than the stationary droplet would also fall, while droplets having more positive charge would rise.

CHAPTER

15

ELECTRONS AND THE PERIODIC TABLE

Intent and Approach

The approach in this chapter stems from a reconsideration of some of the fundamental questions raised in Chapter 6. The student is by now aware that chemical behavior is related to electrons—he has seen how both the halogens and the alkali metals contrive to achieve the inert gas configuration. He has seen the regular trend in chemical properties across a row of the periodic table. In this chapter we attempt to "explain" these important relationships.

Our intent in this chapter is three-fold:

1. To provide a basis for explaining the periodic table (in terms of the hydrogen atom spectrum).
2. To provide a valid picture of the electron distribution of an atom, as currently accepted.
3. To provide a basis for explaining the chemical trends found organized in the periodic table (in terms of ionization energy and its periodic variation).

To achieve the first of these aims, we investigate regularities among the frequencies emitted by hydrogen atoms. After introducing light as a form of energy, these regularities lead quite logically to the energy level diagram (with the aid of a "notched-beam," or "stair-step" analogy). Finally, the connection between the energy levels of the hydrogen atom and the electron population of inert gases establishes these energy levels as a basis for understanding the periodic table.

Our second goal is to implant a valid picture of the electron distribution in an atom, displacing, if necessary, any erroneous views concerning the electron distribution that the student may have acquired. First, our space-filling models convey the impression that the atom has boundary surfaces. We are convinced it does not. Second, the student may have the erroneous view that the term "orbital" means that the electron has a planetary trajectory. Experimental evidence shows this is not correct. There is no advantage in fostering an incorrect idea.

Our third aim, the introduction of the ionization energy, provides a substantial experimental basis for understanding the chemical trends across the periodic table—the trends expressed classically in terms of electronegativity and valence.

Outline

THE HYDROGEN ATOM

1. The connection between light and energy is first developed intuitively and then expressed quantitatively, $E = h\nu$ (15-1.1).
2. The spectrum of the hydrogen atom is used to develop the existence of the hydrogen atom energy level diagram (with the aid of

the notched-beam analogy) (15-1.2 and 15-1.3).

3. Bohr is credited with introducing two important concepts, "stationary states" and "quantization" of energy. These concepts are presented *without* introducing his erroneous planetary model of the atom. This procedure leads to a discussion of "quantum numbers" and a valid view of what is meant by the term "orbital" (15-1.4 and 15-1.5).
4. The energy levels of the hydrogen atom provide the explanation for the first two rows of the periodic table (with the aid of the empirical deduction of the Pauli Principle) (15-1.6).

MANY-ELECTRON ATOMS

5. The distortion of the hydrogen atom energy levels in the many-electron-atom energy levels reveals the origin of the entire periodic table (15-2.1 and 15-2.2).

IONIZATION ENERGY AND THE PERIODIC TABLE

6. The meaning of ionization energy and its measurement are introduced (15-3.1).
7. The "saw-tooth" variation of the ionization energy is displayed and related to chemical trends (15-3.2).
8. The successive ionization energies of a particular atom are related to the number of valence electrons (15-3.3).
9. The first long row of the periodic table is explained (15-3.4).

New Concepts

1. Light is a form of energy. The amount of energy is related to the frequency of the light: $E = h\nu$.
2. Atoms can exist only in certain "stationary states"; each state is characterized by a specific energy. Excitation places atoms in higher energy states temporarily; the emission of light (a form of energy) accompanies the return of the atom to a state of lower energy.
3. The motion of the electron in an atom is described by orbitals characterized by quantum numbers. An "orbital" refers to a spatial distribution of the electron.
4. Atoms have no boundary surfaces; the electron distribution extends to infinity.
5. The ionization energy describes the amount of energy required to remove the most loosely bound electron.
6. Ionization energy increases across a row of the periodic table.
7. The successive ionization energies for a single element explain the number of valence electrons.

Development

INTRODUCTION

In Chapter 6 we presented a brief survey of the organization of the periodic table and noted the existence of a set of inert elements. We then related the properties of the halogens and the alkali metals to the tendency of these elements to attain the electron population of one of the inert elements. "Wondering why" this tendency should be exhibited is the fundamental question this chapter attempts to explain. The explanation given is extended to cover the periodicity of properties illustrated in the periodic table.

Schedule and Related Material

Assignment Prior to Period	Period	Class Work	Ex.	Problems			Topic
				EASY	MEDIUM	HARD	
S 15-1.1/15-1.2 (pp. 253–259)	1	S 15-1.1/15-1.2. Demonstration if spectroscope is available	1–3		1		Periodic table, light-energy, hydrogen spectrum, and the notched-beam analogy
S 15-1.3/15-1.4 (pp. 259–260)	2	Finish above and S 15-1.3/15-1.4	4		2, 3	4	Energy levels
S 15-1.5 (pp. 260–263)	3	S 15-1.5 Film: THE HYDROGEN ATOM AS VIEWED BY QUANTUM MECHANICS	5	5, 6	7, 8	9	Quantum numbers and orbitals
S 15-1.6/15-2.2 (pp. 263–267)	4	S 15-1.6/15-2.2		10, 11			Hydrogen atom and the periodic table. Many-electron atoms
S 15-3/15-3.3 (pp. 267–271)	5	S 15-3/15-3.3	6		12–15	16	Ionization energy
	6	Film: IONIZATION ENERGY					
S 15-3.4 (pp. 271–272)	7	S 15-3.4 Review					The fourth row

THE HYDROGEN ATOM (15-1)

Light—A Form of Energy (15-1.1)

We assume here that the student has had no physics. Hence the relation between light and energy is approached intuitively. Familiar situations are called to mind that will aid the student in accepting the fact that light is a form of energy: the focusing of light to set a piece of paper afire, warmth from the sun, sunburn, photosynthesis. With this basis to lend credibility, the Planck relation, $E = h\nu$, is stated authoritatively. The existence of experimental evidence for $E = h\nu$ is alluded to, but the details are reserved for the physics course.

The relation $E = h\nu$ permits us to analyze the energy content of an atom from measurements of the light frequencies emitted.

The Light Emitted by Hydrogen Atoms and The Energy Levels of a Hydrogen Atom (15-1.2 and 15-1.3)

The intent of this section is to deduce the energy levels of the hydrogen atom from its spectrum as emitted from a glow discharge tube. After accepting the relation $E = h\nu$, the student has only one logical hurdle to pass. He must see how fixed increments of energy imply the energy level diagram.*

It is necessary to see how measurements of differences such as $E_2 - E_1$ can give information about E_2 and E_1 individually. Each frequency emitted reveals the difference in energy between two possible energies the atom can possess. The systematic spacings of the lines within a group (as revealed in Exercise 15-2, p. 255) suggest that these energy differences are related. We can assume, as one possible relation, that each line in a group shows an energy difference relative to the *same* state, E_1. This possible interpretation is communicated via the notched-beam analogy—a familiar device that delivers fixed incremental quantities. The assumption leads to the establishment of the series of notches shown in Textbook Figure 15-5.

We need only find some corroborative evidence that will show that our assumption leads to a useful model. This we find by observing that the notched beam deduced implies that other lines should be possible, and the other lines turn out to be precisely those observed in the visible group.

Quantum Mechanics and the Hydrogen Atom (15-1.4)

A chronological development is given to show how new experimental evidence can force scientists to abandon commonly accepted views. Of course, we use only part of the evidence that led to the quantum mechanical revolt against classical physics. It is that part of the evidence relating to the possible energy states of an atom. Bohr is given credit for postulating "stationary states" to explain experimental data, although acceptance of his postulate meant abandoning classical laws of motion which had remained intact for over 200 years. Observe the significance of this time period. In 1900, every scientist alive was several generations removed from the period when doubt remained about these classical laws. These two centuries had seen many successes as dramatic as the predicted return of Halley's comet and witnessed the development of the mathematical elegance that has immortalized names like LaGrange and Hamilton. Newton's laws and, later, Maxwell's equations had deservedly become accepted as scientific dogma. In this setting, Bohr found it necessary to propose that the laws of motion for an electron interacting with a proton differ from the classical laws of motion. His argument was simple and compelling. With the classical laws of motion,

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* It is instructive to realize that the emission of fixed increments of energy does not prove the existence of discrete energy levels. To see this, we need only think of an analogy in which fixed increments are released from a continuum. There is just such a device which can be attached to a beverage bottle so that the bottle, when tipped, delivers a fixed volume of liquid (a dram is a convenient volume) no matter how much the bottle contains.

the stability of the hydrogen atom, and the well-known hydrogen atom spectrum were inexplicable. Hence Bohr accepted the observed stability of the hydrogen atom and looked for a model in accord with the hydrogen atom spectrum. His success founded quantum mechanics.

There are two important lessons here. First, we see that theories are accepted only as long as they are useful in explaining experimental facts. Second, the longer a theory is used with success, the harder it is to recognize its failings and get new theories accepted.

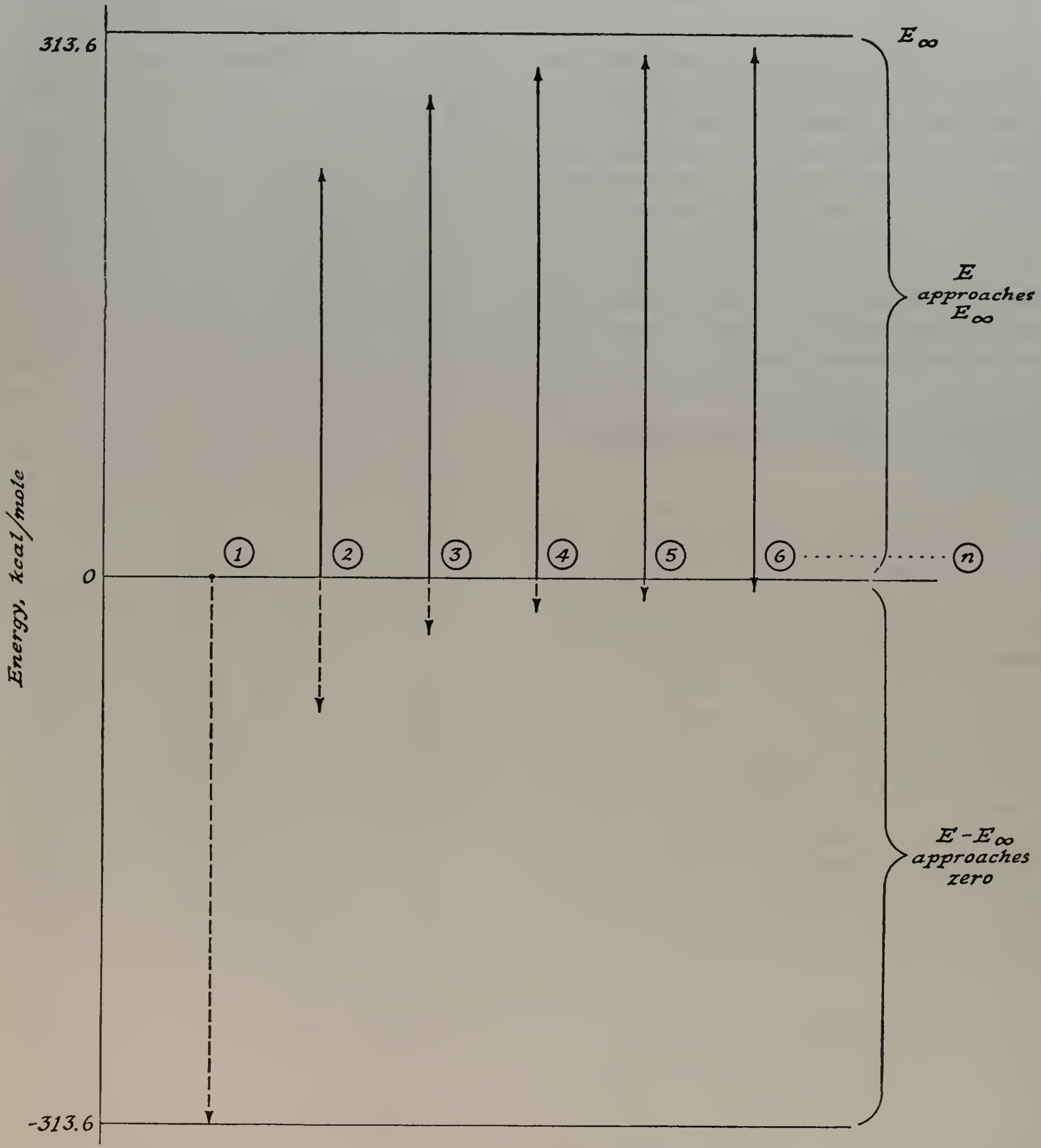
The Hydrogen Atom and Quantum Numbers (15-1.5)

One advantage of the notched-beam analogy is the natural opportunity to name the notches with identifying integers. References to the "first notch," "second notch," etc., lead to the names: notch #1, notch #2, etc. This is intentional, since these numbers are the principal quantum numbers. The principal quantum number fixes the number of nodal surfaces (see *Background Material*) and also the energy of the state it identifies. The simple relationship $-313.6/n^2$ furnishes quite an exciting opportunity for discovery. The students should be encouraged to search for a relation between the energy and the "notch number" prior to assignment of this section. Even if no one finds the correct relation, it is dramatic when the simple relation is revealed. Use a systematic approach to the result in order to convince the student that a logical approach is better than trial and error. Here is a sample line of discussion.

(a) Begin with the plot of Exercise 15-3 (p. 258), showing energy, E, versus notch number. The discussion of the plot should focus on the smooth dependence upon n (which encourages seeking a mathematical formulation) and on the asymptotic behavior as n becomes large (the most important clue to the mathematical relation we seek). Let class discussion lead to an estimate of E_∞, and use the number the class decides upon if it is within three or four kilocalories of the correct value, 313.6 kcal.

(b) On the blackboard, make a table of n versus E and a plot of n versus E. Add the asymptotic value of E for very large n ($n = \infty$). Now observe that it may be more convenient to look for a relation between n and the difference between E and E_∞ instead of between n and E itself. On the plot, this amounts to shifting attention from the solid arrows to the broken arrows. This is simpler because now we are looking for a function that approaches zero as n becomes large. Mathematically, we are changing from E to $E - E_\infty$ as our variable. Now add the third column to the table, calculating $E - E_\infty$.

Column Number	1	2	3	4	5	6
Discussed in paragraph	(a)	(a)	(b)	(c)	(c)	(c)
	n	E	$E - E_\infty$	E_∞/n	E_∞/n^2	E_∞/n^3
	1	(0)	−313.6	−313.6	−313.6	−313.6
	2	235.2	−78.4	−156.8	−78.4	−39.2
	3	278.8	−34.8			
	4	294.0	−19.6	Fill in other entries as discussed in paragraph (d).		
	5	301.1	−12.5			
	6	304.9	−8.7			
	.	.	.			
	.	.	.			
	.	.	.			
	∞	313.6	(0.0)	0	0	0



(c) We now need a function involving E_∞ and n that has the value -313.6 at $n = 1$ and approaches zero as n becomes large. Observe that if we multiply by n or some power of n, the product becomes larger as n becomes larger. On the other hand, if we divide by n or some power of n, the quotient becomes smaller as n becomes larger. Perhaps we are looking for an inverse relation between $E - E_\infty$ and n. Perhaps $E - E_\infty$ is proportional to $1/n^x$.

To see whether this is reasonable, first consider possible values of x, adding columns to the existing table as you proceed, and then demonstrate that every one of these passes through the points E_∞ (when n is taken to be 1) and 0 (when n is taken to be infinity).

(d) Once the reasonableness of an inverse power of n is established we need only fill in enough of the last three columns to see that E_∞/n and E_∞/n^3 do not fit at all but that E_∞/n^2 fits quite closely (even if E_∞ is a few kilocalories in error). Observe that each column is derived from the one to its left simply by dividing by integers. Thus the second entry in column 4 is

$$-\frac{313.6}{2} = -156.8$$

The second entry in column 5 is

$$-\frac{313.6}{2^2} = -\frac{313.6}{2\cdot 2} = -\frac{156.8}{2} = -78.4$$

The second entry in column 6 is

$$-\frac{313.6}{2^3} = -\frac{78.4}{2} = -39.2$$

Thus you can readily complete the table at the blackboard, even with the unfamiliar value for E_∞.

HYDROGEN ATOM ORBITALS

The first point that must be made is to give meaning to the word "orbital." An orbital tells what we know about where the electron "spends its time." The information it contains can be shown by considering the information that would be contained in an instantaneous photograph of three or four bees near a flower. We would see one set of locations of the bees but would receive little information about how the bees move about. If we take a whole succession of photographs, however, we begin to discover where the bees prefer to be in relation to the flower. Many of the photographs would show one or more bees very close to the flower; only a few of the photographs would show a bee a long distance from the center of fragrance. Taking all of the photos together, we have a probability picture of the bees around a flower. If the negatives of the photos are all superimposed, we see a distribution of dots that are quite close together near the flower and far apart away from the flower. The density of dots at any point is proportional to the probability of finding a bee at that point.

This is exactly the meaning of "orbital" in quantum mechanics. Notice that the probability distribution of the bees is continuous and extends to infinity but that this does not mean that the bees have been vaporized into a diffuse bee-cloud. Rather, each bee is at a point at each instant, just as each electron is at a point at each instant. This may be a propitious time to evoke from the class two criticisms of the styrofoam models. The students will probably recognize that the orbitals shown in Figures 15-8 and 15-9 of the Textbook have no boundaries, whereas the models do. In addition, the styrofoam has uniform density and suggests, incorrectly, that the electron is somehow spread out evenly over the volume. (In fact, the term "electron cloud," used by some chemists, is carefully avoided in this text because of the incorrect connotation of the word "cloud.")

Another apt and important property of the analogy is that, although the superimposition of these photographs tells us where the bees are apt to be found, it says nothing about how they get there. We know the bees have energy of motion, but we know nothing of their trajectories. This is exactly the situation we find for an orbital: quantum mechanics tells us where the electrons are (in probability terms); it assures us they have kinetic energy, but it does not reveal their trajectories. (Notice, however, that the distribution clearly rules out a planetary trajectory, since a planetary trajectory never places an electron near the nucleus, whereas this is often a position of high probability for the electron in an atom.)

Having established the meaning of the term "orbital" we must inject the authoritarian statement that, not only does the principal quantum number indicate the energy of an orbital, but it is also related to the number of orbitals with that same energy. Thus the energy of a hydrogen atom orbital with $n = 2$ is $-313.6/2^2$, and there are $n^2 = 2^2 = 4$ different orbitals that have this energy. Paraphrased, this means that there are n^2 *different* spatial distributions of an electron near a proton that all correspond to the same hydrogen atom energy, $-313.6/n^2$. Textbook

Figures 15-8 and 15-9 show the one orbital of principal quantum number $n = 1$ (the 1*s* orbital) and the four orbitals of principal quantum number $n = 2$ (the 2*s* and three 2*p* orbitals).

Emphasize the fact that as *n* becomes larger, the electron spends more and more time far from the nucleus. This is in accord with the fact that the energy of attraction (a negative number) decreases in magnitude as *n* becomes larger. This leads quite naturally to the significance of $n = \infty$. The electron now spends its time at such large distances that it is no longer "attached" to the proton. Exciting the atom to $n = \infty$ corresponds to ionization. Later in the chapter, the energy needed to do this will be called the ionization energy.

Film, THE HYDROGEN ATOM AS VIEWED BY QUANTUM MECHANICS,
fits here. See p. 485 for summary.

The Hydrogen Atom and the Periodic Table (15-1.6)

The crucial aspect of this section is to develop empirically the need for the Pauli Principle. For the purposes of this course, the operative principle is: *one or two electrons, but never more than two, can occupy the same orbital.* This empiricism springs from our attempts to relate the numbers of the hydrogen atom orbitals to the number of elements per row of the periodic table. We observe in the periodic table the row lengths 2, 8, 8, 18, 18, and 32. We observe for the hydrogen atom the numbers of orbitals $1^2 = 1$, $2^2 = 4$, $3^2 = 9$, $4^2 = 16$. Moreover, we find that these numbers, multiplied by 2, give the same numbers found in the periodic table. For the first eleven elements, we demonstrate how the postulation of two electrons per orbital can "explain" the first two rows of the periodic table.*

MANY-ELECTRON ATOMS (15-2)

Energy Levels of Many-Electron Atoms (15-2.1)

At this point, the many-electron energy level diagram is needed. The hydrogen atom levels predict that the third row of the periodic table should have eighteen elements instead of eight. The reason is readily found in the energy level diagrams of many-electron atoms. These diagrams show that electron repulsions (not present in the hydrogen atom) distort the energy levels. The principal quantum numbers are still useful, but now the *s*, *p*, *d*, *f* notation is needed to designate sub-levels of differing energy. The emission spectra of many-electron atoms show just how the energy levels change. Taking these shifts into account, we find the entire periodic table can be "explained" with the aid of the hydrogen atom quantum designations.

The Periodic Table (15-2.2)

This section gives a review of the chapter to this point. Use this to pull the class together in their understanding of the electron configuration and its relation to the periodic table.

IONIZATION ENERGY AND THE PERIODIC TABLE (15-3)

Measurement of Ionization Energy (15-3.1)

This section presents the idea of ionization energy in terms of the energy level diagrams just developed. It may be helpful to motivate interest in this section by first recalling that the difference in the chemistry of alkali metals and that of the halogens was discussed in terms of the atom's tendency to acquire the electron population of an inert gas. This will raise the question of what energy change is implied by such a change in electron population. What energy effect accompanies the change when a neutral sodium atom loses an electron? This process is

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* As an aside, it may be noted that all of the evidence for the Pauli Principle is empirical, just as represented here. Quantum mechanics does not imply the Pauli Principle.

called ionization, and the energy effect is called ionization energy. (Be sure the student realizes that the entire discussion refers to isolated atoms —i.e., gaseous atoms.) By studying ionization energies, perhaps we can understand why sodium loses an electron in a chemical reaction but chlorine does not.

The initial discussion of ionization energy tries to accomplish three objectives:

1. To indicate what "ionization energy" means.
2. To indicate how ionization energies are measured.
3. To relate ionization energies to the energy level diagrams.

A CHEM Study film entitled IONIZATION ENERGY is specifically designed to show the experimental methods used in measuring these important quantities.

Film, IONIZATION ENERGY,
fits here. See p. 485 for summary.

Trends in Ionization Energies (15-3.2)

Ionization Energies and Valence Electrons (15-3.3)

The importance of ionization energies to a chemist comes from their connection to the chemical trends across a row of the periodic table. In Textbook Figure 15-13, the saw-tooth trend in ionization energy clearly defines the periodicity of the periodic table. It explains that the energy needed to remove an electron from an element increases from left to right across a row but suddenly drops at the beginning of a new row. Most important, it explains, in terms of energy effects, why the valence electrons (those in the outermost, partially filled orbitals determine the chemistry of the atom. The energy necessary to disturb the inner electrons is prohibitively high.

The Fourth Row of the Periodic Table (15-3.4)

The chapter concludes by showing how the longer rows of the periodic table are related to the energy level diagram of the many-electron atom.

Supplementary Material

Articles

1. D. DeVault, "A method of teaching the electronic structure of the atom, I," *J. Chem. Education*, 21, 526 (1944).* Excellent for both the advanced student and the teacher. Treats stationary states, electron distribution, periodic table.
2. D. DeVault, "A method of teaching the electronic structure of the atom, II, advanced topics," *J. Chem. Education*, 21, 575 (1944).* Excellent for the teacher, but may confuse students. Treats the variation of energy level spacing with increase in nuclear charge.
3. G. Gamow, "The principle of uncertainty," *Scientific American*, January 1958.† (Offprint No. 212)** For the teacher only. Background reading concerning the wave-particle, dual nature of matter.
4. K. K. Darrow, "The quantum theory," *Scientific American*, March 1952 (Offprint No. 205).† Excellent for teacher; stimulating reading for any student willing to try it. Planck's important role in developing quantum theory is shown; experimental evidence for quantum mechanics is reviewed chronologically.

Books

1. L. E. Steiner and J. A. Campbell, *General Chemistry*, Macmillan, New York (1955). Chapter 14, pp. 174–195, treats ionization energies and periodicity at a level suitable even for average students who desire additional reading.
2. M. J. Sienko and R. A. Plane, *Chemistry*, McGraw-Hill, New York (1961), pp. 46–73. Suitable for the advanced student; useful for the teacher. Treats ionization energy, electron affinity, periodic table.
3. H. H. Sisler, C. A. Vander Werf, and A. W. Davidson, *General Chemistry—A Systematic Approach*, Macmillan, New York (1959), pp. 155–171; 178–185. Suitable for the advanced student, useful for the teacher. The periodic table is considered in terms of energy levels, ionization energies and chemistry.
4. G. M. Barrow, *Physical Chemistry*, McGraw-Hill, New York (1961), pp. 186–201. Provides background in depth for the teacher; too mathematical for students. Covers the Schroedinger equation, and shows explicit forms of hydrogen atom orbitals and discusses the probability distribution.
5. H. H. Sisler, *Electronic Structure, Properties, and the Periodic Law*, Reinhold, New York (1963). Chapter 1 provides good supplementary reading for teachers and students.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

IONIZATION ENERGY A CHEM Study film
Running Time: 22 minutes

This film was produced with the collaboration of Professor Bruce H. Mahan of the University of California at Berkeley. The film provides strong support of the text by showing how ionization energies are measured. Both photoionization and eletron bombardment methods are demonstrated and explained. The photoioninization method is demonstrated using gaseous sodium. The electron bombardment method is shown to give the same value for sodium and is then applied to the inert gases. The saw-tooth periodicity of ionization energy is also developed.

THE HYDROGEN ATOM—AS VIEWED BY QUANTUM MECHANICS A CHEM Study film
Standard Version *Running Time: 13 minutes*

Professor G. C. Pimentel of the University of California, Berkeley is collaborator. This film presents a description of the atom that is in accord with quantum mechanics. This description explains the energy levels and line spectrum of the hydrogen atom and furnishes the basis of contemporary theory of chemical bonding. The electron position in the atom is considered in terms of probability, and the meaning

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* Included in "Supplementary Readings for Chemical Bond Approach"; reprints published by *J. Chem. Education*.

† Included in "Supplementary Readings for Chemical Bond Approach"; reprints from *Scientific American*.

** Available from W. H. Freeman and Co., San Francisco. Order by number.

of a 1*s* orbital is clarified with a digital computer plot, two analogies, and animation.

Advanced Version *Running Time: 20 minutes*

The advanced version includes the complete content of the standard version plus a final section which contrasts the electron distributions of the 1*s*, 2*s*, and 2*p* orbitals. The principal quantum number, *n*, is introduced together with its relation to energy levels, number of orbitals and the number of nodal surfaces.

Background Discussion

This chapter shows how our modern understanding of the hydrogen atom, through quantum mechanics, explains the periodic table and the chemical trends it correlates. Unfortunately, even experienced teachers may feel their own background is weak in this area.

With the expectation that many teachers will wish to supplement their existing knowledge, we present here a rather lengthy background discussion. It goes well beyond the needs of classroom discussion and provides, we hope, some understanding of the advantages that lie in abandoning certain traditional treatments in favor of currently accepted views.

LIGHT AND MATTER: WAVES OR PARTICLES?

Some properties of light are best described in terms of the properties of waves. Other properties of light are best described in terms of particles of light. The same sort of ambiguity in description applies to matter. This wave-particle duality is an essential facet of the modern setting of the physical sciences. In this course, the duality confronts us in our consideration of the properties of light and, again, in our consideration of the quantum-mechanical picture of the atom. Hence we feel that a review of some of the experimental evidence that gives rise to these alternate descriptions—waves or particles—is appropriate.

THE WAVE NATURE OF LIGHT AND MATTER

Geometrical optics deals with the reflection and refraction of light. Precise mathematical description of these can be framed by attributing to light the spatial extension, continuity, and periodic variations of a wave. The description gives detailed explanations of diffraction effects in terms of constructive and destructive summations of waves. The wave view of light is, on the one hand, accurate in that it fits many experimental facts and, on the other hand, appealing in that it provides an intuitive grasp of "what is going on."

Wave-like properties of fundamental particles are now well recognized, too. Diffraction phenomena just like those observed with light have been demonstrated for fundamental particles such as electrons and neutrons. In fact the deduction of crystal structures through neutron diffraction is now an active field. The diffraction patterns can be interpreted in terms of wave phenomena provided the particle is assigned a wavelength fixed by its mass and velocity:

$$\lambda\ (\text{cm}) = h/mv \qquad (1)$$

This wavelength is called the de Broglie (pronounced *de broll-yee*) wavelength.*

The wave nature of matter is most firmly attested, however, by the success of quantum mechanics. The mathematics of quantum mechanics is based upon a modification of the mathematics of classical mechanics. The total energy is written as the sum of the kinetic and potential energies of the fundamental particles, using point positions and momenta as the variables. Then wherever momentum appears, a substitution is made that alters the mathematical character of the equation.† First, the equation takes on the general form of an equation describing waves. Second, it acquires a statistical character, expressing the information it contains in terms of probabilities and averages. More will be said later about the nature of the solutions to quantum mechanical equations, but for the purposes of this paragraph, we can conclude that the

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* Expression (*1*) can be nonrigorously deduced in this way; a light wave of frequency ν has energy $E = h\nu$. But frequency is just the velocity of light divided by wavelength, $\nu = c/\lambda$, thus $E = hc/\lambda$. Einstein related energy and mass in his equation $E = mc^2$, which by substitution gives $\lambda = h/mc$. This is identical in form with expression (*1*) if we recognize that the photon travels with velocity c, whereas the particle travels with velocity v.

† The equation then becomes the celebrated Schroedinger equation. It is obtained by substituting a second derivative wherever momentum appears. Such a change implies that the equation becomes a second-order differential equation. If more than one dimension is involved, it is a partial differential equation.

well-deserved confidence given to quantum mechanics carries an implicit acceptance of the wave description of fundamental particles.

THE PARTICULATE NATURE OF LIGHT AND MATTER

There is no need to argue further in favor of the particulate nature of matter. Chemistry is firmly based on the atomic theory, as the evidence cited in Chapter 14 shows.

Light, too, has properties best treated in terms of a particulate view. Planck was the first to use this view to explain the frequency distribution of the energy radiated by a black body. He found it impossible to devise an experimental model that would fit the experimental facts until he assumed what was then a strange model. He pictured a collection of oscillators, each capable of radiating only a single frequency, and he added that the radiation process released energy in "portions" or "quanta." The energy a given oscillator released per "quantum" was assumed to be fixed by the frequency according to the now-famous relation, $E = h\nu$. The constant h is the same for all frequencies. Planck proposed this model, despite its strangeness, because the experimental facts demanded it.

Another experiment that displays the particulate nature of light, the photoelectric effect, is more easily grasped. When light of frequency ν falls on a metal surface, and the frequency is slowly increased while suitable measurements are made, one discovers that above a critical frequency, ν_0, electrons are ejected from the metal surface. Below this frequency, no electrons are ejected, no matter how long the metal is illuminated. At frequencies above ν_0, the energies of the ejected electrons can be measured. All electron energies observed at a particular frequency are the same. Changing the intensity of the light changes the number of electrons ejected per second, but not their energies. This behavior and the frequency dependence of these energies are readily understood in terms of the quantum view of light. Light is considered to be made up of "packages" of energy, $E = h\nu$. As ν is increased, the energy per package increases. Finally, a frequency ν_s is reached at which the photon package of energy is sufficient to wrench an electron out of the metal surface. At still higher frequencies, the photon contains even more energy, and hence the electron is wrenched out of the metal surface, and the excess energy appears as kinetic energy. A very simple relation between kinetic energy and frequency is observed experimentally and is predicted by this model:

$$\text{K.E.} = h\nu - h\nu_0 \qquad (\nu > \nu_0)$$

Changing the intensity of the light merely increases the number of photons in the beam, but does not affect the energy per photon.

Finally, we must mention that interpretations of spectroscopic studies almost always require the Planck relation, implying the particulate nature of light. Hence every successful interpretation of the absorption or emission of light by a molecule or an atom confirms the view that light comes in packages called photons.

A CONTRAST OF $E = h\nu$ AND $E = mc^2$

The Planck relation indicates that the amount of energy per photon is intimately related to the frequency. The relation $E = h\nu$ can be verbalized: "Energy is proportional to frequency, and the proportionality constant is h." We could verbalize the Einstein relation, $E = mc^2$, in a similar way: "Energy is proportional to mass, and the proportionality constant is c^2." Each of these statements is correct, as far as it goes, but the use of the term "proportional" is objectionable because it fails to make clear the essential relationships conveyed by the expressions. It gives no clue to subtle and important differences in the two relations, $E = h\nu$ and $E = mc^2$.

To begin, let us explore a meaning of the word proportional that is not applicable to either $E = h\nu$ or $E = mc^2$. Consider the statement: "The number x of shoes needed is proportional to the number of individuals, y, to be shod," or, mathematically, $x = ny$. Two aspects of this proportionality relation make it very different from our two expressions $E = h\nu$ and $E = mc^2$.

First, the word "proportional" tells how x depends upon y, but it leaves unsaid whether x depends upon other factors. Is n a number that varies, or is it an absolute constant? Clearly, n in $x = ny$ is the number of feet per individual—it is two per individual if humans are considered; four per individual if horses are considered. In general, a proportionality constant can vary—as it does in the relation, "weight is proportional to mass" (upon what planet is m placed?) and in the relation, "food consumption is proportional to population" (population of mice? moose? men?). But neither h nor c^2 can vary. Each of these is considered to be a fixed and absolute constant. This information is not implied by the word "proportional." The second difference is that $x = ny$ expresses a dependence of the number of shoes upon the number of individuals, but it surely does *not* imply that shoes and individuals are the same thing. In contrast, light *is* a form of energy, and energy *does* have mass. Neither of these equivalence relations is implicit in a statement of proportionality.

Thus the relations $E = h\nu$ and $E = mc^2$ contain much different information than the example $x = ny$. Moreover, we can add that $E = h\nu$ and $E = mc^2$ differ in a subtle and important way. First, consider $E = h\nu$. This expression tells us that a measurement of the frequency of a photon gives its energy and that a measurement of the energy of a photon gives its frequency. Thus the frequency and the energy of a photon convey exactly the same information. In fact frequency bears the same relationship to heat energy as does electrical energy. The operations by which electrical energy is usually measured (e.g., by measuring current and voltage) differ from the operations by which heat is usually measured (e.g., by calorimetric measurements). The operations by which frequency is measured (e.g., by spectroscopic measurements) are different from either of the others. Yet light, electrical energy, and heat are all manifestations of energy. The different units used, cycles per second, joules, or calories, have historical significance in that they suggest the use of a particular operational technique in their measurement. But the energy per photon can be measured calorimetrically just as readily as can electrical energy. The question of what units to use in expressing the results is purely semantic and rests upon convenience. For example, consider the conservation of energy in a photochemical reaction:

$$\text{heat content of reactants} + \text{energy of light absorbed} = \text{heat content of products} + \text{heat}$$

Any one of these four quantities can be calculated if the other three are known—provided, of course, that all four are expressed in the same units, be they kilocalories, ergs, or cycles per second.

Hence the essential message of $E = h\nu$ is that *light is a form of energy*. The amount of energy per photon can be indicated by specifying its frequency or by specifying other units related to the frequency through conversion factors; $h = 6.624 \times 10^{-27}$ erg-sec if ergs per photon are the desired units, or $h = 9.54 \times 10^{-14}$ kcal-sec if kilocalories per mole of photons are the desired units.

The relationship $E = mc^2$ is not quite the same. This expression tells us that energy has associated with it the property we call mass and that mass has associated with it the property we call energy. *Any* form of energy has mass equal to E/c^2 (if E is expressed in ergs). Thus after a molecule emits light, the molecule has less mass, the decrease being related to the mass of the photon. A chemical change can occur involving any of the various forms of energy, but whatever forms of energy are involved, they *all* have mass. A kilocalorie of energy has the same mass whether the energy form is heat content, rest mass, light, heat, etc. This is true even though the mass of a kilocalorie is too small to be weighed in a conventional weighing operation.

Thus the essential message of $E = mc^2$ is that *energy and mass are equivalent*. Conventional ways of measuring energy also measure mass, and conversely. Energy and mass are the same thing—one cannot exist without the other. A student will be aided in using $E = h\nu$ and $E = mc^2$ if he learns early the complete meanings of these two relations, as conveyed quite simply by the following language:

$E = h\nu$: *Light is a form of energy.* The amount of energy per photon, as fixed by its frequency, can be expressed in other units through the conversion factor, h.

$E = mc^2$: *Energy and mass are equivalent.* The mass of an amount of energy E is E/c^2. The energy associated with a mass m is mc^2.

CLASSICAL MECHANICS AND THE HYDROGEN ATOM

Inevitably, the deduction of the nuclear atom led, within classical mechanics, to a satellite, or planetary, model of the hydrogen atom. This model seems to provide a mechanical basis for the stability of the atom. The electron is pictured as a frictionless planet circling a proton sun. The centrifugal force of the circling electron just balances the attractive electrostatic force between the two charged particles.

Unfortunately this model contains a false premise. Such a planetary system cannot be considered frictionless, because the two bodies possess electric charge. According to classical electrodynamics, an accelerated charge radiates light, losing energy. A circling electron is continuously accelerated as it moves in a curved trajectory. Hence an electron circling a proton in a hydrogen atom should radiate energy continuously. This loss of energy would slow the electron, reduce the centrifugal force, and cause the electron to spiral toward the nucleus. Thus the theoretical scientist of 1910 could predict that nuclear atoms should collapse. He could even calculate that this collapse would occur in a small fraction of a second, shortly after atoms started behaving according to the well-established laws of physics that govern the behavior of macroscopic bodies. Fortunately for the universe, atoms have stubbornly refused to behave according to these laws.

THE BOHR ATOM

Bohr first built into a useful theory the obvious experimental fact that the nuclear hydrogen atom does not collapse. He proposed that the electron in the hydrogen atom can possess only certain angular momenta—integral multiples of $h/2\pi$. Bohr "forbade" the electron to radiate by confining its angular momentum to one of a set of discrete and separated values. This model was chosen because, with only this one arbitrary change, the classical calculation of orbital motion led to the experimentally observed energy levels of the hydrogen atom. A dozen years later, the de Broglie wave picture of matter was proposed. Then it was realized that Bohr's rule corresponded to periodic electron movement in orbits, such that the distance traveled in each orbit is equal to a whole number of de Broglie wavelengths.

The Bohr model of the hydrogen atom filled two important and, possibly, essential roles. First, it introduced the idea of stationary states—an idea that set the stage for the development of modern quantum mechanics. Second, it provided a bridge between the classical planetary model of the atom and the modern quantum-mechanical model. The Bohr model, together with the de Broglie wavelength, furnished an intuitively acceptable evolutionary step in the development of the theory of the atom. Scientists who had learned to think of the atom in terms of a planetary model found it helpful to retain as much of the planetary model as the facts would tolerate.

Successes of the Bohr Atom

We can enumerate two successes of the Bohr model of the atom, one of which was immediately apparent, the other of which is important in retrospect.

1. The Bohr model reproduced exactly the energy levels of the hydrogen atom, hence it explained the till-then mysterious line spectrum of the hydrogen atom. This furnished great impetus to the ultimate development of quantum mechanics, because the simple but totally unexplained numerical relationships among the hydrogen atom

frequencies had haunted physicists for almost three decades. For the first time, an explanation seemed imminent.

2. The Bohr model formulated explicitly the concept of "stationary states." At the time, this could not be counted a success; it was merely an unfamiliar premise apparently required by the experimental facts. In retrospect, we see this as one of the crucial steps toward the break with the classical laws of motion in the treatment of fundamental particles.

Failures of the Bohr Atom

The failures of the Bohr atom are more numerous than successes, though they have become apparent only slowly as the atomic theory has evolved. We can now say that the Bohr atom gives a simple physical picture of the atom, but one that is qualitatively incorrect.*

1. The Bohr atom uses a planetary model of the atom involving circular or elliptical trajectories. Quantum mechanics and experiments both show that the electron does *not* move in such trajectories. It is true that quantum mechanics remains noncommittal concerning the electron trajectory, but it does indicate the average spatial distribution of electron positions. This spatial distribution is incompatible with the Bohr trajectories. The most obvious difference is that *s* orbitals place the electron near the nucleus with high probability. There is ample experimental evidence proving that quantum mechanics is correct in this regard. Two phenomena giving data on this point are electron-capture by the nucleus (a kind of nuclear transmutation) and the nuclear spin-nuclear spin interactions displayed in nuclear magnetic resonance spectra. Each phenomenon is understandable provided the electrons spend a considerable time near the nucleus, as predicted by quantum mechanics and denied by the Bohr trajectories.

   It is sometimes noted that Bohr arbitrarily "threw away" the trajectories with zero angular momentum and that these discarded orbits *do* pass through the nucleus. The inclusion of these trajectories solves one problem only to raise another. The Bohr atom fits the hydrogen atom energy levels *without* the zero angular momentum trajectories. Adding a new set of energy levels detracts from the only real success of the model.
2. The calculational scheme chosen to explain the energy levels of the one-electron, or hydrogen-like, atom failed to explain the energy levels of any other atom.
3. The Bohr model of the atom gives no clue to the origin of chemical bonding.
4. The basic Bohr assumption concerning angular momentum of the electron is not correct, even though it does lead to the correct hydrogen atom energy levels. Whereas Bohr assumed angular momentum equal to $n(h/2\pi)$, in which $n = 1, 2, 3, \cdots$, quantum mechanics shows it to be $\sqrt{l(l+1)}(h/2\pi)$, in which $l = 0, 1, 2, \cdots$. The results are compared in Table 15-I.

Table 15-I

Comparison of Bohr's Assumed Angular Momenta with Calculated Quantum-mechanical Averages for the Hydrogen Atom (in units of $h/2\pi$)

Quantum Number		Angular Momentum	
Bohr	QM	Bohr	· QM
$n = 1$	$l = 0$	1	0
$n = 2$	$l = 1$	2	1.41
$n = 3$	$l = 2$	3	2.45
$n = 4$	$l = 3$	4	3.46

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* Some of the failures listed for the Bohr atom are based upon its discordance with results drawn from quantum mechanics. This is well justified, since quantum mechanics has proven to be in accord with every atomic property for which mathematical tractability has permitted a meaningful calculation. This statement applies to many-electron atoms and molecules as well as to the hydrogen atom.

5. The Bohr atom provides no basis for understanding either quantization or the failure of the orbiting electron to radiate its energy. Both are simply assumed.

The Persistence of the Bohr Model

It is not surprising that the part classical, part quantum-mechanical Bohr atom strongly influenced the popular conception of the atom during the developmental period of quantum mechanics. The Schroedinger wave equation was proposed in 1926 and was developed through research done during the 1930's. Most scientists (certainly most chemists) found it convenient to adopt the Bohr atom during this period of trial as a "step in the right direction" while waiting to see what success and impact the more abstract wave mechanics would have. This permitted them to benefit from recognition of the quantization of atomic properties without abandoning their intuitively satisfying planetary view of the atom.

What is surprising is the retention of emphasis on the Bohr atom now, almost three decades after it became clear that the planetary model is not a correct picture of the atom. This can hardly be argued to be beneficial to the novice in chemistry as a bridge between his planetary view of the atom and a more correct view. *The novice has no prior basis for believing that the atom is planetary.* We cannot justify presenting the Bohr atom as a "natural" introduction to quantization, for the planetary model does not "naturally" include quantization; such an approach requires that quantization be imposed as a necessary element foreign to the model. Nor can the Bohr model be supported on the grounds that it successfully explains the hydrogen atom spectrum when it conflicts with correct predictions of another theory that also explains the hydrogen atom spectrum.

To be sure, there remains the benefit of the "case history" approach. This example offers a classic opportunity to display the path of scientific progress. Nevertheless, a very large fraction of the value is lost if the example must be presented without the mathematical detail, beginning with the classical equations, continuing through the Bohr atom, and ending with a display of the ultimate quantum-mechanical postulates and equations.

We have sought a middle ground. We present the dilemma formed by the classical predictions (collapse of the nuclear atom) and the discrete energy level diagram of the hydrogen atom. Bohr's valuable proposal of stationary states is emphasized, together with his numerical success in explaining the hydrogen atom spectrum. We proceed immediately, then, to a discussion of electron distribution in the hydrogen atom—a discussion that is valid in the light of quantum mechanics.

Thus we carefully refrain from displaying Bohr's planetary model to avoid shaping the student's first impression of atomic structure in an incorrect mold. First impressions are lasting, and there is a real disadvantage in beginning with the easy lie of the planetary model, which must later be supplanted by the more difficult truth of quantum mechanics.

QUANTUM MECHANICS AND THE HYDROGEN ATOM

A classical calculation of the motion of charged particles offers definite answers; it tells the time dependence of the potential energies, kinetic energies, and trajectories for each particle. Such classical calculations, though detailed, do not describe correctly the properties of electrons within atoms. The quantum-mechanical solution to such a problem is less informative. The quantities it does predict, however, are in accord with experiment. Quantum-mechanical solutions do not tell us everything we would like to know about the atom, but we can believe with confidence what they do tell us.

We shall discuss the following topics, using the minimum amount of mathematical detail:

1. The relation between classical mechanics and quantum mechanics.
2. The nature of a quantum mechanical orbital.
3. Some properties of the hydrogen atom orbitals:

   (a) the significance of n, the principal quantum number;
   (b) dependence of average radius upon Z, n;
   (c) dependence of energy upon Z, n.
4. The Pauli Principle and electron spin.

The Schroedinger Wave Equation and Classical Mechanics

The relation between the wave equation and classical mechanics is shown here in bare outline. Our intent is two-fold. First, we wish to show that the equation retains the classical dependence upon potential energy. Second, we wish to show the origin of the wave function ψ (psi), a function that tells, in terms of probability, where the electron is to be found in an atom.

As mentioned earlier, the formulation of the mathematics of quantum mechanics has a direct relationship to classical mechanics. The classical laws of motion are based upon the energy concept:

$$\text{(kinetic energy)} + \text{(potential energy)} = \text{(total energy)}$$

or

$$\text{K.E.} + \text{P.E.} = E \qquad (2)$$

The energies in equation (2) are expressed in terms of positions (x, y, z) and velocities (v_x, v_y, v_z) or, equally well, in terms of positions (x, y, z) and momenta (p_x, p_y, p_z).* If, for example, we apply the classical laws of motion to a hydrogen atom, the kinetic energy is fixed by the electron velocity, and the potential energy is fixed by the electrostatic interaction between the electron and the proton:

$$\text{K.E.} = \tfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \qquad (3)$$

Equation (3) can be written in terms of momenta:

$$\text{K.E.} = \frac{1}{2}m\left(\frac{p_x^2}{m^2} + \frac{p_y^2}{m^2} + \frac{p_z^2}{m^2}\right)$$

$$= \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \qquad (4)$$

The potential energy depends upon the distance r between the electron and the proton and upon the electrostatic charges of the particles:

$$\text{P.E.} = -\frac{e^2}{r} \qquad (5)$$

If we take the proton position as the origin, (5) becomes

$$\text{P.E.} = -\frac{e^2}{\sqrt{x^2 + y^2 + z^2}} \qquad (6)$$

Thus equation (2) can be written in classical form,

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - \frac{e^2}{\sqrt{x^2 + y^2 + z^2}} = E \qquad (7)$$

Equation (7) provides a basis for formulating the Schroedinger equation via a simple recipe. Wherever momentum appears, a derivative is substituted. For example,

$$p_x^2 = -\frac{h^2}{4\pi^2}\frac{d^2}{dx^2}$$

The potential energy is not changed.

At this point we have made a change that gives an incomplete expression:

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{\sqrt{x^2 + y^2 + z^2}}\right] = E \qquad (8)$$

In expression (8), the derivatives are "operators"—they give us instructions to differentiate something. We must provide in the equation a function that can be differentiated. Hence a new function ψ is brought into (8), which acts rather like a multiplier (on both sides, to maintain the equivalence):

$$\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{\sqrt{x^2 + y^2 + z^2}}\right]\psi = E\psi$$

or

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) - \left(\frac{e^2}{\sqrt{x^2 + y^2 + z^2}}\right)(\psi) = E\psi \qquad (9)$$

Equation (9) is the Schroedinger Wave Equation for the hydrogen atom. The quantity ψ depends upon x, y, and z. Solving the equation means

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* The symbols v_x and p_x mean the component of the velocity and momentum along the x-direction.

finding all possible functions, ψ, that make the equation valid.

The worst is over. Now we can compare the classical equation (*7*) to the quantum-mechanical equation (*9*). First we note that the potential energy term, $-e^2/\sqrt{x^2 + y^2 + z^2}$, is present in both equations. This term tells us that the electron-proton electrostatic interaction is no different in the quantum-mechanical atom than it was in the classical atom. Specifically, the electron has not been vaporized into a charge cloud. The contribution to the potential energy at any instant is like that of a point electron interacting with a point proton separated by some definite distance, $r = \sqrt{x^2 + y^2 + z^2}$. This shows that the terms "electron cloud" and "charge cloud" are unfortunate and misleading. A more apt expression is "probability distribution."*

Next we focus our attention on the function ψ. This function is chosen so as to satisfy equation (*9*). Mathematical analysis shows that there is not just one but a set of solutions ψ_1, ψ_2, ψ_3, $\cdots$, and each solution satisfies equation (*9*), provided we substitute the correct one of a set of numerical values of the energy parameter, E_1, E_2, E_3, $\cdots$. To each solution ψ_1 there is one and only one mathematically acceptable value of the energy, E_1. The Schroedinger equation (*9*) interests us because the acceptable values of E are the exact energy levels of the hydrogen atom.

By solving equation (*9*), then, we learn the possible energy levels from the values of E. All other information about the atom is contained in ψ. This function, called the wave function, tells us only averages and probabilities. It tells us the probability that the electron will be found at a particular point, but not how it would get there (its trajectory) nor how long it will remain nearby (its velocity passing through the point). That is, ψ contains the information that would be contained in a time exposure of an atom. From this "time exposure" we can tell where the electron spends lots of time, where it spends little time, its average kinetic energy, average momentum, average dipole moment, etc. Yet such a time average is completely noncommittal as regards instantaneous properties. It gives us no information about instantaneous movement of the electron. We can postulate, if we wish, that the electron has a trajectory—it has an average kinetic energy—but if we do, it must be a trajectory whose average agrees with the known time average. (This requirement spells out the complete unsuitability of the Bohr trajectories.) But quantum mechanics does not imply there is a trajectory. Indeed, it places limitations on what we can know about the electron movement through the Uncertainty Principle. As regards quantum mechanics (and ψ) there is no need to discuss the electron trajectory in the atom, since, as far as we know, it cannot be detected.

Thus the wave function, ψ, describes the probability distribution of the electron in space.* Such a probability distribution is called an *orbital.*

The Nature of a Quantum-mechanical Orbital

The evolution of thinking with regard to a particular physical phenomenon is sometimes told in its terminology. This is so for atomic structure. The energy levels of the hydrogen atom, for example, are designated *s*, *p*, *d*, *f*, etc. These letters are not now considered as abbreviations, but once they were. The symbols originally classified an atomic spectral line in accordance with its appearance in a spectral photograph: *s* meant "sharp," and *d* meant "diffuse." The symbol *p* meant "principal," reflecting the then current belief that these lines had a special significance. When the Bohr atom was proposed, it became clear that the lines corresponded to transitions between two energy states of the atom. Connections between the spectral lines and the hydrogen atom energy

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* Even our space-filling models of an atom can be misinterpreted as suggesting (incorrectly) that the electron is everywhere in the atom at once.

* More accurately, $\psi^2 dV$ gives the probability of finding the electron in a volume element dV, provided ψ has been "normalized"—multiplied by a constant so that the total probability over the entire space is unity: $\int \psi^2 dV = 1$.

levels led to a natural transfer of these symbols to the Bohr energy levels.*

At this time, the planetary model of the atom placed an indelible imprint on atomic nomenclature. The electron trajectory of the Bohr atom was, quite naturally, called an orbit, or orbital. As quantum mechanics developed, the function ψ supplanted the Bohr trajectory as our statement of what is known about the position of the electron. The term orbital was transferred to the probability distribution defined by ψ. The etymological unsuitability of the term is more of a detriment than is that of the symbols *s*, *p*, and *d*, however. The word orbital directly suggests a type of electron motion that conflicts with the true meaning of ψ.

Actually, ψ predicts time averages of atomic properties—the average electron momentum, the average electron kinetic energy, the average electron-proton distance, the average angular momentum. In addition, it gives probability information on the instantaneous electron position. For example, it predicts that if many separate experiments are performed to locate the electron in a hydrogen atom, 90% of the experiments will find it at a point closer than 1.42 Å from the proton. Moreover, 90% of the experiments will find the electron farther than 0.29 Å from the proton. The radius at which the electron is most likely to be found is 0.53 Å (the radius of the first Bohr orbit!), but there is a 2% probability that the electron will be either as close as 0.1 Å or as far from the proton as 2.24 Å.

The wave function ψ does *not* tell us that the electron will surely be at a particular point at any particular time. Neither does it insist that the electron moves from point to adjacent point in a systematic trajectory. It simply makes no statement about trajectory. What, then, should be said about trajectory? Probably it is best to de-emphasize it, laying stress instead upon the fact that quantum mechanics tells us in terms of probability how the electron occupies the space around the proton. There is no question that probability distribution is a concept of deep significance in quantum mechanics. It remains to be seen whether the notion of trajectory is really needed on the atomic scale. It is even conceivable that the notion of trajectory is merely an anachronism that persists while we get used to thinking about quantum-mechanical counterparts of kinetic energy and angular momentum without it.

The function ψ is called the "wave function." Its square fixes the spatial probability distribution that is called an orbital. This function is identified by integer numbers called quantum numbers. Each possible set of quantum numbers defines a probability distribution, hence an orbital.

The Significance of Hydrogen Atom Quantum Numbers

The hydrogen atom wave functions are identified by four quantum numbers, n, l, m, and s. Of these, only n needs to be mentioned explicitly in an introductory course. The value of l is implicitly contained in the *s*, *p*, *d* notation. The *principal* quantum number, n, has possible values 1, 2, 3, 4, 5, and so on. The angular momentum quantum number, l, is related to the shapes of the probability distribution. Its value is limited by n; it may have values equal to $(n - 1)$. If the value of l is 0, the electron distribution has spherical symmetry, as shown in Textbook Figure 15-8 (p. 262), and the orbital is called an *s* orbital. If the value of l is 1, the distribution has the angular shape shown in Textbook Figure 15-9 (p. 263), and the orbital is called a *p* orbital. For *d* orbitals, $l = 2$, and for *f* orbitals, $l = 3$. The shapes of the *d* and *f* orbitals are more complex than those of *s* and *p* orbitals.

The magnetic quantum number, m, indicates the possible orbital orientations in a magnetic field. This quantum number must also be an integer, and its value can be any number from $+l$ to $-l$. Hence the number of possible values of m is $(2l + 1)$. For an *s* orbital, $l = 0$, there is only a single value for m, $m = 0$. For a *p* orbital ($l = 1$) there are *three* values, $m = +1, 0, -1$. These three values identify three possible orientations of the orbitals, called p_x, p_y, and p_z.

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* The higher symbols, *f*, *g*, ··· were added later in an alphabetical continuation from *d*. The letter *e* was skipped because of its other uses as a symbol.

For *d* orbitals ($l = 2$) there are *five* values for m, and for *f* orbitals ($l = 3$) there are *seven* values.

The spin quantum number, s, indicates the orientation of an electron's spin with respect to a magnetic field. This quantum number can take only two values, $+\frac{1}{2}$ or $-\frac{1}{2}$.

An orbital is completely fixed when n, l, and m are specified. According to the Pauli Principle, only two electrons can occupy the same orbital. We can now add that these two electrons must have different values of s. Hence the Pauli Principle can be restated in the form: "No two electrons can have the same values of all four quantum numbers n, l, m, and s."

Some students may wonder why it should be that the complicated probability distributions can be characterized so simply by integers. An appropriate and meaningful model can be based upon a vibrating string fixed at both ends. At low vibration frequencies, there is one loop, or antinode. As the vibration frequency is raised, a node appears at the center, and two antinodes appear. At successively higher frequencies, three, then four, antinodes appear. The most natural way of differentiating these vibrational motions consists in representing, by an integer, the number of nodes or antinodes. The integer is analogous to a quantum number.

This is the significance of the integral values taken on by n, the principal quantum number, which tells the number of nodal surfaces—surfaces at which the probability of finding the electron becomes zero. For $n = 1$ there is but one nodal surface, and that surface is at infinity. Every orbital includes this node at infinity. For $n = 2$ there are two nodal surfaces, one in addition to the node at infinity. The 2*s* orbital has spherical symmetry, but there is a finite value of r at which the probability becomes zero, $r = 1.06$ Å. The fact that $\psi = 0$ at $r = 1.06$ Å means that the electron is never to be found at that particular radius. The 2*p* orbitals also have two nodes, one node in addition to the one at infinity. The pictures of the 2*p* orbitals, Figure 15-9 (p. 263) show that this nodal surface can be taken as one of the planes defined by pairs of axes. For the $2p_z$ orbital it is the *yz*-plane; for the $2p_y$ orbital, it is the *xz*-plane. For 2*p* orbitals, no nodes are fixed solely by r, except the one at infinity.

In general, the *ns* orbitals have spherical symmetry and n different values of r, at which the wave function becomes zero (including the one at infinity). For *np* orbitals, one of these r-nodal surfaces is lost, and one of the coordinate-axis planar nodes substitutes for it. For *nd* orbitals two of the r-nodal surfaces are lost, and two more-complicated (or "angular") nodes substitute.

The connection between the number of nodal surfaces and n can be made meaningful in terms of a tangible model, the vibrating string. This connection can furnish a satisfying relief from the abstract quality of the Schroedinger equation, the wave function, and the probability distribution.

The Hydrogen Atom Orbitals

The hydrogen atom problem is more appropriately called the one-electron, or hydrogen-like, atom problem. It is applicable to any two-body problem involving a nucleus with charge Z and a single electron. Thus two important properties of the orbitals, the energy and the average electron-proton distance, depend upon Z as well as upon the quantum numbers. Much of our understanding of chemical periodicity is based upon these dependencies.

The energy of a hydrogen-like atom depends upon Z and upon the principal quantum number n, but not upon the l or m quantum numbers:

$$E = -R\frac{Z^2}{n^2} \qquad (10)$$

$$R = -313.6 \text{ kcal/mole}$$

The average electron-proton distance, or average radius, depends upon Z and upon two quantum numbers, n and l.

$$\bar{r}_{n,l} = 0.529\frac{n^2}{Z}\left[\frac{3}{2} - \frac{l(l+1)}{2n^2}\right] \qquad (11)$$

$\bar{r}_{n,l}$ being in Ångstrom units.

The expressions (*10*) and (*11*) show how E and $\bar{r}$ would vary for the elements if the outermost electron had the properties of the electron in a

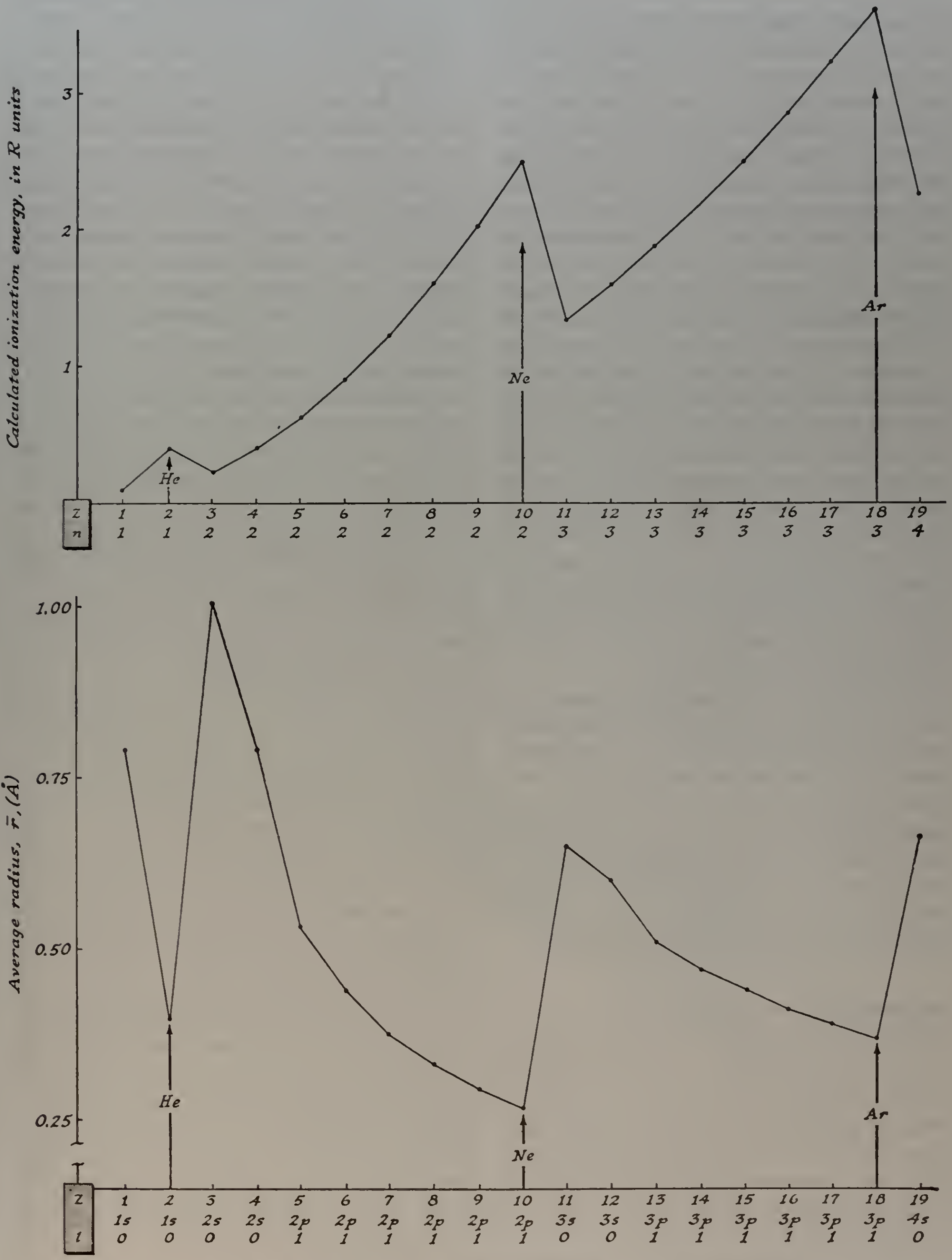


Fig. 15-1. **Ionization energy and average atomic radius versus** Z, n, **and** l *for hydrogen-like atoms.*

hydrogen-like atom. These are shown in Figure 15-1, where the energy is plotted as ionization energy in units of $R = -313.6$ kcal/mole. The plots do not agree quantitatively with experiment, but they show certain qualitative features of the observed trends in ionization energy and effective atomic radius. The actual ionization energies are shown in Textbook Figure 15-13 (p. 268). The major discontinuities that occur at each inert gas and the gradual rise across each row of the periodic table are present both in the experimental data (Textbook Figure 15-13) and in the calculated values (Figure 15-1). It is clear that the gradual increase in nuclear charge accounts for the rising ionization energy (and hence, electronegativity) across a row of the periodic table. The valence electrons are more strongly bound as Z increases. When n changes, starting a new row of the periodic table, a large drop occurs in ionization energy. The reason for this large effect of n on ionization energy is evident in the plot of average radius. An increase in n moves the valence electrons much farther from the nucleus, reducing the electrostatic attraction to the nucleus.

The quantitative discrepancies between the ionization energy trends and the calculated values are due to the assumption of a one-electron model. The presence of many electrons adds repulsive electrostatic forces in addition to the nuclear attractive terms. One way to express the electron-electron repulsive effects is in terms of an effective nuclear charge, Z^*. The full nuclear charge is not felt by the valence electrons, because the inner electrons "screen" the nucleus.

The Pauli Principle and Electron Spin

The Pauli Principle can be stated in various degrees of sophistication. The relatively simple statement given in the Textbook, "A single orbital can accommodate, at most, two electrons," offers a real advantage as an introductory formulation. It emphasizes the empirical basis for the principle and points to the most important piece of evidence requiring it—the periodic table. We do not use a statement in terms of quantum numbers (no two electrons can have the same values for all four quantum numbers). This definition has some subtle disadvantages. It is stated in abstract terms, and it suggests, incorrectly, that the Pauli Principle is derivable from quantum mechanics. The many-electron problem, as formulated in quantum mechanics, does *not* yield the Pauli Principle. It must be added as an empirical principle based upon the periodic table and upon spectroscopic evidence. Moreover, the electron spin quantum number must be discussed—another new concept, which adds complexity without contributing toward an understanding of the Pauli Principle.

Another common statement of the Pauli Principle is: "At most, two electrons can occupy an orbital, and these electrons must have opposite spin." Again the concept of electron spin must be defined, hence attention is directed to the fact that two electrons with the same spin cannot occupy the same orbital, but with opposite spin they can. Yet the interaction between the two electrons seems to have little to do with the Pauli Principle. Calculations of this interaction show it to be quite negligible.

A quantum-mechanical statement of the Pauli Principle is: "The wave function of a many-electron atom must be antisymmetric with respect to exchange of the coordinates of any two electrons." This statement means that the wave function is changed by a factor of -1 if the coordinates of two electrons are interchanged. This mathematical property is not required by quantum mechanics. It is an empirical restriction imposed on the wave function to fit the experimental facts mentioned earlier.

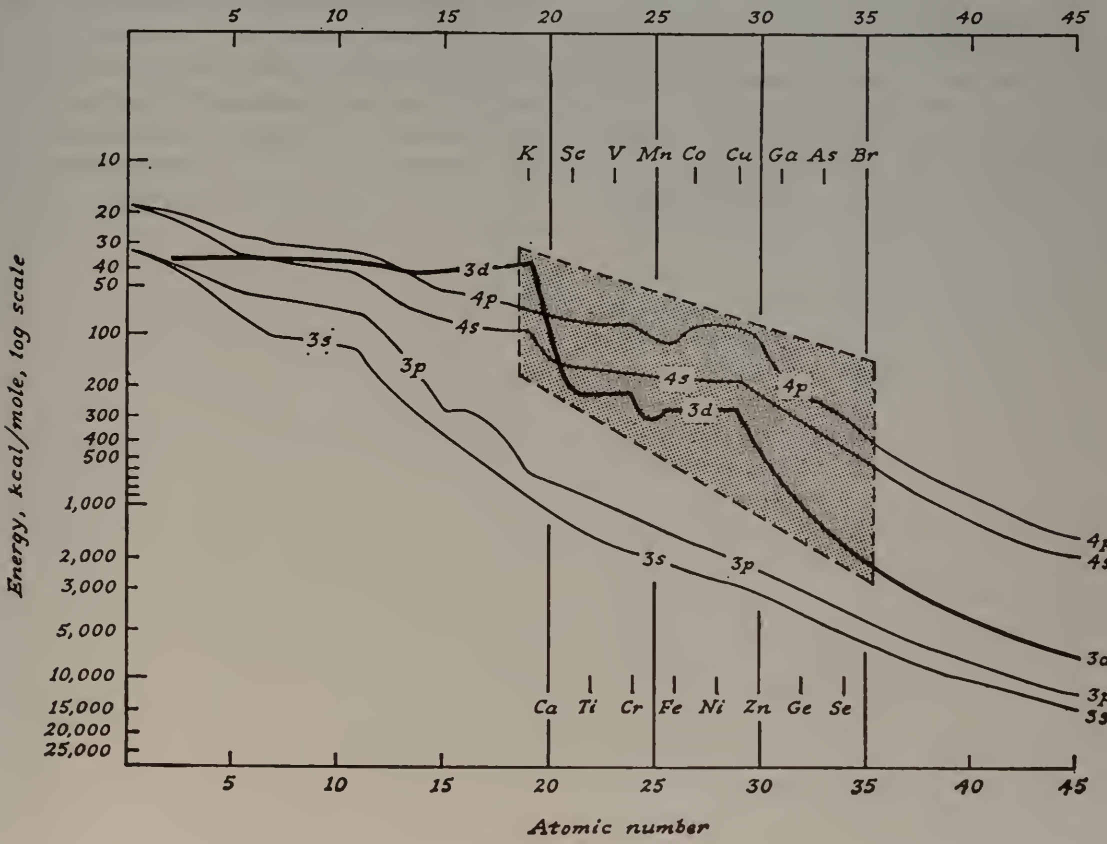
The Pauli Principle is fundamental as defined on Textbook p. 78. Experimental observations showed it to be true many years ago, but no explanation has yet become apparent. In this sense, this important principle, even in its most abstract formulation, is completely empirical. Make this absence of explanation clear—it does not detract from the principle, but adds a challenge. Surely someday an explanation will be forthcoming, conceivably from the generation you are teaching.

ENERGY LEVELS AND THE PERIODIC TABLE

Chapter 15 shows how the energy levels of the hydrogen atom lead to an understanding of the periodic table. The energy levels must be displaced somewhat to fit many-electron atoms, but these displacements are verified by spectroscopic studies, as were those for the hydrogen atom. The final energy levels explain the periodic table with an empirical "filling rule" called the *aufbau* principle. According to this rule, the electron configuration with the lowest energy is found by assigning electrons to the lowest levels in sequence, two to a level.

The Textbook contains, in Figure 15-11 (p. 266), a schematic energy level diagram that displays the important energy level relationships which depend upon Z and upon electron-electron repulsions. Both of these factors change from atom to atom and as more and more electrons are added. Thus the two energy level diagrams shown in Figure 15-14 (Textbook) for magnesium and sodium atoms are quite different. Textbook Figure 15-11 shows the approximate energy level relationships for each energy level that matters—that is, for each energy level that corresponds to a valence orbital. An energy level corresponds to a valence orbital when all lower levels are filled and higher energy levels are empty. To a chemist, it is important that the $3d$ energy level in iron has about the same energy as the $4s$ and $4p$ levels, but it is much higher in energy than the $3p$ orbitals and much lower in energy than the $4d$ orbitals. From the chemist's point of view, the very different energy relationships among the $3p$, $3d$, $4s$, $4p$, and $4d$ orbitals that exist for lithium or for uranium atoms are

Fig. 15-2. **Energy of the 3*d* orbitals** *for the first 45 elements.*



unimportant. The chemistry of lithium is fixed by the close spacing of the 2*s* and 2*p* levels and the wide separations of the 1*s* and 3*s* levels. The 3*d* level plays no important role in the chemistry of lithium (or in the chemistry of uranium).

Nevertheless, there are some interesting trends in the energy level spacings of the neutral atoms as a function of atomic number. These are developed in the two supplementary references by DeVault (see *Supplementary Material*). For example, the energy of a particular orbital increases in magnitude rapidly with increase in atomic number. Meanwhile, the relationships among levels of a given principal quantum number change. Figure 15-2 shows the energy of the 3*d* level as a function of atomic number. For atomic number 1, the 3*s*, 3*p*, and 3*d* energy levels have the same energy, and 34.8 kcal are required to ionize a 3*d* electron.* For atomic number 3 (the element lithium) the energy that a 3*d* electron would have is still about 35 kcal, but the 3*s* energy level has dropped about 10 kcal, and the 3*p* energy level has dropped about 2 kcal. For iron (atomic number 26) the energy of a 3*d* electron is about 275 kcal, and now the 3*s* and 3*p* energy levels are more than 1000 kcal below the 3*d* level. On the other hand, the 4*s* level has dropped down near the 3*d* level. For the higher atomic numbers, the 3*d* energy level has dropped even more, and the 3*s*, 3*p*, and 3*d* levels have about the same energy again. The 3*d* energy levels act as valence orbitals for atomic numbers 19 to about 30, and in this range of atomic number the energies are approximately as shown in our schematic energy level diagram.

IONIZATION ENERGIES

The term "electronegativity" has a long history in chemistry, and the term remains useful today, though it has sometimes been used with vagueness and ambiguity of meaning. There are two quantitative definitions of electronegativity. Pauling's definition is based upon bond energies of diatomic molecules (and will not be discussed here). The second definition, Mulliken's, defines electronegativity as the sum of ionization energy and electron affinity, $I + E$. These concepts are discussed in the Guide for Chapter 16 (p. 531).

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* In standard references, ionization energies are usually expressed in electron volts. The electron volt is the energy change associated with the movement of one electron through a one volt potential. Since this definition has little meaning to a student who has had no physics, we use kilocalories exclusively in the text.

1 ev = 1 electron volt = 23.062 kcal/mole

Answers to Exercises and Problems

Ex. 15-1. To see that these numbers have regularity, consider the series of numbers 2–8–18–32. (We shall forget, for the time being, that 8 and 18 each appear twice in the series.)

(a) If you were to consider this series incomplete, would you expect the next number (after 32) to be even or odd?

(b) The numbers 2–8–18–32 were obtained by subtracting electron populations (that is, by taking differences). Take differences again, and use them to predict the next number beyond 32 in the series.

(c) Divide the numbers 2–8–18–32 by two. Use these numbers as a basis for predicting the next number beyond 32 in the series by another method than taking differences.

Answer

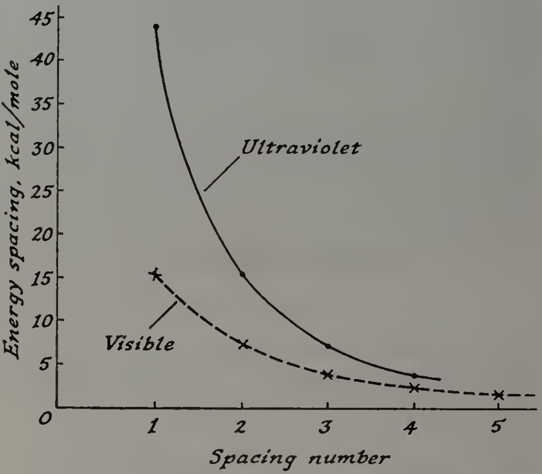
(a) The next number would probably be even.

(b) The second set of differences is: 6, 10, 14. The next number in this set is probably 18. This would make 50 the next number in the set 2–8–18–32.

(c) Division of the given set by two produces the set 1–4–9–16. This is a series made up of the squares of the integers. The next number of this series would be 25, which when doubled produces 50, the same number predicted in (b).

Ex. 15-2. Complete the following table for all of the ultraviolet lines listed in Figure 15-3. Plot the energy spacing against the arbitrary spacing number assigned in the last column to convince yourself that there is regularity in the spacings of these lines. Make the same sort of a table for the lines in the visible group.

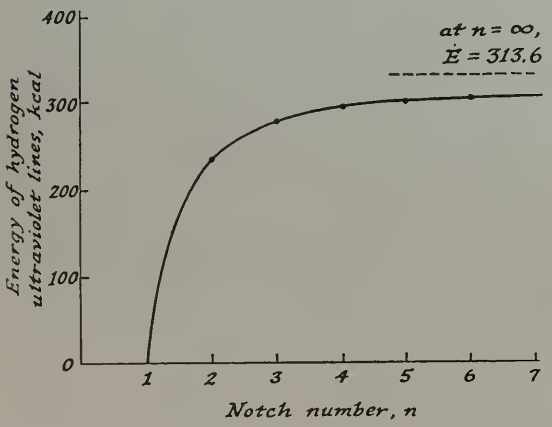
Group	Energy per Mole of Photons	Energy Spacing	Spacing Number
Ultraviolet lines (Given in Ex.)	235.2 kcal		
		43.6 kcal	1
	278.8		
		15.2	2
	294.0		
		7.1	3
Answer	301.1		
		3.8	4
	304.9		
Visible lines	43.6		
		15.2	1
	58.8		
		7.1	2
	65.9		
		3.8	3
	69.7		
		2.4	4
	72.1		
		1.5	5
	73.6		



Notice that the student is not asked to plot the visible spacings or to relate them to the ultraviolet spacings. The former is left to his initiative; the latter, for his discovery. The correspondence of the spacings should excite interest and should lead, through class discussion, to agreement that the two sets of lines probably have a common origin (e.g., the same set of notches on the notched beam). Interesting speculation can be raised on whether there is a separation 2.3 kcal in the ultraviolet group. Let the discussion lead to the prediction of where the next line should be. The situation can be left in doubt till the notched beam is developed. Although such a line exists, experimental difficulties make its detection difficult. In this spectral region, even air absorbs heavily, interfering with spectroscopy.

Ex. 15-3. Plot the energy of each line of the ultraviolet group against notch number, *n*, using the higher of the two notch numbers assigned to that line in Figure 15-3. For example, plot 235.2 kcal on the vertical axis against 2 on the horizontal axis. Assign to notch #1 the arbitrary value zero, and draw a smooth curve through all of the points, including the point for notch #1. Estimate the energy value that would be observed for a notch with very high notch number, as suggested by the curve. (Call this "notch # infinity," $n = \infty$.)

Answer



As the notch number increases, the energy of the line approaches 313.6 kcal. Student estimates should be in the range 310–315.

Ex. 15-4. Calculate the energy change that occurs between notch #1 and notch #2, *using the right-hand scale in Figure 15-7.* (Remember that the energy change is the energy of the final level *minus* the energy of the initial level. Pay careful attention to algebraic signs.) Repeat the calculation for the energy change between notch #2 and #3. Compare your calculations with the numbers shown in Figure 15-6.

Answer

On the right-hand scale in Figure 15-7 the notch numbers are assigned the following energies:

notch #1	−313.6 kcal/mole
notch #2	−78.4
notch #3	−34.8

$$\Delta E = (-78.4) - (-313.6) = +235.2 \text{ kcal}$$
notch #2 − notch #1

$$\Delta E = (-34.8) - (-78.4) = +43.6 \text{ kcal}$$
notch #3 − notch #2

Comparing these numbers to Textbook Figure 15-6, we find the same numbers, 235.2 and 43.6 kcal. Hence the student learns that the *differences* are not influenced by the arbitrary choice of zero on the energy scale.

In discussing this exercise, emphasize the arbitrariness of this choice of zero. A useful analogy can be developed in terms of the height of a light fixture in a room with a 10.0 foot ceiling height. We could say the fixture is 7.5 feet above the floor or that it is 2.5 feet below the ceiling. In the first case, our coordinates are: floor, 0.0 feet; light fixture, +7.5 feet; ceiling, +10.0 feet. In the second case, our coordinates are: floor, −10.0 feet; light fixture, −2.5 feet; ceiling, 0.0 feet. We could even call sea level our reference and use the coordinates, floor, +470 feet; light fixture, +477.5 feet; ceiling, +480 feet. Any of these sets of coordinates places the light fixture 7.5 feet above the floor, where no one will bump his head.

The significance of the two possible choices deserves mention. Assigning zero to notch #1 means that the most stable state of the hydrogen atom is taken as zero. Assigning zero to the hypothetical notch #∞ means that the zero on the scale refers to the energy of an electron and a proton separated by an infinite distance. Whichever zero is taken, the energy of the hydrogen atom ground state is 313.6 kcal below (more stable than) the energy of the completely separated proton and electron. In practice, the zero is usually assigned to the separated proton and electron.

Ex. 15-5. From the information that the numbers of *s*, *p*, and *d* orbitals are 1, 3, and 5, how many of the next higher (*f*) orbitals would you expect? Verify your answer by calculating n^2 for $n = 4$ and comparing to your sum of the numbers of *s*, *p*, *d*, and *f* orbitals.

Answer

Since the numbers 1, 3, 5 are the first odd integers, in order, one would expect the next to be 7. If $n = 4$, then $n^2 = 16$. Since the sum of $1 + 3 + 5 + 7$ is 16, the two expectations agree.

Ex. 15-6. Explain why chemists say that boron has three valence electrons and that chlorine has seven. How many valence electrons has fluorine? Oxygen? Nitrogen?

Answer

The electron configuration of boron is

$1s^2\ 2s^22p^1$. The highest partially filled cluster is the $2s2p$ cluster. The exponents show us that three electrons are in this cluster ($2s^22p^1$). Hence chemists say boron has *three* valence electrons, the three in the highest partially filled cluster of energy levels. These are much more easily removed than the remaining electrons.

The electron configuration of chlorine is $1s^2\ 2s^22p^6\ 3s^23p^5$. The highest partially filled cluster is the $3s3p$ cluster. There are seven electrons in the cluster ($3s^23p^5$). Hence the number of valence electrons is 7.

Notice that a chemist decides the valence by looking at the electron configuration, not by looking at ionization energies. The ionization energies show *why* the electrons in the highest energy level cluster determine the chemistry, but it isn't necessary to look up these ionization energies to decide the number of valence electrons.

	Electron Configuration	Number Valence Electrons
Fluorine	$1s^2\ 2s^22p^5$	7
Oxygen	$1s^2\ 2s^22p^4$	6
Nitrogen	$1s^2\ 2s^22p^3$	5

Pr. 1. Which of the following statements concerning light is FALSE?

(a) It is a form of energy.
(b) All photons possess the same amount of energy.
(c) It cannot be bent by a magnet.
(d) It includes the part of the spectrum called X-rays.

Answer

Choice (b) is false.

Pr. 2. Use the energy level diagram in Figure 15-7 to calculate the energy required to raise the electron in a hydrogen atom from level #1 to level #2; from level #1 to level #3; from level #1 to level #4. Compare these energies with the spectral lines shown in Figure 15-3, p. 255.

Answer

In general, the energy required to bring about any change is

$$\begin{matrix}\text{energy}\\\text{required}\end{matrix} = \begin{pmatrix}\text{energy of}\\\text{final state}\end{pmatrix} - \begin{pmatrix}\text{energy of}\\\text{initial state}\end{pmatrix}$$

Using this expression keeps the signs straight. This format might be used if the negative signs bother any of the students.

level change	(energy of final state)	−	(energy of initial state)	=	(energy required)
$1 \longrightarrow 2$	(−78.4)	−	(−313.6)	=	+235.2
$1 \longrightarrow 3$	(−34.8)	−	(−313.6)	=	+278.8
$1 \longrightarrow 4$	(−19.6)	−	(−313.6)	=	+294.0

The changes correspond to the energies of the first three lines in the ultraviolet region of the hydrogen atom spectrum. In your discussion, demonstrate that either the left- or the right-hand energy scale in Textbook Figure 15-7 can be used.

Pr. 3. Your plot in Exercise 15-2 suggested that the energy levels given in Figure 15-7 are systematically related. To explore this relationship further, divide the energy of each level by that of the first level (using the right-hand scale). How are the fractions so obtained related to the numbers of the energy levels?

Answer

When *assigning* this problem, tell the students that decimal fractions are not wanted. Fractions with a numerator of one are most useful.

$$\frac{-313.6}{-313.6} = 1 \qquad \frac{-78.4}{-313.6} = \frac{1}{4}$$

$$\frac{-34.8}{-313.6} = \frac{1}{9} \qquad \frac{-19.6}{-313.6} = \frac{1}{16}$$

$$\frac{-12.5}{-313.6} = \frac{1}{25}$$

Notice that the student is led near the discovery that the fractions so obtained are the reciprocals of the squares of the identifying numbers of the energy levels. Give the students an opportunity to contemplate these fractions before assigning and discussing Sec. 15-1.5.

Pr. 4. Calculate, using frequency units (cycles per second) and Figure 15-3, the lines predicted by the notched beam due to changes beginning in notch #3. Use the complete light spectrum shown in Figure 14-14 (p. 247) to decide in what spectral region these additional lines were found. (It was this sort of prediction that actually led to the discovery of this set of lines.)

Answer

The answer to this question is requested in frequency units so that the student can discover from Figure 14-14 that the predicted lines fall in the infrared region. The student should construct a table as in Exercise 15-2, but should use frequency units. For example, the expression

notch #3 ⟶ notch #4

$$294.0 - 278.8 = 15.2 \text{ kcal}$$

must be converted to the analogous expression in cycles per second by replacing each energy term by the corresponding frequency taken from Figure 15-3.

notch #3 ⟶ notch #4

$$(3.081 \times 10^{15}) - (2.922 \times 10^{15}) = 0.159 \times 10^{15} \text{ cycles/second}$$

Notch Change	Corresponding Frequency Change
$4 \longrightarrow 3$	$(3.081 - 2.922) \times 10^{15} = 1.59 \times 10^{14}$ cycles/sec
$5 \longrightarrow 3$	$(3.149 - 2.922) \times 10^{15} = 2.27 \times 10^{14}$
$6 \longrightarrow 3$	$(3.196 - 2.922) \times 10^{15} = 2.74 \times 10^{14}$

Referring back to Figure 14-14 the student will find these frequencies between the visible and infrared regions. This spectral region is part of the infrared region and is usually called the "near infrared" to indicate that it is that part nearest the visible.

Pr. 5. According to the quantum-mechanical description of the 1*s* orbital of the hydrogen atom, what relation exists between the surface of a sphere centered about the nucleus and the location of an electron?

Answer

This question refers to any *s* orbital. Any particular surface represents positions having equal probability of being occupied by an electron. Be sure that the student realizes that the probability is different from that on another spherical surface.

Pr. 6. What must be done to a 2*s* electron to make it a 3*s* electron? What happens when a 3*s* electron becomes a 2*s* electron?

Answer

Energy must be added to a 2*s* electron in a hydrogen atom to make it a 3*s* electron. In becoming a 2*s* electron, a 3*s* electron must lose energy. It can do so by emitting light or by converting the energy into heat through collisions.

Pr. 7. If the energy difference between two electronic states is 46.12 kcal/mole, what will be the frequency of light emitted when the electron drops from the higher to the lower state?

Planck's constant = 9.52×10^{-14} (kcal sec)/mole.

Answer

$$E = h\nu$$

$$\nu = \frac{E}{h} = \frac{46.12}{9.52 \times 10^{-14}} \frac{\text{kcal/mole}}{\text{(kcal sec)/mole}}$$

$$= 4.84 \times 10^{14} \frac{\text{cycles}}{\text{sec}}$$

Pr. 8. Determine the value of E_n for $n = 1, 2, 3, 4$, for a hydrogen atom using the relation $E_n = -313.6/n^2$. For each E_n, indicate how many orbitals have this energy.

Answer

$$E_n = -\frac{313.6}{n^2}$$

Corresponding to each E_n, there are n^2 orbitals.

n	E_n	n^2
1	−313.6	1
2	−78.40	4
3	−34.84	9
4	−19.62	16

Pr. 9. The quantum mechanical description of the 1*s* orbital is similar in many respects to a description of the holes in a much-used dartboard. For example, the "density" of dart holes is constant anywhere on a circle centered about the bullseye, and the "density" of dart-holes reaches zero only at a very long distance from the bullseye (effectively, at infinity). What are the corresponding properties of a 1*s* orbital?

In the light of your answer, point out erroneous features of the following models of a hydrogen atom (both of which were used before quantum mechanics demonstrated their inadequacies).

(a) A ball of uniform density.
(b) A "solar system" atom with the electron circling the nucleus at a fixed distance.

Answer

The two properties of the "density" of dart holes both have counterparts in the 1*s* orbital of a hydrogen atom. The probability of finding an electron is constant on a spherical surface and corresponds to the constant "density" of dart holes on a circle. Moreover, the probability of finding an electron at a given radius decreases to zero only at an infinite radius, as is also true for the "density" of dart holes.

From these properties, the erroneous features of the two models can be deduced.

(a) The ball of uniform density has the following erroneous features:

1. The electron probability distribution is the same everywhere within the spherical volume of the ball.
2. The electron probability distribution reaches zero at a finite radius and is zero everywhere outside this radius.
3. The feature just mentioned implies the atom has a boundary.

(b) The "solar system" atom has the following erroneous features.

1. The electron probability distribution is concentrated at a single radius and is zero both at smaller radii and at larger radii.
2. The feature just mentioned implies that the atom has a boundary and that the electron never approaches the nucleus.

Notice that the student may be picturing the atom as one of these two models. The first is encouraged by our space-filling models, and its most glaring defect is that it attributes to the atom a boundary surface. The second model is encouraged by representations of atoms commonly seen in advertising (and, perhaps, in pre-high school science courses). The "solar system" model places the electron in a spherical shell, again implying a boundary and a particular electron trajectory, both inconsistent with the quantum mechanical description and experimental facts (see *Background Discussion*). The best use of this problem may come in the class discussion of the erroneous features of models of the atom.

Pr. 10. Name the elements that correspond to each of the following electron configurations

$1s^2$
$1s^2\ 2s^1$
$1s^2\ 2s^22p^1$
$1s^2\ 2s^22p^3$
$1s^2\ 2s^22p^6\ 3s^23p^6\ 4s^1$

Answer

helium	$1s^2$
lithium	$1s^2\ 2s^1$
boron	$1s^2\ 2s^22p^1$
nitrogen	$1s^2\ 2s^22p^3$
potassium	$1s^2\ 2s^22p^6\ 3s^23p^6\ 4s^1$

Pr. 11. Make a table listing the principal quantum numbers (through 3), the types of orbitals, and the number of orbitals of each type.

Answer

Principal Quantum Number	Type of Orbital	Number of Orbitals
1	*s*	1
2	*s*	1
	p	3
3	*s*	1
	p	3
	d	5

Pr. 12. The electron configuration for lithium is $1s^22s^1$, and for beryllium it is $1s^22s^2$. Estimate the approximate ionization energies to remove first one, then a second electron. Explain your estimates.

Answer

The first ionization energy for lithium should be low, about 100 kcal, like that of sodium. The second electron is very difficult to remove because it must be removed from a 1*s* orbital. Hence the second ionization energy is expected to be about 1000 kcal.

In contrast, the first ionization energy for beryllium should be low, about 200 kcal, larger than that of lithium because of the higher nuclear charge. The second ionization process still removes a $2s$ electron, hence is only a little more difficult than removing the first electron, requiring about 400 kcal. The second ionization requires more energy than the first because of the charge of the ion from which the electron is removed.

The experimental ionization energies are:

$$\mathrm{Li}(g) \longrightarrow \mathrm{Li}^{+}(g) + e^{-}(g) \qquad E_1 = 124 \text{ kcal}$$
$$\mathrm{Li}^{+}(g) \longrightarrow \mathrm{Li}^{+2}(g) + e^{-}(g) \qquad E_2 = 1743 \text{ kcal}$$

$$\mathrm{Be}(g) \longrightarrow \mathrm{Be}^{+}(g) + e^{-}(g) \qquad E_1 = 215 \text{ kcal}$$
$$\mathrm{Be}^{+}(g) \longrightarrow \mathrm{Be}^{+2}(g) + e^{-}(g) \qquad E_2 = 419 \text{ kcal}$$

Pr. 13. What trend is observed in the first ionization energy as you move from lithium down the column I metals? On this basis, can you suggest a reason why potassium or cesium might be used in preference to sodium or lithium in photoelectric cells?

Answer

The energy required to remove the first electron and ionize the atom in the column I metals shows a decreasing trend down the column, as indicated by the ionization energy in kcal/mole. See Textbook Table 15-III, p. 268. The reason for this decrease is that the outer electron is farther from the nucleus in each succeeding row and is therefore not as tightly held.

The operation of a photoelectric cell involves the absorption of light and the ejection of an electron to produce an electric current. Only photons with energy greater than the threshold energy needed to pull an electron through the metal surface can cause the photoelectric effect. The lower the ionization energy of the metal, the lower will be this threshold energy. Hence potassium will produce photocurrent over a wider spectral range (extending to lower frequencies) than will either sodium or lithium. Cesium would have an even wider spectral range of sensitivity.

Pr. 14. Consider these two electron populations for neutral atoms

$A \quad 1s^2 \;\; 2s^2 2p^6 \;\; 3s^1;$
$B \quad 1s^2 \;\; 2s^2 2p^6 \;\; 6s^1.$

Which of the following is FALSE?

(a) Energy is required to change A to B.
(b) A represents a sodium atom.
(c) A and B represent different elements.
(d) Less energy is required to remove one electron from B than from A.

Answer: Choice (c) is false.

Pr. 15. How many valence electrons has carbon? Silicon? Phosphorus? Hydrogen? Write the electron configurations for neutral atoms of each element.

Answer

Carbon: 4	$1s^2\ 2s^2 2p^2$
Silicon: 4	$1s^2\ 2s^2 2p^6\ 3s^2 3p^2$
Phosphorus: 5	$1s^2\ 2s^2 2p^6\ 3s^2 3p^3$
Hydrogen: 1	$1s^1$

Pr. 16. The first four ionization energies of boron atoms are as follows:

$E_1 = 191$ kcal/mole;
$E_2 = 578$;
$E_3 = 872$;
$E_4 = 5962$.

Explain the magnitudes in terms of the electron configurations of boron, and deduce the number of valence electrons of boron.

Answer

E_1 removes a $2p$ electron from a neutral atom. E_2 removes a $2s$ electron from an atom with $+1$ charge. E_2 exceeds E_1 both because a $2s$ electron is removed instead of a $2p$ electron and because the atom now has a $+1$ charge.
E_3 removes another $2s$ electron. E_3 exceeds E_2 because the charge on the atom has increased ($+1$ to $+2$).
E_4 removes a $1s$ electron. E_4 exceeds E_3 because a $1s$ electron must be removed instead of a $2s$ electron and because the charge on the atom has increased ($+2$ to $+3$).

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

1. Whenever sodium compounds are volatilized in a burner flame, the characteristic yellow flame color is always present. Account for this in terms of electron energy.

   Answer
   One of the "allowed" jumps for electrons in sodium atoms has a frequency in the yellow part of the visible light spectrum. Quantized "bundles" of energy are emitted as electrons release energy in changing from a condition of higher energy, E_2, to a condition of lower energy, E_1. The "bundle" of light energy is given by

   $$h\nu = E_2 - E_1$$

2. (a) Calculate the energy of the photon emitted if the frequency of the line is 5.2×10^{14} cycles/sec. This is in the yellow region of the visible spectrum. (Planck's constant, $h = 9.52 \times 10^{-14}$ (kcal-sec)/mole.)
   (b) Chemical bonds have energies of about 100 kcal/mole. Would they be dissociated by light of this energy?

   Answer
   $$E = h\nu = \left(9.52 \times 10^{-14}\,\frac{\text{kcal-sec}}{\text{mole}}\right)\left(5.2 \times 10^{14}\,\frac{1}{\text{sec}}\right)$$
   (a) $E = 49.5$ kcal/mole.
   (b) No.

3. Diagram the electron configuration for the highest energy level containing any electrons for each of the following in their lowest energy state. (Use circles to represent orbitals; use diagonal lines to represent electrons. Label orbitals $1s$, $2s$, $2p$, etc.):
   (a) sodium atom, Na;
   (b) sodium ion, Na^+;
   (c) bromine atom, Br;
   (d) bromide ion, Br^-;
   (e) krypton atom, Kr;
   (f) oxygen atom, O;
   (g) nitrogen atom, N.

   Answer

   (a) $3s$: ⊘
   (b) $2s$: ⊗ $2p$: ⊗⊗⊗
   (c) $4s$: ⊗ $4p$: ⊗⊗⊘
   (d) $4s$: ⊗ $4p$: ⊗⊗⊗
   (e) $4s$: ⊗ $4p$: ⊗⊗⊗
   (f) $2s$: ⊗ $2p$: ⊗⊘⊘
   (g) $2s$: ⊗ $2p$: ⊘⊘⊘

4. Is more or less energy required to remove an electron from an atom of gaseous sodium than from an atom of gaseous neon?

   Answer
   Much less for sodium than for neon.

5. Calculate the energy of the photon emitted when the electron in a hydrogen atom changes from the fourth energy level to the second energy level. Refer to Figure 15-7 (p. 258) for energy values. This light appears in the blue part of the visible

spectrum. Express your answer in kcal/mole.

Answer

$$\begin{aligned} h\nu &= E_2 - E_1 \\ &= -78.4 \text{ kcal/mole} - (-19.6 \text{ kcal/mole}) \\ &= -58.8 \text{ kcal/mole} \end{aligned}$$

The negative sign indicates energy is lost by the electron.

6. Suppose there are two electronic transitions, one involving 100 kcal/mole and the other 10 kcal/mole. What frequencies will be observed? In what spectral region will they be seen?

   Answer

$$\frac{100}{9.52 \times 10^{-14}} = 10.5 \times 10^{14}$$

$$= 1.0 \times 10^{15} \frac{\text{cycles}}{\text{sec}}$$

ultraviolet region

$$\frac{10}{9.52 \times 10^{-14}} = 1.0 \times 10^{14} \frac{\text{cycles}}{\text{sec}}$$

infrared region

The electron configurations for the following neutral atoms are given for use in Questions 7–11:

A $1s^2 \quad 2s^2 2p^6 \quad 3s^2$
B $1s^2 \quad 2s^2 2p^6 \quad 3s^1$
C $1s^2 \quad 2s^2 2p^6$
D $1s^2 \quad 2s^2 2p^5$
E $1s^2 \quad 2s^2 2p^3$

7. Which of the electron configurations given above would you expect to have the lowest ionization energy?

   Answer: B.

8. Which of the electron configurations given above would you expect for an inert gas?

   Answer: C.

9. List the five configurations in predicted order of increasing ionization energy (lowest first).

   Answer
   The question is directed to the large-scale upward trend in ionization energy from left to right within a row. Thus the order is *B*, *A*, *E*, *D*, *C*.

10. Predict the configuration that should have the highest second ionization energy.

    Answer: B.

11. Predict the configuration that should have the lowest second ionization energy.

    Answer: A.

12. As atomic number increases in a given row of the periodic table, does ionization energy generally tend to increase or decrease?

    Answer
    It tends to increase, but small decreases often occur when atomic number increases by unity.

13. Two experimental methods of providing an atom with a measured amount of energy to cause ionization are photoionization and electron bombardment. Describe briefly how it is possible to measure ionization energy by each of these methods.

    Answer
    Photoionization: The frequency of light striking the gas sample is increased until it shows a sudden increase in conductivity. This increase is interpreted to mean electrons are available: ionization has occurred. The energy may be calculated by using light of known frequency or wave length.

$$E = h\nu$$

    Electron bombardment: Use easily measured and controlled electrical voltages to accelerate electrons to sufficient energy to produce ionization. Ionization is detected by a large increase in the conductivity of the sample.

14. Consider a neutral atom with the electron configuration

$$1s^2 \quad 2s^2\, 2p^5 \quad 3s^1$$

    Which of the following is *false*?
    (1) The atom has atomic number 10.

(2) The atom is not in the most stable configuration.
(3) The atom must gain energy to change to $1s^2 \quad 2s^2 2p^6$.
(4) The $1s$ and $2s$ orbitals are filled.

Answer
Statement (3) is false, the atom will lose energy as the $3s^1$ electron returns to give the more stable $1s^2 \quad 2s^2 2p^6$ configuration.

15. If there could be but one electron per orbital in an energy level diagram like Figure 15-11 in the Textbook, which of the following would be inert gases?
(1) Element 1 only.
(2) Elements 2, 10, 28 and 60 only.
(3) Elements 2, 10, 18, 36 and 54 only.
(4) Elements 1, 5, 9, 18, 27 and 43 only.

Answer: (4).

CHAPTER

16

MOLECULES IN THE GAS PHASE

Intent and Approach

This chapter and the next present the heart of chemical bonding and how it affects molecular properties. The material is quite important because a good understanding will serve as a strong basis for any further work, both in this course and later.

We have adopted an explanation of chemical bonding that may be new to you. It uses the phrase **electrons are attracted simultaneously to two nuclei** to explain *all* chemical bonds. This means that the same principles that explain the stability of covalent bonds also explain the stability of ionic bonds.

This material should be developed naturally from Chapter 15. The electron orbital filling and the tendency toward inert gas structure can occur in several ways to give molecules that contain "satisfied" atoms, and hence stable structures. The valence orbitals determine the possible structures, since they fix the number of bonds an atom forms and determine the bond angles. A large amount of structural information is condensed in a few simple bonding rules, from which the student should gain substantial predictive ability.

From this chapter the student should learn:

1. why molecules are more stable than separated atoms;
2. to predict how many bonds can be formed by an atom in the first three rows of the periodic table;
3. to predict the approximate bond angles a given atom will display;
4. to predict whether a bond between two atoms will have a polar character (i.e., whether it will be part ionic);
5. to predict whether a molecule will have zero electric dipole because of symmetry; and
6. that multiple bonds can form.

Outline

1. The origin of the stability of a chemical bond is pinpointed. Among the attractive and repulsive electrostatic forces, the electron-nucleus terms *always* furnish the attractive forces. The possibility of simultaneous proximity of one or more electrons to two nuclei accounts for the fact that two atoms are more stable when near one another than when far apart. The possibility of simultaneous proximity is determined by the filling of valence orbitals (16-1.1, 16-1.2).
2. The orbital and electron dot representations of chemical bonding are introduced (16-1.3) and used to discuss the bonding of fluorine atoms (16-1.4).
3. The role of the valence orbitals and electron configuration in fixing the bonding capacities of the second-row elements is treated (16-2.1 to 16-2.6).
4. Ionization energies are used to explain and predict ionic character of bonds (16-3.1, 16-3.2).

5. It is shown that the ionic character of bonds to hydrogen is not predicted correctly from its ionization energy. Section 16-3.3 suggests an *apparent* ionization value of 200 kcal/mole.
6. Section 16-3.4 indicates the relation between electric dipole and bond energy.
7. The bond angles found in the second row fluorides are related to the available valence orbitals (16-4.1 to 16-4.6).
8. The absence or presence of nonzero molecular dipoles is discussed in terms of molecular shape (16-4.7).
9. The existence of multiple bonds (double bonds only) is shown, using O_2 and ethylene as examples (16-5.1, 16-5.2).

New Concepts

1. Chemical bonding can be explained in terms of electron-nucleus attraction.
2. Electron affinity is treated (reduced type).
3. Bonding capacity is related to electron configuration.
4. Covalent and ionic bonds are treated in terms of ionization energies.
5. Molecular shape is related to orbital shape.
6. Molecular dipoles are treated as vector sums of bond dipoles.
7. Electric dipole is related to bond energy.
8. The existence of double bonds is revealed.
9. The possibility of *cis-trans* geometric isomers is shown.

Development

THE COVALENT BOND (16-1)

The Hydrogen Molecule (16-1.1)
Interaction Between Helium Atoms (16-1.2)

To explain the existence of stable bonds, we must go back to the parts of the atom and their properties. This leads us to why chemists are interested in electrical forces. The attractive (and repulsive) forces that exist between the charged parts of the atom offer a basis for "explaining" a chemical bond. The text describes bonding via attraction between orbital electrons and their nuclei. Remind the student that he studied the attractions and repulsions among electric charges in Chapter 5 (5-3.1 to 5-3.5).

A most important point is made on p. 275—the simultaneous attraction of electrons to two protons (nuclei) accounts for the stability of the chemical bond. It is stated in terms of protons because the hydrogen molecule is the example used, but the statement is generally applicable. Generalize the expression to "· · · to two nuclei simultaneously" after the idea is fixed. This idea is visually reinforced in Textbook Figure 16-3, where the overlap region represents the electrons being attracted to both nuclei. This figure also explains some of the limitations to bonding. Each orbital has a fixed capacity—2 electrons. Bonds form through combinations which help supply this maximum for each orbital. Atoms like the inert gases, or others that have attained filled valence orbitals, do not share electrons effectively; there is no available space near the nucleus. Hence bonding is extremely weak—so weak that we say chemical bonding does not occur (van der Waals forces result).

The concept of overlap is a valuable one in chemistry, particularly in reference to covalent bonding. From our simplified point of view, it emphasizes that there must be a region in which electrons occupy valence orbitals of both atoms at once (this is the region in which they are simultaneously attracted to both nuclei). In the most conventional quantum-mechanical approximations the treatment emphasizes this overlap in quantitative terms that have exactly the sig-

Schedule and Related Material

Assignment Prior to Period	Period	Class Work	Ex.	Problems			Topic
				EASY	MEDIUM	HARD	
S 16-1/16-1.2 (pp. 274–278)	1	S 16-1/16-1.2 Film: CHEMICAL BONDING		2, 3	1		The Covalent Bond
S 16-1.3/16-1.4 (pp. 278–281)	2	S 16-1.3/16-1.4		4	5		Representation of Chemical Bonding
S 16-2/16-2.7 (pp. 281–286)	3, 4	S 16-2/16-2.7	1–5	10, 11	6–9		Bonding Capacity 2nd row, Predictions of Molecular Formulas
S 16-3/16-3.4 (pp. 286–290)	5	S 16-3/16-3.4	6		12, 13		Trends in Bond Types, Covalent and Ionic
S 16-4/16-4.7 (pp. 290–294)	6	S 16-4/16-4.7 Film: SHAPES AND POLARITIES OF MOLECULES		15	16–18	14, 19	Molecular Architecture
S 16-5/16-5.2 (pp. 295–297) Expt. 26 (optional)	7	S 16-5/16-5.2. Start Expt. 26, $\frac{1}{2}$ period			20, 21		Molecular Architecture, Double Bonds and Isomers
	8	Finish Expt. 26, $\frac{1}{2}$ period. Review.					

Note: You may schedule the film A RESEARCH PROBLEM: THE INERT(?) GAS COMPOUNDS to be shown along with this chapter or at any time later, as convenient.

nificance implied by the qualitative statement about simultaneous attraction to two positive centers.*

The first sentence in Sec. 16-1.2 can lead to questions which are answered by this argument. The density of helium is 4 g/22.4 liters, and that of hydrogen is 2 g/22.4 liters. Since Avogadro's Hypothesis tells us there are equal numbers of particles in the samples (*P* and *T* are the same), each particle of helium must be twice as heavy as each particle of hydrogen. Or, since hydrogen gas is diatomic, one particle of helium weighs as much as four hydrogen atoms. The atomic weight values show that one atom of helium is four times as heavy as one atom of hydrogen, therefore helium gas is monatomic.

Film, CHEMICAL BONDING,
fits here. See p. 523 for summary.

Representations of Chemical Bonding (16-1.3)

There are numerous ways to represent atoms and their combinations in molecules. Be sure that the students realize these pictures are only pictures—drawn for convenience, and as convenience dictates. This means that different uses may dictate different representations. Don't attach importance to pictorial aspects of the representations (for example, the fact that squares or circles could be used to represent orbitals). Emphasize that these simple pictures are useful because they provide a reliable and easily used basis for predicting formulas of stable compounds. It is appealing to the student that, by learning a few simple operating rules based upon these (or similar) representations, he can avoid the necessity of memorizing thousands of molecular formulas.

Both the electron dot and the orbital representations of chemical bonding retain importance. The orbital representation gives more information but is somewhat more difficult to write. Both are used by practicing chemists as shorthand notations for discussing the chemical bonding in a molecule. The line representation of a chemical bond is another graphic aid. Although it is the one most used in designating structures, it presents the least information about the chemical bonding itself. Be sure to relate the orbital representation to the energy level diagram used in discussing ionization energy (Textbook Figure 15-10, p. 264).

The Bonding of Fluorine (16-1.4)

This section gives the first examples of the orbital and electron dot representations. This is a good place to stress the relation between the energy level diagram and the orbital representation. Students may ask which electrons are in valence orbitals. This question can be answered by referring to the diagram. The discard of the higher orbitals later in the chapter (beginning on p. 283) is justified by the energy gap shown on the energy level diagram. Contrast the electron dot and orbital representations, and emphasize that they are merely two different ways of representing the bonding.

BONDING CAPACITY OF THE SECOND-ROW ELEMENTS (16-2)

The Bonding Capacity of the Second-row Elements (16-2.1 to 16-2.5)

These sections provide a systematic movement across the second row and show how the bonding capacity is fixed by the electron occupancy of the valence orbitals. Of course, the orbital and electron dot representations play an important role here. They were devised specifically to aid in discussing and predicting these bonding capacities.

Notice that the examples introduce successively the complications involved in discussing the trend in bonding capacity. Fluorine is sim-

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* In one approximate treatment of chemical bonding, the "atomic orbital" approximation, the quantitative terms referred to are the so-called *overlap* and *exchange* integrals. In the "molecular orbital" approximation, these are called *overlap* and *resonance* integrals.

plest, since the valence orbitals are filled except for one electron. Oxygen atom, with two electrons less than a filled valence orbital group offers two alternative electron configurations. The $2s^22p_x^22p_y2p_z$ configuration is lower in energy because the electrons are farther apart which provides a basis for examining it in preference to the alternate, $2s^22p_x^22p_y^2$. This same argument suffices for the nitrogen atom, for which the $2s^22p_x2p_y2p_z$ configuration is important whereas the $2s^22p_x^22p_y$ is not. The carbon atom is used to introduce two new ideas. First, bonding one carbon and two hydrogen atoms into CH_2 gives a group which has chemical activity because a valence orbital, a region near the nucleus, remains vacant. Next, to explain the four equivalent bonds found in many carbon compounds, it is postulated that one electron of the pair in the 2*s* orbital is moved to the empty 2*p* orbital. This process involves an energy input not present in oxygen or nitrogen, the energy difference between the 2*s* and 2*p* orbital. This second new idea, called "promoting" an electron, can be discussed with the aid of the energy level diagram.

Now we have all of the ideas necessary to discuss the bonding of the remaining atoms in the gas phase. The compound BH_3 is reactive (forming B_2H_6). We can explain this by observing that boron requires promotion of a 2*s* electron, but even then the reactivity of a vacant orbital remains. Beryllium forms BeH_2, again with the aid of promotion, and again reactive because of empty valence orbitals. Lithium forms LiH, sharing one pair of electrons, but retaining reactivity because of its vacant orbitals.

TREND IN BOND TYPE AMONG THE SECOND-ROW FLUORIDES (16-3)

The Bonding in Gaseous Lithium Fluoride (16-3.1)
Ionic Character in Bonds to Fluorine (16-3.2)

After explaining the underlying idea that *all* chemical bonds are formed for the same reason—a sharing of electrons between two nuclei—introduce the concept that the electrons need not be shared equally. The attraction an atom displays toward electrons varies from atom to atom. Hence the sharing may be more effective (give a lower energy) if it favors one atom somewhat more than the other. Ionization energies provide a basis for showing that atoms hold electrons with varying tightness and for predicting when electron sharing will tend to favor one atom over another to which it is bonded. The atom with the higher ionization energy tends to attract the electrons. Note that this statement applies to bonds containing hydrogen, but only if you use the empirical ionization energy described in Sec. 16-3.3.

Taking ionization energy as a basis for discussing the unequal sharing tendency, we see that the *difference* in ionization energy between two bonded atoms is the influential factor. When this difference is very small or zero, the electrons are shared equally. Such a bond is called covalent. When this difference is very large, the electrons are strongly pulled toward one of the atoms. But among chemical bonds we can expect to find all magnitudes of differences. Hence we can expect to find a continuous range of bond types from covalent to ionic. By no means is it desirable to attempt to classify all bonds as one or the other, covalent or ionic. We must base our discussion of bonding on the recognition of a continuous range of bond types. This is the content of Textbook Table 16-II (p. 289).

The dipole moment is introduced somewhat gingerly. The idea of "moment" is never introduced, the term electric dipole being used exclusively. Experiments do not reveal how much charge is separated by what distance; they only show the product of charge times distance. The "moment" idea is difficult under any circumstances and is even more confusing when there is no basis for deciding how far apart the separated charges really are. In this first treatment, it is sufficient to speak of the electric dipole and to picture it as centered on the atomic centers. The important idea to emphasize is that, as ionic bond character increases, charge separation (hence, electric dipole) increases.

Ionic Character in Bonds to Hydrogen (16-3.3)

This section is calculated to give the student a consistent basis upon which to estimate the ionic nature of bonds. Without a special handling of hydrogen, incorrect conclusions will be made.

Bond Energies and Electric Dipoles (16-3.4) (reduced type)

One object of this section is to show why chemists are concerned about the extent of the bond's ionic character. So far in the chapter we have stressed the common basis for all bonds, but now we shall begin to consider whether the bond is expected to be covalent, partially ionic, or largely ionic. The more ionic its character, the stronger will be the bond. The difference in ionization energies, $E_1(Na) - E_1(Cl)$, is taken to be a qualitative index of this ionic character (provided hydrogen is assigned an empirical "effective" ionization energy). In your discussion of this subject, be sure that the student is not led to expect an "either-or" relation between covalent and ionic bonds. Instead, let him realize that we encounter a continuous range of bond types from one extreme to the other, with the extra stability due to ionic character also ranging from zero to many tens of kilocalories.

You will recognize, in the calculations used to fill in Textbook Table 16-III, the Pauling definition of electronegativity. This concept is not introduced specifically, but the more able student may be told about it. An extensive section of the *Background Discussion* is devoted to this subject (pp. 531–534).

MOLECULAR ARCHITECTURE (16-4)

Orbitals and Shapes of Molecules (16-4.1 to 16-4.6)

These sections provide a basis for predicting qualitatively the shapes of molecules. Treat the correlations as empiricisms, emphasizing that they are useful because they work. We do not wish to say that H_2O *must* be a bent molecule *because* of the orbitals used in its bonding. Instead we note the correlation between the use of two *p* orbitals in the bonding and the resulting bent structure. From this correlation we can predict that a molecule will be bent if the electron configuration of the central atom provides only these two orbitals for bonding. The bonding in the molecule is then called p^2, a convenient name because it tells us not only which type of orbitals are involved but the molecular structure as well.

The perpendicularity of *p* orbitals of the hydrogen atom provides a reasonable basis for discussing bent structures for H_2O and F_2O (and pyramidal structures for NH_3 and NF_3). It does not prove that the structures must be bent (or pyramidal); indeed, the structures can be explained in quite another way (see the *Background Discussion*).

The empiricism involved in discussing molecular architecture is most important in treating the tetrahedral bonding of carbon and the planar trigonal bonding of boron. Here again we find that an atom can bond to four other atoms when one *s* and three *p* orbitals are available. When this is the case, we find that these bonds are tetrahedrally oriented. Hence we can associate with confidence the label sp^3 (indicating that these four orbitals are half-filled) and the tetrahedral geometry. This is true for unsymmetrical compounds, such as CH_3F, as well as for CH_4 and CF_4.

A set of Cartesian coordinates is helpful for demonstrating the spatial arrangements of the bonds. Two balloons tied together make a convincing *p* orbital, and two or three of these pairs can be used together to illustrate p^2 and p^3 orbital arrangements. Ball and stick models of NF_3, CF_4, and BF_3 are more helpful than blackboard drawings.

Molecular Shape and Electric Dipoles (16-4.7)

In a molecule more complicated than a diatomic molecule, there must be two or more chemical bonds. Each of these bonds can have associated with it some ionic character (depending upon the atoms connected), hence it is reasonable to attribute an electric dipole to each bond. The total molecular electric dipole can then be discussed in terms of these individual "bond dipoles." This is regularly done because a significant understanding of molecular dipoles results from making simple vector sums of hypothetical "bond dipoles."

According to this view, two factors determine the molecular dipole: the degree of ionic character of individual bonds and the geometrical way in which the bond dipoles are oriented relative to each other. For example, the bonds in both F_2O and BeF_2 show some ionic character, but the difference in ionization energies indicates that the bonds in BeF_2 are more ionic. The molecular dipole, however, is the vector or geometrical sum of two bond dipoles in each molecule. In BeF_2, the linear arrangement results in exact cancellation and in a net zero molecular dipole (as shown in Textbook Figure 16-15, p. 294). For F_2O, the bent structure leaves a net molecular dipole directed along the bisector of the angle formed by the two bonds (as shown in Textbook Figure 16-17, p. 295).

The more complicated examples, BF_3 and CF_4, involve the same principles used in the F_2O-BeF_2 comparison. Discussion of BF_3 may be aided by using a travel analogy. The result of two straight-line airplane flights can be likened to a vector sum. For BF_3, the succession of three flights, properly directed, brings the traveler back to his starting place. It is probably not worthwhile trying to apply such a travel analogy to a non-planar molecule (though it can be done).

Film, SHAPES AND POLARITIES
OF MOLECULES,
fits here. See p. 523 for summary.

DOUBLE BONDS (16-5)

Double Bonds and Isomers (16-5.1 and 16-5.2)

The student should have little trouble grasping the basic idea of double bonds, since this type of bonding is just an extension of what the student has been drilling on. To form double bonds there must be (a) enough empty orbitals for two pairs of electrons to be shared and (b) appropriate geometry. Because the second factor is often not completely fulfilled, double bonds are more reactive—that is, they "break" more easily to form other bonds.

The rigidity of the double bond in ethylene can be clarified as follows. Use your forefingers to represent orbitals from two atoms. Touch the tips of these fingers to represent overlap, reminding the student that this is an energetically favored situation. Now twist one hand, keeping your fingertips in contact. Overlap is not affected, hence rotation can occur around a single bond (as, for example, in ethane). Now use your forefingers and middle fingers to represent two pairs of orbitals forming a double bond. Show that rotation about one of the bonds "breaks" the other bond. Since rotation can occur only with the absorption of enough energy to break the other bond, there is an energy barrier to the rotation. This barrier causes the double bond structure to be rigid. We discover empirically that this rigidity favors a planar structure in the compound ethylene.

If you cover the subject of carbon–carbon isomerism (reduced type), you will find that ball and stick models aid in classroom discussion. This is the student's first contact with the term "isomers"—different compounds having the same molecular formula. This is an important idea, and the fact that isomers can be separated and have different chemistry should be stressed. If Expt. 26 is done it will provide a basis for discussion, since the student has opportunity to measure some of the properties of these compounds. More discussion can be based upon consideration of the physical properties, including the expected molecular dipoles of the three dichloroethylene isomers shown in Textbook Figure 16-18 (p. 297).

	Density (g/ml)	m.p. (°C)	b.p. (°C)
$CH_2{=}CCl_2$	1.250	—	31.7
cis-$CHCl{=}CHCl$	1.291	−80.5	60.1
trans-$CHCl{=}CHCl$	1.265	−50	48.4

Emphasize that these substances are *different* compounds only because their structures differ. This shows dramatically how important molecular structure is in chemistry.

Expt. 26, INVESTIGATION OF PROPERTIES OF A PAIR OF *CIS-TRANS* ISOMERS (Optional), fits here. See p. 519 for guide.

EXPERIMENT 26 INVESTIGATION OF SOME OF THE PROPERTIES OF A PAIR OF *CIS-TRANS* ISOMERS

(*Optional—appropriate with material in reduced type*)

PURPOSE. To illustrate the different properties of two substances having the same molecular formula but different molecular structures. To review the use of melting point for characterization and the use of titration for quantitative analysis.

PRELAB DISCUSSION. Tell the student that empirical formulas can be determined in the lab and are found to be CHO for both these acids. Their properties, however, are different. Remind students of the formulas of acetic acid and formic acid, both of which have been given in the Textbook, and point out that the —COOH group accounts for acid properties. Have models available.

TIMING. Assign this experiment at the end of Chapter 16 if material on *cis-trans* isomers is included.

EQUIPMENT NEEDED (PER INDIVIDUAL OR GROUP)

9 g maleic acid, reagent grade (to use anhydride see lab hint 4)
15 ml 12 *M* HCl
0.1 g fumaric acid (if desired for melting point confirmation)
6 cm magnesium ribbon
0.2 g sodium carbonate (solid, either anhydrous or hydrate)
Orange IV (see Expt. 18) or *p*H paper (see lab hint 1)
100 ml 0.5 *M* NaOH, phenolphthalein indicator, and titration apparatus (one 50 ml buret)
balance (±0.01 g)
ring stand, ring, screen
burner
aspirator (not essential)
melting point apparatus: flask, stopper, thermometer, capillary tube, oil (see lab hint 2 and *Precautions*)
100 ml beaker
250 ml beaker
25 ml graduate
watch glass
funnel and filter paper
wash bottle
2 test tubes (18 × 150 mm)
3 test tubes (13 × 100 mm)

TIME REQUIRED. This experiment requires $1\frac{1}{2}$ periods, split between two days to allow for drying after (f). This time is sufficient if titration is omitted, but $2\frac{1}{2}$ periods are needed if the titration is included. Convenient stopping points: In Part I, after (b), after (e), after (f) (recommended); in Part II, after (a) or after (b).

PRECAUTIONS. Avoid breathing HCl vapors in (b) of Part I. Remind students not to exceed the limit of the thermometer during the melting point determination. This will also prevent excessive heating of the vegetable oil. If thermometers that read to 300°C are used, silicone oil should be used instead of vegetable oil to avoid danger of fire. A silicone vacuum pump oil is excellent. Warn the student about handling the melting point apparatus when it is hot.

LABORATORY HINTS

1. Have a set of standards ranging from *p*H 1 to 4 for whatever indicator is used.
2. Demonstrate the use of the melting point apparatus and the filling of capillary tubes. A two foot length of 6 mm glass tubing, down which the capillary tube may be dropped, helps to get the powder well packed.

3. In the titration, 1.0 gram of acid is 0.0086 mole and requires 0.017 mole of NaOH. This means 34 ml 0.50 *M* NaOH are needed per titration.
4. Crystallization should occur in I c without cooling. Nevertheless, the solution should be cooled to increase the yield of solid. If difficulty is experienced here, this may be due to insufficient heating in Part I b. To convert maleic anhydride to the acid, add 300 grams to 400 cc of hot water, stir to dissolve, cool, and filter. Dry the acid gently (aspirator at 30–40°C), check its melting point, and store it in the dark. Prepare the acid only a few days before it is to be used.

PHYSICAL DATA

	Maleic (*cis*)	Fumaric (*trans*)
Melting Point	130.5°C (decomposes at 135°C)	287°C (boils at 290°C and sublimes at 200°C)
Solubility in water		
at 25°C;	78.8 g/100 g	0.70 g/100 g
at 97°C	393 g/100 g	9.8 g/100 g
Density	1.59 g/ml	1.64 g/ml
*p*H of solution	0.1 *M*, ~1.4	
	0.06 *M*, ~1.5	saturated (~0.06 *M*), ~3
K_1	1.2×10^{-2}	1.0×10^{-3}
K_2	6×10^{-7}	4×10^{-5}

RESULTS. Emphasize the need to summarize differences and similarities, as indicated in the Laboratory Manual. Be sure that either you do the titration as a demonstration or assign it to some students if all are not doing it.

ANSWERS TO QUESTIONS

1. Assuming that equilibrium concentrations were achieved in Part I, which acid would you classify as the more stable with respect to the transformation of one into the other?

   Answer: Since 5–6 grams of fumaric acid are obtained from 6 grams of maleic acid, fumaric acid must be more stable than maleic acid.

2. What do each of the following experiments contribute to your knowledge of the structure of each isomer?
   (a) The reactions with magnesium and with sodium carbonate.
   (b) The titration data, that is, the number of moles of base required to titrate each acid.
   (c) The reactions of solutions of each acid with an indicator.
   (d) The melting point determination.

   Answer:

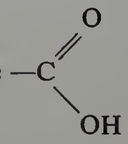
   (a) These reactions indicate that each is an acid. Both reactions are faster with maleic acid.
   (b) The titration data show that, for each compound, two moles of H^+ are available for each mole of the acid.
   (c) The indicator shows that the *p*H for maleic acid solution is lower (*p*H ~1.5 for

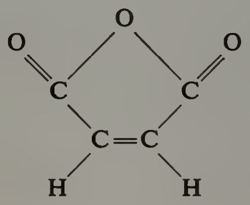
0.06 *M* maleic acid and ~3 for 0.06 *M*, a saturated solution, of fumaric acid). This is due to the higher first dissociation constant of the *cis* form.

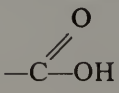
(d) The difference in melting points indicates that the two are different compounds.

The validity of the results obtained in (c) of Part II depends upon the complete removal of HCl, by washing and/or evaporation, from the fumaric acid.

3. Maleic acid can lose a molecule of water from each molecule of acid when its two carboxyl groups react to form an anhydride. Which structural isomer, *cis* or *trans*, do you predict it is? Fumaric acid cannot do this. Explain.

Answer: Because of the proximity of the  $-\mathrm{C}(=\mathrm{O})\mathrm{OH}$ groups in the *cis* form, one would predict that this isomer would form an anhydride. This fact enables the student to predict that maleic acid is the *cis* form and fumaric is the *trans* form. The anhydride has the structure



This is not normally possible for the *trans* form, because the  $-\mathrm{C}(=\mathrm{O})-\mathrm{OH}$ groups are not adjacent. Maleic acid forms the anhydride and then, on hydrolysis, returns to maleic acid. Under vigorous treatment the fumaric acid can form an anhydride, but it is the same anhydride obtained from maleic acid, and it hydrolyzes to give maleic acid instead of the starting material, fumaric acid. Vigorous treatment causes isomerization to maleic acid and then formation of the anhydride.

A QUESTION TO WONDER ABOUT. Compare the molecular models of the *cis* and *trans* isomers. Considering their structure, attempt to account for observed differences in solubility and melting point.

Discussion: In Chapter 17 we discuss the formation of intramolecular hydrogen bonds in maleic acid. The fumaric acid forms only intermolecular bonds. Thus maleic acid can form only half as many intermolecular H bonds and a weaker, less completely interlocked crystal structure results. The less stable crystal has a lower melting point and a higher solubility in water.

Molecular shape also influences physical properties. With reference to solubility, the more extended *trans* form probably breaks up the stable hydrogen bond network of water more than does the compact *cis* form. This would tend to make the solubility of the *trans* form lower. On the other hand, the *trans* structure can form hydrogen bonds more extensively because its hydrogen bonding groups are both exposed. This factor works in the other direction, tending to increase the solubility of the *trans* form. The dominant effect is undoubtedly the hydrogen bonding in the crystals.

For purposes of further discussion, some data on other *cis-trans* isomers follows. It may be noted that the melting points of the *trans* form are consistently higher. Solubility and density do not follow a pattern.

	m.p. (°C)	Solubility (g/100 g H_2O at 25°C)	Density (g/ml)
Crotonic acid (*trans*)	72	8.3	1.02
Isocrotonic acid (*cis*)	15	40	1.03
Elaidic acid (*trans*)	51	—	0.85
Oleic acid (*cis*)	14	—	0.90
Cinnamic acid (*trans*)	133	0.1	1.25
Allocinnamic acid (*cis*)	68	0.94	1.28

POSTLAB DISCUSSION. This experiment provides an opportunity to relate observed chemical behavior to molecular structure and to review several techniques. The idea that a catalyst can be used to lower the activation energy for the maleic acid to fumaric acid equilibrium, the use of melting points in identification, and the information gained by titration were all studied earlier and used here. With the evidence available, the student can relate the behavior of these isomers to their structure. It should be made clear, however, that, although these data are all consistent with the proposed isomerization reaction, they do not provide decisive evidence either that this reaction did occur or that the structures are as shown in Figure 26-1. The most valuable experiment to show that the postulated reaction occurred (and that HCl acted only as a catalyst) would be a molecular weight determination. A determination of the second ionization constant would furnish additional evidence to show that the reactant is the *cis* form because it is generally true that an intramolecular hydrogen bond lowers the second ionization constant by a factor of 10–100.

The experiment helps establish the "reality" of *cis-trans* isomerism and of the relation between structure and properties. It also serves as an introduction to the hydrogen bond discussion in Chapter 17 and gives more experience with organic compounds as an introduction to Chapter 18.

Supplementary Material

Articles

1. C. R. Noller, "A physical picture of covalent bonding and resonance in organic chemistry," *J. Chem. Education*, 32, 23 (1955).* Introduces the molecular orbital view and explains bonding and resonance in these terms. Excellent for teachers; suitable for very good students.
2. G. E. Kimball, and E. M. Loebl, "A quantum mechanical theory of complex ion formation," *J. Chem. Education*, 36, 233 (1959). Explains bonding in terms of quantum mechanics. Good background reading for teachers and good students.
3. I. Cohen, "The shape of the 2*p* and related orbitals," *J. Chem. Education*, 38, 20 (1961). Corrects the erroneous view conveyed by most contemporary textbooks that the 2*p* electron probability distribution is well represented by two spheres in contact.
4. A. B. Burg, "Bonding in boron compounds and in inorganic polymers," *J. Chem. Education*, 37, 482–490 (1960). Displays the reactivity associated with a vacant valence orbital in terms of boron chemistry. Good supplementary reading for the interested student.

Books

1. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press (1960). This third edition retains the basic content and clarity of the original 1938 version. The book remains valuable because of its strong influence on the advances made in the theory of chemical bonding within the last two decades. This book is written in such a way that much of it can be assimilated by an outstanding student.
2. M. J. Sienko and R. A. Plane, *Chemistry*, McGraw-Hill, New York (1961). Chapter 4, pp. 77–99, provides excellent supplementary reading for the above-average student.
3. J. A. A. Ketelaar, *Chemical Constitution*, Elsevier Publishing Co. (distributed by Van Nostrand, Princeton) (1958). Chapter III is an excellent fundamental article for teachers. Although it presents some mathematical detail, readability is not impaired even if the mathematics is not meaningful to the reader. Unfortunately it does not connect ionic and covalent bonding. Too advanced for the student.
4. C. A. Coulson, *Valence*, Oxford University Press, New York (1951). Contrasts the atomic and molecular orbital points of view. Excellent background reading for the teacher who can cope with the mathematics.
5. D. J. Cram, and G. S. Hammond, *Organic Chemistry*, McGraw-Hill, New York (1959). Chapter 6 presents a good treatment, with clear figures, of rotation around single and double bonds and of *cis-trans* isomerism. Useful for selected students, but only after they have studied Chapter 18. Good background reading for teachers.
6. G. M. Barrow, *Physical Chemistry*, McGraw-Hill, New York (1961), pp. 287–303. A fundamental discussion of dipole moment. Suitable for teachers.
7. G. M. Barrow, *The Structure of Molecules*, Benjamin, New York (1963). Good supplementary reading for teachers and students.
8. G. E. Ryschkewitsch, *Chemical Bonding and the Geometry of Molecules*, Reinhold, New York (1963). Good supplementary reading for teachers and students.
9. H. H. Sisler, *Electronic Structure, Properties, and the Periodic Law*, Reinhold, New York (1963). Good supplementary reading for teachers and students.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE.

CHEMICAL BONDING A CHEM Study film

Running Time: 16 minutes

This is another film made in collaboration with Professor G. C. Pimentel, University of California, Berkeley. It makes use of and extends the concepts developed in the film THE HYDROGEN ATOM (see p. 485), applying to the formation of a molecule of hydrogen and emphasizing the cause of bond formation as discussed in the Textbook. Extensive use of animation helps correct the impression of electron immobility which might be gained from the static sketches of molecules required in the Textbook.

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* Included in "Supplementary Readings for Chemical Bond Approach," reprints from the *J. Chem. Education*.

SHAPES AND POLARITIES OF MOLECULES

A CHEM Study film

Running Time: 18 minutes

This film was made with the collaboration of Professor David Dows, University of Southern California, Los Angeles. Observations of electrical effects lead to the concept of electrical polarity. There are two types of results for covalent substances: some show very marked interactions with electric charges, whereas others give little effect. A model is developed that is based on considerations of bond polarity and molecular symmetry which correlate the electrical effects and their change as temperature is varied. The molecular dipole model is extended to explain differences in solubility, conductivity, and chemical reactivity.

A RESEARCH PROBLEM: THE INERT(?) GAS COMPOUNDS

A CHEM Study film

Running Time: 20 minutes

This film shows the inception of an actual research problem, its pursuit via discussion, equipment assembly, and experimentation to the point of the first successful identification of krypton difluoride. The film ends by reaching a tentative conclusion and outlining further tests. Professor G. C. Pimentel and Dr. James Turner of the University of California, Berkeley, collaborated on this film.

The central idea of this film is to show how new knowledge is gained and to convey the excitement inherent in the process. With this theme, the film does not have to be shown at a particular point in the course; it can be shown in Chapter 16 or later as time is available.

Background Discussion

Though some gases, the inert gases, are found to be monatomic, most are not. Gaseous hydrogen contains molecules of H_2, not separate atoms of H; chlorine contains molecules of Cl_2, not separate atoms of Cl. Turning to compounds, we find gaseous molecules containing oxygen and hydrogen with formulas H_2O and H_2O_2, whereas nitrogen and hydrogen form molecules with formulas NH_3 and N_2H_4. What holds these clusters of atoms together? Why are these particular molecular formulas observed but not others? It is the purpose of this chapter to answer such questions, and it is the purpose of this background section to provide a deeper understanding of the answers given. Depth of understanding is particularly needed in this chapter. First, the chemistry teacher needs a deep insight into the origin of chemical bonding because of its all-pervading importance in chemistry. Second, a modern treatment of this subject must eliminate a large amount of obsolescent but traditional material. You, and other able teachers, will insist upon justifying arguments that guarantee that the present treatment is valid and has real advantages over alternate treatments to be found in other textbooks.

THE EMPHASIS UPON ENERGY

In gaseous hydrogen at room temperature, the number of free hydrogen atoms present is minute—at equilibrium, the atoms are almost completely combined in particles of formula H_2. Chemists find that two factors fix equilibrium conditions: randomness and energy. Randomness tends to be maximized, whereas energy tends to be minimized. The tendency toward maximum randomness favors free atoms. (A high degree of organization exists in a system arranged such that each atom is located at just the right distance from a neighbor.) Since randomness favors H atoms, not H_2 molecules, the explanation of the existence of H_2 must lie in the other factor, the tendency toward minimum energy. Two hydrogen atoms remain together in H_2 because the energy is lower than if they separate. Thus we emphasize energy considerations in our explanation of the stability of certain molecular aggregates.

POTENTIAL ENERGY VERSUS KINETIC ENERGY

A stable bond will form between two (or more) atoms if the energy is lower when the atoms are in proximity. This statement refers, of course, to the total energy—that is, the sum of kinetic energy and potential energy. The kinetic energy can be attributed almost wholly to electron motion, but there is some in the vibrational movements of the nuclei. The potential energy consists of several parts: electron–electron repulsions, nucleus–nucleus repulsions, and electron–nucleus attractions. To account for chemical bond formation, we would like to discover which of these interactions help lower the energy as the atoms come together and which do not.

We are aided here by a very general theorem, equally valid in classical mechanics and in quantum mechanics, called the Virial Theorem. In the form given below, it applies to any system of particles interacting with electrostatic forces (and hence to any molecule). The theorem is derived directly (and rather simply) from Newton's second law and from the statement that all forces in the system depend upon particle separation as $1/r^2$. There results a connection between average kinetic energy, $(\overline{\text{K.E.}})$ and the average potential energy, $(\overline{\text{P.E.}})$.

$$(\overline{\text{P.E.}}) = -2(\overline{\text{K.E.}}) \qquad (1)$$

Equation (*1*) states that the potential energy is twice as large as the kinetic energy *and opposite in sign*. We can use this relationship to express total average energy, $\bar{E}$, in terms of either potential or kinetic energy.

$$\bar{E} = (\overline{\text{P.E.}}) + (\overline{\text{K.E.}}) = -2(\overline{\text{K.E.}}) + (\overline{\text{K.E.}})$$
$$= -(\overline{\text{K.E.}})$$

or

$$\overline{E} = (\overline{\text{P.E.}}) + (\overline{\text{K.E.}}) = (\overline{\text{P.E.}}) - \tfrac{1}{2}(\overline{\text{P.E.}}) = \tfrac{1}{2}(\overline{\text{P.E.}})$$

giving

$$\overline{E} = \tfrac{1}{2}(\overline{\text{P.E.}}) \qquad (2)$$

we also have

$$\overline{E} = -(\overline{\text{K.E.}}) \qquad (3)$$

Equation (*2*), or (*3*), can be applied to a pair of separated atoms, *A* and *B*, and also to the two atoms bound as a molecule, *AB*.

$$\begin{aligned} \overline{E}_A &= \tfrac{1}{2}(\overline{\text{P.E.}})_A \\ \overline{E}_B &= \tfrac{1}{2}(\overline{\text{P.E.}})_B \\ \overline{E}_{AB} &= \tfrac{1}{2}(\overline{\text{P.E.}})_{AB} \end{aligned}$$

The change in energy as *A* and *B* come together is then

$$\begin{aligned} \Delta\overline{E} &= \overline{E}_{AB} - (\overline{E}_A + \overline{E}_B) \\ &= \tfrac{1}{2}(\overline{\text{P.E.}})_{AB} - [\tfrac{1}{2}(\overline{\text{P.E.}})_A + \tfrac{1}{2}(\overline{\text{P.E.}})_B] \\ &= \tfrac{1}{2}[(\overline{\text{P.E.}})_{AB} - (\overline{\text{P.E.}})_A - (\overline{\text{P.E.}})_B] \end{aligned}$$

or

$$\Delta\overline{E} = \tfrac{1}{2}\Delta(\overline{\text{P.E.}}) \qquad (4)$$

we also find

$$\Delta\overline{E} = -\Delta(\overline{\text{K.E.}}) \qquad (5)$$

Equations (*4*) and (*5*) are most pertinent to a consideration of chemical bonding. If a stable bond is formed in the reaction of *A* and *B*, then $\Delta\overline{E}$ must be negative; heat must be evolved; and the products must contain less energy than the reactants. In order for $\Delta\overline{E}$ to be negative, the change in average potential energy must be negative, since $\Delta\overline{E} = \frac{1}{2}\Delta(\overline{\text{P.E.}})$. *A bond can form when two atoms approach only if the potential energy is lowered.* Equation (*5*) adds that if the potential energy drops, the kinetic energy must rise, $-\Delta\overline{E} = +\Delta(\overline{\text{K.E.}})$. Hence the change in kinetic energy works *against* bond formation, but because the change of the potential energy is twice as large, the potential energy dominates.

Thus we see that in forming a stable molecule, the potential energy lowers the total energy, and the kinetic energy raises the total energy. The potential energy holds the atoms together in opposition to the kinetic energy, which favors separating them. To discover, then, a valid explanation of why bonds form, we must understand the factors that determine the potential energy change as atoms come together. If we can discover the conditions that cause the potential energy to be lowered, we have discovered conditions necessary for chemical bonding.

THE POTENTIAL ENERGY TERMS

The Schroedinger Equation was presented to show that the potential energy function merely expresses the classical electrostatic interactions (see p. 493). Hence we can readily write down the contributions to the average potential energy. If we consider a molecule *AB*, there will be three types of contributions.

Electron–electron Repulsions

Electrons have the same charge, hence work must be done to bring electrons close together. There are some electron–electron repulsions in atom *A* and others in atom *B*. As the atoms approach each other, these are still present, but there are also *new* electron–electron repulsions. When the electrons of atom *A* get close enough to feel the electrons of atom *B*, the average potential energy rises. Electron–electron repulsions cannot lower the potential energy as atoms come together.

Nucleus–nucleus Repulsions

Nuclei have the same charge, hence work must be done to bring them close together. Again we have a term that raises $(\overline{\text{P.E.}})$. Nucleus–nucleus repulsions cannot lower the potential energy as atoms come together.

Nucleus–electron Attractions

Electrons and nuclei have opposite charge, therefore they attract each other, and energy is released as electrons move closer to a nucleus. There are electron–nucleus attractions in atom *A* and others in atom *B*, but in the molecule there are *new* electron–nucleus interactions.* These new interactions lower the potential energy as

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* This statement does not mean that the interactions possessed by separated atoms are unaltered in the molecule. When rather slight electron redistribution occurs on bond formation (as in the covalent bond), these terms do not change much. The case in which the redistribution is large is considered in the next section.

the atoms come together. Since they are the only new terms that can lower potential energy, they must be responsible for the stability of a chemical bond. *The lowering of the potential energy on bond formation results from the fact that electrons are attracted to both nuclei at once rather than to only one of the nuclei at a time, as in the separated atoms.*

The argument can be reviewed in four steps:

1. The average energy change, $\Delta\overline{E}$, *must be negative* for a stable bond to form.
2. *If* $\Delta\overline{E}$ *is negative,* $\Delta(\overline{P.E.})$ *must be negative.* By the Virial Theorem, $\Delta\overline{E}$ and $\Delta(\overline{P.E.})$ have the same sign (as shown in expression *2*), whereas $\Delta(\overline{K.E.})$ has the opposite sign (as shown in expression *3*).
3. *Electron–nucleus attractions must account for a negative value of* $\Delta(\overline{P.E.})$. The other contributions to the potential energy of the system make $\Delta(\overline{P.E.})$ go *up* as atoms come together.
4. Electron–nucleus attractions can result in a negative value of $\Delta(\overline{P.E.})$ because each electron is attracted simultaneously to two positive nuclei in the molecule, but only to one nucleus in the separated atoms.

ELECTRONS SIMULTANEOUSLY ATTRACTED TO TWO NUCLEI: A GENERAL EXPLANATION OF BONDING

We need to investigate whether this argument is generally applicable. For example, the arguments 3 and 4 could, conceivably, not apply to ionic molecules. It is at least conceivable that the drastic redistribution of electrons in ionic bond formation could reduce the net magnitude of the electron repulsions even though there are more of them than there were prior to bond formation. It is also conceivable that the contribution of the simultaneous attraction of an electron to two nuclei is not an important factor at all. To investigate these possibilities, let us consider the formation of one of the most ionic diatomic molecules known, LiF, from a separated lithium atom and a fluorine atom. Fortunately we can consider this bond formation in a hypothetical series of steps for which we know, experimentally, all of the energy values.

$$\mathrm{Li}(g) \rightleftharpoons \mathrm{Li}^+(g) + e^-(g) \qquad \Delta H = +124\ \text{kcal} \qquad (6)$$

$$\mathrm{F}(g) + e^- \rightleftharpoons \mathrm{F}^-(g) \qquad \Delta H = -83\ \text{kcal} \qquad (7)$$

$$\mathrm{Li}^+(g) + \mathrm{F}^-(g) \rightleftharpoons \mathrm{LiF}(g) \qquad \Delta H = -178\ \text{kcal} \qquad (8)$$

$$\text{Net reaction:}\quad \mathrm{Li}(g) + \mathrm{F}(g) \rightleftharpoons \mathrm{LiF}(g) \qquad \Delta H = -137\ \text{kcal} \qquad (9)$$

First, let us consider reaction (*8*), the formation of a bond between gaseous Li^+ and gaseous F^-. Since the electron distribution of $\mathrm{LiF}(g)$ is quite similar to that of a pair of spherical ions in proximity, *no large electron redistribution is involved in reaction (8).* Hence the entire discussion of the previous section is applicable. The electron–electron repulsions present in the separated ions are also present in the molecule, *in addition to some new ones.* These new repulsions work against bond formation. The nucleus–nucleus repulsion also works against bond formation between Li^+ and F^-. The electron–nucleus terms must account for the energy lowering as Li^+ and F^- are brought together. Since electron distribution doesn't change much during reaction (*8*), the electron–nucleus attractions of the ions don't change much as the ions come together. Hence the energy must drop, because, in the molecule, the electrons of each ion are also close to the nucleus of the other ion. In particular, the largest contribution is due to the electrons of F^-, which are near the fluorine nucleus, simultaneously attracting the lithium nucleus. Thus the energy lowering in reaction (*8*) is clearly due to the simultaneous placement of electrons near two nuclei.

It only remains to investigate the energy effects required to obtain the electron distribution of Li^+ and F^-. This is the sum of the energies of reactions (*6*) and (*7*), +41 kcal. We see that energy is *absorbed* in achieving the electron distribution of Li^+ and F^-. Hence the bond formation between a neutral lithium atom and a neutral fluorine atom must be explained in terms of the energy drop in reaction (*8*), which we have seen is caused by simultaneously placing electrons near two nuclei.

To extend the generality of this argument, observe that the remarks in this and the previous section need not be restricted to a diatomic molecule, nor even to a small molecule. The quantum-mechanical equation is of the same general form for solid sodium chloride and for solid sodium metal as for gaseous Cl_2. Hence the explanation posed here is applicable to all bonds, strong or weak, in simple or complex systems.

This discussion must not be interpreted to mean that it is useless to recognize different bond types. Despite the fact that the same potential energy terms account for bonding in LiF as in F_2, it is a decided advantage to recognize that in gaseous LiF the complicated mathematics describing the molecule can be well approximated in terms of the interaction of two singly charged ions. Even more important, with our present mathematical skills, we would be able to calculate very little about solid lithium fluoride *without* applying this approximation.

Even van der Waals effects are covered by this discussion. The difference between chemical bonding and van der Waals attractions is understandable if we consider how close two atoms with filled valence orbitals can approach each other. Two helium atoms attract each other only weakly, not because different interactions are present, but because the electrons near one nucleus can't get very close to a second nucleus. Again, this is not a denial of the advantage in seeking acceptable approximations stated in terms of tractable mathematics to treat this type of weak interaction (e.g., the London treatment). Yet it gives insight into the growing reluctance among chemists to make ironclad differentiations between chemical interactions and so-called physical interactions.

THE SIMPLEST MOLECULES, H_2^+ AND H_2

The Schroedinger equation for a molecule is much easier to write than it is to solve. In general, a many-particle problem can be treated only by successive approximations. Only within the last few years have accurate calculations become available for molecules even as simple as lithium hydride, which has only two nuclei and four electrons. We can expect this calculational obstacle to be bypassed gradually as digital computers become available.

Fortunately, the calculations for the two simplest molecules, H_2^+ and H_2, are extremely informative about the nature of the covalent bond. (The hydrogen molecule ion, H_2^+, consists of two protons held together by one electron.) The confidence to be placed in the calculations is indicated by comparing calculated and experimental bond energies (the bond energy is the energy necessary to disrupt the bond). These

Table 16-I. **Comparison of Calculated and Experimental Bond Energies of H_2^+ and of H_2**

Reaction	Degree of Approximation	Calculation (kcal/mole)	Experiment* (kcal/mole)	% Error
$H_2^+ \longrightarrow H + H^+$				
	best available	64.25	64.37	0.2
$H_2 \longrightarrow H + H$				
	5 terms	103.7	108.65	5
	11 terms	107.85		0.8
	13 terms	108.15		0.5
	estimated for more terms	108.7 ± 0.3		<0.3

* These numbers differ from those in Table 16-III because they include the zero-point vibrational energy.

Table 16-II. **A Contrast of Energy Effects Due to Particle Interactions in H_2^+ and in H_2**

	H_2^+			H_2		
	Separated Atoms (kcal)	Molecule (kcal)	Net Effect (kcal)	Separated Atoms (kcal)	Molecule (kcal)	Net Effect (kcal)
$\overline{\text{P.E.}}$						
Electron–electron repulsions	none present			0	+681	+681
Nucleus–nucleus repulsions	0	+313	+313	0	+449	+449
Electron–nucleus attractions	−627	−1069	−442	−1254	−2601	−1347
$(\overline{\text{P.E.}})$	−627	−756	−129	−1254	−1471	−217
$(\overline{\text{K.E.}})$	+313.5	+378	+64.5	+627	+735.5	+108.5
$\bar{E}$	−313.5	−378	−64.5	−627	−735.5	−108.5
r_e	1.06 Å			0.74 Å		

are shown in Table 16-I. For H_2, the calculated energies are shown for successively better approximations (as indicated by the number of terms retained in the expansion of the solution of the Schroedinger equation) together with an estimate of the effect of adding many more terms.

The close agreement between experimental and calculated values shown in Table 16-I gives us confidence that the calculational breakdown of this energy into the various contributions is meaningful and valid. These contributions are listed in Table 16-II and are contrasted for H_2^+ and H_2. The equilibrium bond lengths, r_e, are given as well. In considering the significance of the energy terms, we must remember that the bond length is much shorter in H_2 than in H_2^+.

Considering H_2^+ first, we see that a stable chemical bond is formed, even though only one electron is present. The larger magnitude of the electron–nucleus attraction in H_2^+ (−1069 kcal) over that in the H atom (−627 kcal) accounts entirely for the chemical bond. Both kinetic energy and nucleus–nucleus repulsion work against chemical bond formation. In addition, we see that the net kinetic energy effect (+64.5 kcal) is much smaller than is the net nucleus–nucleus repulsion effect (+313 kcal). There are, of course, no electron–electron interactions, since there is but one electron.

Turning to H_2, we see that with two bonding electrons, the bond is roughly twice as stable as the one-electron bond of H_2^+ (bond energies are −109 kcal for H_2 compared to −64.5 kcal for H_2^+). Since the bond is stronger, the bond length is shorter,* accounting for the 40% rise in the nucleus–nucleus repulsion. This shorter internuclear distance also accounts for the fact that the net change in the electron–nucleus attraction in H_2 (−1347 kcal) is more than twice that in H_2^+ (−442 kcal). There is a new interaction, the electron–electron repulsion (+681 kcal), but it is more than offset by the enlarged electron–nucleus attraction. Again, the rise in kinetic energy as the atoms come together is relatively small compared to the electron–electron repulsion and proton–proton repulsion.

Since the bond energy of H_2, which has two bonding electrons, is roughly double that of H_2^+, which has one bonding electron, there is every reason to expect that the same explanation should account for chemical bond formation in these two molecules. This is an important observation because it discriminates against explanations of bonding based on some sort of interaction between the two electrons. For example, "electron exchange" and "overlap" are two commonly used terms that should not be

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* This inverse relationship between bond energy and bond length holds reasonably well for any pair of atoms.

misinterpreted. Overlap, for example, means that a bonding electron can occupy a region of space that is simultaneously an important part of two valence orbitals. The overlap of orbitals contributes to bonding because the bonding electron then simultaneously occupies the valence orbitals of two atoms. If there is but one bonding electron in the overlapping orbitals, a second bonding electron can still be accommodated, thus the molecule, though stable, will be reactive. If two bonding electrons occupy the overlapping orbitals, the bond is stable *in spite of* the electron interactions, not because of it. At all internuclear distances, the forces between electrons tend to push the atoms *apart*, and the energy of this interaction tends to make the molecule *less stable.*

One more conclusion is contained in calculations of the type shown in Table 16-II. The equilibrium bond length is the internuclear distance at which the energy is a minimum—that is, at which the attractive forces are exactly equal to the repulsive forces. The attractive forces are entirely due to electron–nucleus attractions. Three contributions tend to force the atoms apart: electron–electron repulsions, nucleus–nucleus repulsions, and electron kinetic energy.* Of these three, the nucleus–nucleus repulsion becomes infinite as the internuclear distance approaches zero, whereas the other two contributions remain finite. Hence, at distances shorter than the equilibrium distance, where the energy increases quite sharply, the nucleus–nucleus repulsion term dominates the other terms. At the equilibrium distance it is as important as the other two terms.

Thus the consideration of H_2^+ and H_2 through quantum mechanics shows us the nature of the covalent bonding in these two prototype molecules. Any valid discussion of chemical bonding must be consistent with this reference point. We have reached these conclusions:

1. Chemical bonds are stable because of electron–nucleus attractions.
2. Electron kinetic energy, electron–electron repulsions, and nucleus–nucleus repulsions all act to decrease the stability of the chemical bond.
3. Orbital overlap is a useful concept because it gives importance to the region of space in which an electron is simultaneously close to two nuclei.
4. Orbital overlap does *not* imply that the electron–electron interaction contributes to lowering the energy of the system as atoms come together.
5. At the equilibrium distance, the nuclei are subjected to zero net force, because attractive forces are equal to repulsive forces. One of the most important repulsive terms is the nucleus–nucleus repulsion.

In view of these conclusions, we see that it is unfortunate that a number of current textbooks de-emphasize or fail to mention the role of the nucleus in explaining why two atoms attract each other but do not fall together. It is even implicit in the popular (and useful) space-filling molecular models that only the electron clouds need be considered. The best present theories lead to the opposite conclusion: a stable chemical bond would not exist unless a nucleus interacted with electrons close to a second nucleus, and the nuclei would collapse together without nuclear–nuclear repulsions.

ORBITAL AVAILABILITY AND BONDING CAPACITY

Chemical bonding has been explained in terms of simultaneous proximity of the bonding electrons to two or more nuclei. We have yet to discuss the condition which will give a stable bond.

In a sense, the electrons in any pair of atoms experience orbital overlap as the atoms approach each other. For example, the 1*s* electrons of a helium atom overlap the empty 2*s* and 2*p* orbitals of a second, nearby helium atom. They

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* The electron kinetic energy varies with the assumed internuclear distance. This treatment is valid in the "Born-Oppenheimer" approximation, in which the nuclei can be considered to be motionless with respect to the extremely rapid electron motion.

cannot, however, overlap significantly the 1*s* orbital of the second helium atom; these orbitals are full. The atoms cannot approach closely, so the only overlap occurs between the valence orbitals of one atom and the extra-valence orbitals* of the other. This type of overlap gives the weak interactions that determine the heats of vaporization of the inert gases, all less than 4 kcal/mole.

If there are vacant valence orbitals on one or both of the atoms, the situation is found to be different. The atoms move together until the valence orbitals of the two atoms overlap significantly. Then the energy of interaction is much larger. It may be as high as 100 kcal/mole.

Because these two situations involve such different amounts of energy, a distinction between them is useful and convenient. When two nuclei share electrons in valence orbitals, the attraction is called chemical bonding; when two nuclei share electrons only in extra-valence orbitals, the attraction is called van der Waals attraction.

As defined above, then, chemical bonding can occur when two atoms approach each other with partly filled valence orbitals. We need only consult the electron occupancy of the valence orbitals to predict whether chemical bonds can form. There are three favorable situations we might find. First, two atoms may approach with one atom possessing a vacant valence orbital and the other having a half-occupied valence orbital (as in H_2^+). Then a one-electron bond forms, with a bond energy about half as large as that of a two-electron bond between similar atoms. Second, two atoms may approach with each atom containing a half-occupied valence orbital (as in H_2). This two-electron bond is the normal chemical bond, with a bond energy in the range 10 to 100+ kcal/mole. Third, two atoms may approach with one atom containing a vacant valence orbital and the other containing a filled valence orbital (not already used in some other bond). Here again, a pair of electrons can be shared between the two atoms, but one atom provides (donates) both electrons. For example, the boron atom in BF_3 has a vacant valence orbital. The nitrogen atom in NH_3, on the other hand, has an unused pair of electrons in a valence orbital. In such a situation we can predict that a stable bond can form between these two molecules. Generally such a bond energy is found to be less than 50 kcal/mole.* Such a bond is sometimes called a coordinate bond, a Lewis acid–base interaction, or a dative bond, though some chemists do not feel a distinctive name is needed.

In our attempt to place bounds upon the coverage of the Textbook, we have not made a definition of this type of bonding. The way has been prepared, however, in our emphasis upon the residual bonding capability represented by a vacant valence orbital. Specific examples are present in the text, but the bonding is not discussed. Many of the oxyacids are of this type. Thus the oxygen in HOCl is unlike the added oxygen in HOClO. The bonding of the second oxygen can be considered to arise from the sharing of one unused electron pair from the chlorine atom of HOCl in the vacant valence orbital of an oxygen atom. The complexes formed by the transition elements, discussed briefly in Secs. 22-2.1 and 22-2.2 (Textbook p. 392) can also be treated in such a fashion.

Table 16-III shows some chemical bond energies. These illustrate the range of these energies and provide a basis for further discussion of ionic bond character.

IONIC BONDING AND ELECTRONEGATIVITY

When two hydrogen atoms come together, the energy is lowered by 103.2 kcal, because two bonding electrons are simultaneously near the two protons a good part of the time. When two bromine atoms come together, the energy is lowered by 45.5 kcal, because two bonding electrons are simultaneously near the two bromine nuclei a good part of the time. What, then, should we expect the energy decrease to be when a hydrogen atom and a bromine atom come

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* "Extra-valence" orbitals are those (unoccupied) orbitals outside the valence orbitals.

* The energy absorbed in the following reaction is 42 kcal/mole.

$$H_3N\text{—}BF_3(g) = NH_3(g) + BF_3(g)$$

Table 16-III. **Some Chemical Bond Dissociation Energies (ΔH at 0°K)** *

Reaction (all gases)	ΔH (0°K) (kcal/mole)	Reaction (all gases)	ΔH (0°K) (kcal/mole)
$H_2 = 2H$	103.2	$HF = H + F$	134
$F_2 = 2F$	36	$HCl = H + Cl$	102.2
$Cl_2 = 2Cl$	57.1	$HBr = H + Br$	86.5
$Br_2 = 2Br$	45.5	$HI = H + I$	70.5
$I_2 = 2I$	35.6	$CH_4 = CH_3 + H$	101
$Li_2 = 2Li$	25	$CH_3F = CH_3 + F$	108
$Na_2 = 2Na$	17.3	$CH_3Cl = CH_3 + Cl$	80
$K_2 = 2K$	11.8	$CH_3Br = CH_3 + Br$	67
$Rb_2 = 2Rb$	10.8	$CH_3I = CH_3 + I$	54
$CH_3{-}CH_3 = 2CH_3$	85	$LiF = Li + F$	137
$HO{-}OH = 2OH$	51	$LiCl = Li + Cl$	115
		$LiBr = Li + Br$	101
		$LiI = Li + I$	81
		$ClF = F + Cl$	60.5
		$BrF = F + Br$	55
		$BrCl = Cl + Br$	52.1
		$ICl = Cl + I$	49.6
		$IBr = Br + I$	41.9

* As compiled by T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworth Scientific Publications, London (1958). The energy is absorbed in the reactions as written. The quantity ΔH (0°K) is usually symbolized D_0.

together? In this situation two bonding electrons will be simultaneously near one proton (instead of two, as in H_2) and one bromine atom (instead of two, as in Br_2). It is reasonable to expect that a perfect sharing of the electron pair would give at least half the energy of bond formation in H_2 plus half the energy of bond formation in Br_2.

$$\text{Expected covalent bond energy} = \frac{103.2 + 45.5}{2} = 74.3 \text{ kcal} \qquad (10)$$

In an unsymmetrical molecule like HBr, however, there may be some *additional* energy lowering associated with a redistribution of the electrons so as to favor one atom over the other. Although the electrons in a stable bond must be simultaneously close to two nuclei (even in such molecules as LiF), they do not have to be equally close to each. Should the electrons favor one atom over the other, the center of negative charge will be displaced from the center of positive charge, giving the molecule an electric dipole and the bond some ionic character. By this argument, then, the energy required to break the bond in HBr should be 74.3 kcal or *greater*, the amount greater being a measure of how much the electron distribution is skewed away from equal sharing or covalent distribution.

This discussion is all based upon the empirical regularity, first recognized and interpreted by Linus Pauling, that the bond energy of a molecule *AB* always exceeds somewhat the algebraic mean of the bond energies of A_2 and B_2. The amount of excess is interpreted as a measure of ionic character of the bond, and Pauling was successful in using this type of data in founding an electronegativity scale. Before considering Pauling's electronegativities, let us examine the expected "equal-sharing" bond energies and the experimental values of some of the molecules given in the right-hand column of Table 16-III. These are given in Table 16-IV, and they verify the generalization that experimental bond energies exceed the calculated values.

Table 16-IV. **"Equal-sharing" Bond Energies Compared to Experimental Values (All Values in kcal/mole)**

Molecule	Observed $D(AB)$	Algebraic Mean $\frac{1}{2}[D(A_2) + D(B_2)]$	Excess Energy, $D(AB) - \frac{1}{2}[D(A_2) + D(B_2)]$
BrCl	52.1	51.3	+0.8
IBr	41.9	40.5	+1.4
ICl	49.6	46.3	+3.3
IF	46	35.8	+10
BrF	55	40.7	+14
ClF	60.5	46.5	+14
HI	70.5	69.4	+1.1
HBr	86.5	74.3	+12.2
HCl	102.2	80.1	+42
HF	134	69.6	+64
LiI	81	30.3	+51
LiBr	101	35.2	+66
LiCl	115	41	+74
LiF	137	30.5	+106

Pauling reasoned that the amount of excess energy should be fixed by the *difference* in electronegativities of the two atoms. Since the chemistry of atoms is fixed by energy relations, he attempted to use excess energy as a means of defining an electronegativity scale. He found that a self-consistent scale of electronegativity emerged if a square dependence was assumed:*

$$\begin{aligned} \text{Excess energy} &= (x_A - x_B)^2 \\ &= D(AB) - \tfrac{1}{2}[D(A_2) + D(B_2)] \qquad (11) \\ x_A &= \text{electronegativity of atom } A \\ x_B &= \text{electronegativity of atom } B \end{aligned}$$

It must be recognized that equation (*11*) defines x_A. There are only two verifications of the scale. First, the set of x values so obtained is self-consistent, fitting a large amount of data. Second, the relative magnitudes of the x values so obtained correlate well with our intuitive ideas about relative electronegativities as shaped by the huge mass of known descriptive chemistry. The value of Pauling's scale is attested by its persistence today, three decades after its proposal. Figure 16-1 shows the most reliable portion of the relative scale, on which fluorine is 4.0.

Despite its usefulness, we have not presented the bond energy electronegativity scale in the Textbook, nor have we used the rather abstract term "electronegativity." We have instead laid a basis for relating the formation of ionic bonds to differences in ionization energy. This quantity more obviously relates to the charge distribution. The clear-cut connection suggests that ionization energy should provide a basis for defining an electronegativity scale. So it does.

The use of ionization energy as a basis for electronegativity was proposed by R. E. Mulliken, who devised a scale that is in reasonably close agreement with the Pauling scale. Since Mulliken's ionization energy scale more obviously relates to charge movement, it has clearer intuitive significance. It has not found the wide use given Pauling's bond energy scale, however, because there are few known experimental values of ionization energies of negative ions (i.e., of electron affinities).

Two important practical results come from a consideration of electronegativity. First, the existence of a large electronegativity difference permits the prediction of extra bond stability over that expected for a covalent bond. This will be noticed in such properties as molecular stability, bond length, and vibrational frequency.

* Later, Pauling shifted to the geometric mean, $\sqrt{D(A_2)D(B_2)}$, instead of the algebraic mean in (*10*) to eliminate a few negative values of excess energy. But this results in little change in the scale.

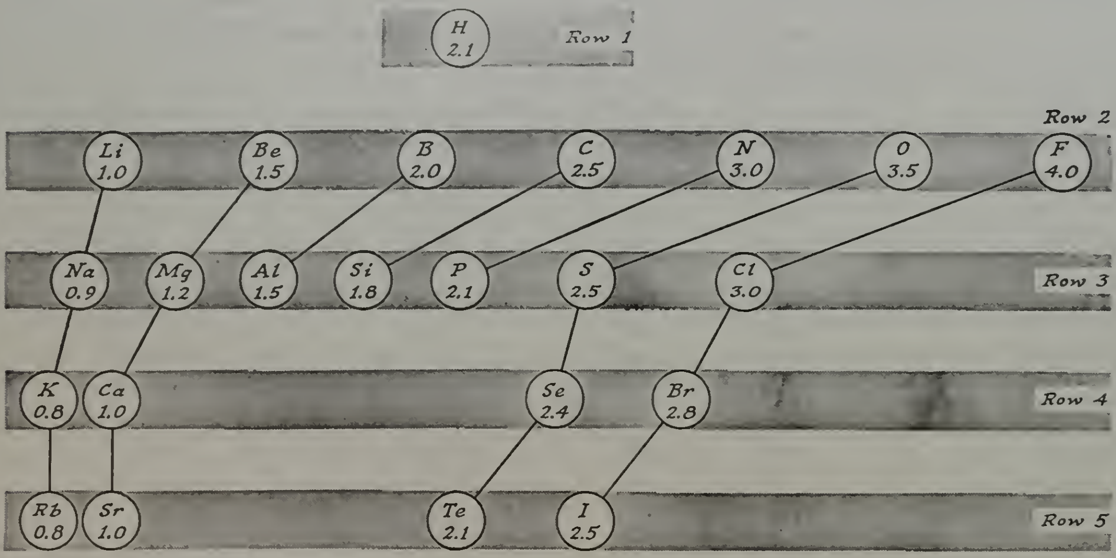


Fig. 16-1. **An electronegativity scale.**

Second, the electronegativity difference leads us to expect an electric dipole in the molecule. It suggests the magnitude of the bond dipole and indicates the direction of charge shift. Care must be used, however, in deciding whether the electronegativity scale is applicable to any particular case. The concept is defined in terms of normal single bonds in which each atom furnishes one electron to the electron-pair bond. Multiple bonds, electron donor-acceptor bonds, and molecules involving resonance need separate consideration in predicting charge distribution. As two examples, note that neither carbon monoxide, CO, nor nitric oxide, NO, have appreciable dipole moments.

BOND ANGLES

Two relatively popular models are used to explain the bond angles formed in polyatomic molecules. One is based upon the angular distributions of the hydrogen atom orbitals; it is called the "hybridization" model. The other model is based upon the electrostatic repulsions among the bonding and nonbonding valence electrons. We shall call it the "electrostatic" model. The discussion given in the text is, deliberately, neither of these, though it is closer to the hybridization model. Either model furnishes a basis for understanding the qualitative aspects of molecular structure (linear or bent? planar or nonplanar? etc.). Both are ambiguous in explaining variations among bond angles for molecules with similar electron configurations. At this stage in the development of these models, an empirical view of bond angles seems most appropriate. Such a view is presented in the Textbook.

There is method in our choice of an empirical treatment based on the hydrogen atom orbitals. It permits the interested student to become familiar with the hybrid orbital notation, since he is certain to encounter it in his outside reading.

THE HYBRIDIZATION MODEL

In this model, the angular distributions of the hydrogen atom orbitals are presumed to persist in many-electron atoms and to be influential in determining the angles between bonds formed by a central atom. "Hybridization" is a term intended to indicate that when bonds having different types of orbitals are formed, the angular properties are to be explained on the asumption that some "mixing" of the different orbital types occurs to form "hybrid orbitals." Thus if an *s* and a *p* orbital are available for bonding, two bonds will form at angles appropriate to two "hybrid orbitals," each of which has part *s* and part *p* character. In this fashion, an explanation is framed for the empirical observation that two identical bonds are formed by an atom having an *s* and a *p* orbital available for bonding, though two different types of bonds might have been expected. A systematic movement across the periodic table displays the argument.

Fluorine

The halogens have but one bonding orbital and do not raise the question of bond angle.

Oxygen

The oxygen family has the valence orbital electron configuration $ns^2np_x^2np_y^1np_z^1$. The two bonding orbitals, p_y and p_z, are directed at right angles, and lead to an expected 90° bond angle. We do not need to invoke the hybridization idea to explain the bonding of oxygen. Experimentally the data for the oxygen family compounds (shown in Table 16-V) are qualitatively compatible with this proposal. The hydride bond angles are in the range 104.5° to 90°. A convenient explanation of the angles greater than 90° is furnished by assuming that the bonding electrons of the peripheral atoms repel each other. This effect should decrease as the central atom becomes larger, a comfortable explanation of the large reduction of bond angle between H_2O and H_2S and the very slight further reduction in H_2Se and H_2Te.

The bond angles for the three compounds Cl_2O, Cl_2S, and Br_2Te mesh smoothly with this explanation. Since chlorine is much larger than hydrogen, we might expect greater repulsion in Cl_2O than in H_2O and, hence, a somewhat larger bond angle in Cl_2O. The same argument, however, would lead us to expect an F_2O bond angle between that for H_2O and Cl_2O. The observed 102° angle is not readily explained without some new argument.

Nitrogen

The nitrogen family has, in the valence orbitals, the electron configuration $ns^2np_x^1np_y^1np_z^1$. Three bonding orbitals are available, directed at right angles, and lead to an expectation of a 90° pyramidal arrangement without hybridization. Again, experiment is in comfortable agreement, the hydrides presenting the same trend shown by the oxygen family. The halogen compounds are also compatible except, again, for the small angle observed for NF_3.

Carbon

Each element of the carbon family is found, experimentally, to form four equivalent bonds. The available orbitals can explain this *number* of bonds if we assume the electron configuration $ns^1np_x^1np_y^1np_z^1$. Without other evidence, however, the bonding orbitals suggest there might

Table 16-V. **Experimental Bond Angles for Some Compounds in the Oxygen and Nitrogen Families**

H_2O	104.5°	F_2O	102°	Cl_2O	111°	—	—
H_2S	92°	—	—	Cl_2S	102°	—	—
H_2Se	91°	—	—	—	—	—	—
H_2Te	89.5°	—	—	—	—	Br_2Te	98°
NH_3	107°	NF_3	102°	—	—	—	—
PH_3	93°	—	—	PCl_3	100°	PI_3	98°
AsH_3	91.5°	AsF_3	102°	$AsCl_3$	98°	$AsBr_3$	101°
SbH_3	91.3°	SbF_3	88°	$SbCl_3$	99.5°	$SbBr_3$	97°
—	—	—	—	$BiCl_3$	100°	$BiBr_3$	100°

be three equivalent bonds formed at right angles, which use the p_x, p_y, and p_z orbitals, and a fourth, different bond formed at an undetermined angle by the spherically symmetrical s orbital. To eliminate this conflict with experiment, it is assumed that each of the four bonding orbitals is a mixture, or "hybrid," of the available bonding orbitals. Linear combinations of the available orbitals are considered ($as + bp_x + cp_y + dp_z$), and the coefficients a, b, c, and d are selected with two criteria in mind. Four sets of coefficients must be found (one set for each hybrid orbital), and these four sets must be selected so that they are *equivalent* and so that they are *mutually oriented at tetrahedral angles* (109°28′). You will recall that in discussing the orientation of a p_x orbital (which really occupies all space), we were guided by the angular properties. This orbital is considered to be oriented *along* the x-axis, because the probability of finding the electron is greater along this line than along any other line passing through the nucleus. In deciding how the hybrid orbitals will be oriented, we should follow the same reasoning—discover along what line the probability is a maximum. Our four bonds will be equivalent if the probability distribution along the four "bond-lines" are identical, and they will be properly oriented if the four "bond-lines" are directed through the vertices of a regular tetrahedron.

Upon this basis, we deduce the following set of hybrid orbitals:

$$(sp^3)_1 = \tfrac{1}{2}(s + p_x + p_y + p_z) \qquad (12)$$
$$(sp^3)_2 = \tfrac{1}{2}(s + p_x - p_y - p_z) \qquad (13)$$
$$(sp^3)_3 = \tfrac{1}{2}(s - p_x + p_y - p_z) \qquad (14)$$
$$(sp^3)_4 = \tfrac{1}{2}(s - p_x - p_y + p_z) \qquad (15)$$

Perhaps one of the most convincing aspects of the hybridization scheme is that these four sp^3 hybrid orbitals are not only equivalent and tetrahedrally oriented, but *they also represent the best possible combinations for concentrating the probability distribution along the "bond-lines."* The concentration of probability along the "bond-line" is used by Pauling as a measure of bond strength, because a high directionality along a bond line implies a high overlap with the bonding orbital of an adjacent atom.

In summary, when the carbon family elements form four single bonds, they are tetrahedrally oriented, no matter what atoms are attached. This can be explained by considering that the bonding occurs through hybrid bonding orbitals, each of which is a linear combination of the available valence orbitals, s, p_x, p_y, and p_z. Confidence in the hybridization scheme derives from the observation that *the requirement of tetrahedral orientation produces maximum directionality* of the hybrid orbitals.

Boron

Each element of the boron family forms three equivalent bonds in the same plane and directed at the vertices of an equilateral triangle. Again, "mixing" of the available bonding orbitals is necessary to explain the number and orientation of the three bonds. The procedure for seeking suitable linear combinations of the s, p_x, and p_y orbitals follows the pattern given for carbon. Again the technique is successful. Suitable linear combinations are found, and the planar and equivalent sp^2 hybrid orbitals turn out to have maximum directionality.

Beryllium

Each element of the beryllium family forms two equivalent bonds in a linear arrangement. The hybrid orbitals are simple in form and easy to visualize.

$$(sp)_1 = \frac{1}{\sqrt{2}}(s + p_x) \qquad (16)$$

$$(sp)_2 = \frac{1}{\sqrt{2}}(s - p_x) \qquad (17)$$

It is clear that these two hybrids are both directed along the x-axis. Since the s orbital is spherically symmetric, the p_x orbital determines completely the angular properties. The difference in algebraic sign of the p_x contribution in $(sp)_1$ and $(sp)_2$ causes the two hybrids to be oppositely directed. The equivalence of the two hybrids is indicated by the fact that each contains the same "admixture" of s orbital.

Lithium

The alkalis have but one bonding orbital and do not raise the question of bond angle.

Hybrids Involving *d* Orbitals

The same procedure is applicable to atoms whose valence orbitals involve *d* as well as *s* and *p* orbitals. Suitable linear combinations exist to explain the structures found in molecules involving transition elements (which use *d* orbitals in bonding). The geometries of some of these hybrid orbitals are shown in Table 16-VI.

Table 16-VI

Geometrical Properties of Some Hybrid Orbitals

Number of Bond Orbitals	Hybrid	Structural Geometry	An Example
2	sp	linear	BeF_2
	p^2	bent	H_2O
3	sp^2	trigonal, planar	BF_3
	p^3	trigonal, pyramidal	NH_3
4	sp^3	tetrahedral	CH_4
	dsp^2	tetragonal, planar	$Ni(CN)_4^{-2}$
5	dsp^3	trigonal bipyramid	PCl_5
6	d^2sp^3	tetragonal bipyramid (octahedron)	$Fe(CN)_6^{-3}$

THE ELECTROSTATIC MODEL

The repulsions between pairs of valence electrons (whether used for bonding or not) provide an alternate basis for explaining the observed geometries in the simple molecules. In the electrostatic model, the tendency for electrons to stay as far apart as possible is taken to be the predominant factor in fixing bond angles. The principal advantage of this model is its simplicity, as shown again in a sweep across the periodic table (this time, from left to right).

Lithium

The alkalis involve but one electron pair in bonding, hence do not raise the question of bond angle.

Beryllium

Each element in the beryllium family forms two bonds, hence involves two pairs of bonding electrons. These two pairs are separated as far as possible when the two bonds are oppositely directed along a line. Hence this model predicts a linear molecule, in agreement with experiment.

Boron

Each element in the boron family forms three bonds, hence involves three pairs of bonding electrons. These three pairs are separated from each other as far as possible when the three bonds are in the same plane and directed at 120° angles to each other. The model is again in agreement with the observed structures of BF_3, BCl_3, etc.

Carbon

Each element in the carbon family forms four bonds, hence involves four pairs of bonding electrons. These four pairs are farthest separated in the tetrahedral orientation, in accord with the facts.

Nitrogen

Each element in the nitrogen family forms three bonds, but has another pair of electrons in a valence orbital. Here, too, each has four pairs of electrons, and a tetrahedral orientation of the four pairs is expected. The three bonds should be found along three of the four tetrahedral directions, forming a trigonal pyramid with 109°28′ angles. This is in qualitative, but not quantitative, agreement with experiment, as shown in Table 16-V. Ammonia is quite close to the tetrahedral value, 107°, but PH_3, AsH_3 and SbH_3 are all near 92°. Perhaps the tetrahedral shape is not found because the electron pairs are nonequivalent. One pair is not used in bond formation. We can postulate that this extra pair exerts stronger repulsion on the bonding electrons than the bonding pairs exert on each other. Unfortunately it is difficult to explain why this effect should be almost negligible for NH_3 but very large and about the same for PH_3, AsH_3, and SbH_3.

Oxygen

Of the four pairs of electrons in the bonding orbitals of oxygen, two pairs are shared in chemical bonds, and two pairs are unused in bonding. If these four pairs are tetrahedrally oriented, a bent molecule is expected. Turning again to the actual angles, we find they are all smaller than the tetrahedral angle of 109°28′. The same effect that accounts for the closing of the NH_3 angle to 107° ought to be present, although to a greater degree, in water (in which there are two unused pairs of electrons pushing the HOH bond angle to a smaller size). This argument is in nice agreement with experiment, since water deviates from the tetrahedral bond angle by just about twice as much as does ammonia. The pleasure this observation brings is quite shattered, however, by observing the experimental angles of H_2S, H_2Se and H_2Te. These angles are practically identical to the 92° bond angles observed in PH_3, AsH_3, and SbH_3. If these large deviations from 109°28′ are explained in terms of nonequivalent interactions between unused pairs and bonding pairs, then somehow the rationale for the large deviations must be compatible with the almost constant bond angles near 90°.

Fluorine

The halogens form but one bond and do not raise the question of bond angle.

HIGHER NUMBERS OF VALENCE ELECTRONS

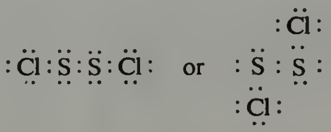
The idea that electron–electron repulsions are a factor in determining bond angles can be extended to the case of six electron pairs near an atom. The tetragonal bipyramid, or octahedral geometry, places the pairs far apart. If one of the pyramid apex positions is occupied by an unused electron pair, a tetragonal pyramid structure results among the bonds. If both of the pyramid apex positions are occupied by electron pairs, a square planar structure results.

In summary, both the hybridization and the electrostatic schemes furnish bases for qualitative explanation of observed bond angles. Each model presents some difficulty in dealing with the quantitative aspects, with the result that predictions made in the absence of experimental data have proven to be unreliable. At the introductory level, an empirical presentation is warranted. The deviations from the predictions require a much more sophisticated treatment.

Answers to Exercises and Problems

Ex. 16-1. Predict the structure of the compound S_2Cl_2 from the electron dot representation of the atoms. After you have predicted it, turn back to Figure 6-12, p. 103, and check your expectation.

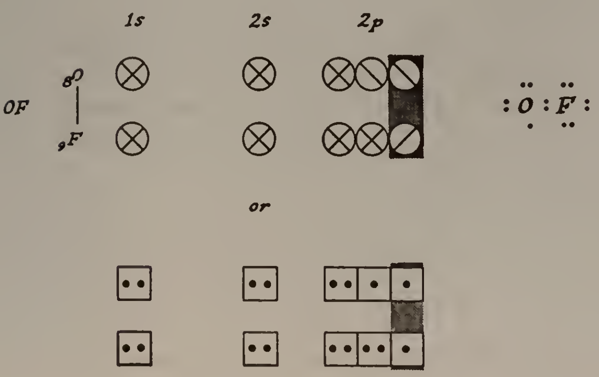
Answer

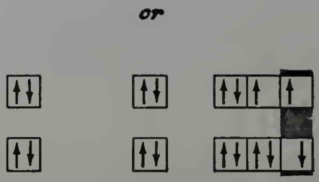


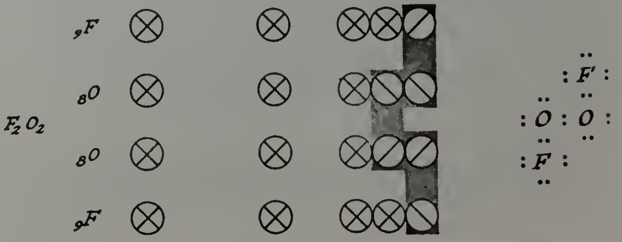
The electron dot representation leads to a structure in which the two sulfur atoms are bonded, sharing a pair of electrons. The orbital representation for sulfur is $1s^2\ 2s^22p^6\ 3s^23p^4$, showing two partially occupied p orbitals available for bonding, hence sulfur is divalent (like oxygen). Chlorine, with but one partially occupied p orbital for bonding, is monovalent (like hydrogen). Hence the bonding is similar to that of H_2O_2. Later in the chapter the student will learn that p^2 bonding gives a bent, rather than a linear, configuration. At this time, however, the student has no basis for preference between the two structures considered here. Show them both, and raise, but don't answer the question of which structure is correct.

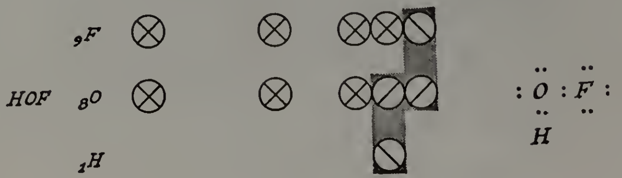
Ex. 16-2. Draw orbital and electron dot representations of each of the following molecules: OF, F_2O_2, HOF, HFO_2. Which of these is apt to be the most reactive?

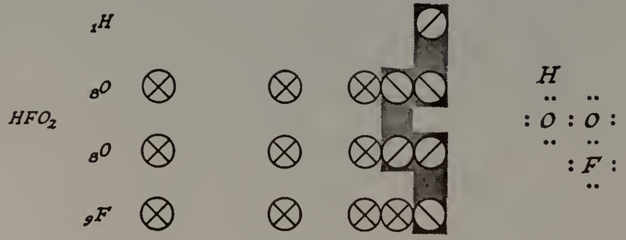
Answer









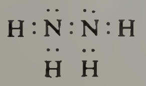


Notice that in the figure the answers generally follow the text in pictorial details of the representation. But do not lead the student to believe that this notation is unique. Stress this point in class discussion by presenting alternate notations such as those shown for OF. Do not, however, introduce the idea of spin to justify the arrows.

The molecule OF, with its remaining half-filled orbital, is apt to be the most reactive. Every one of the other molecules can be drawn in a structure that places near each atom the number of electrons required to fill its valence orbitals.

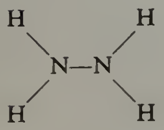
Ex. 16-3. The molecule NH_2 has residual, unused bonding capacity and is extremely reactive. The molecule N_2H_4 (hydrazine) is much more stable. Draw an electron dot representation of the bonding of hydrazine. Draw its structural formula (show which atoms are bonded to each other).

Answer



$$\begin{array}{ccccccc} H & : & \underset{\cdot\cdot}{\ddot{N}} & : & \underset{\cdot\cdot}{\ddot{N}} & : & H \\ & & H & & H & & \end{array}$$

(electron dot representation)

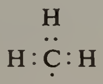


(structural formula)

Ex. 16-4. Draw electron dot formulas for the molecules CH_3, CF_3, CHF_3, CH_2F_2, CH_3F. Which will be extremely reactive?

Answer

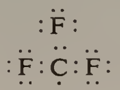
CH_3



$$\begin{array}{ccccc} & & H & & \\ H & : & \underset{\cdot}{\ddot{C}} & : & H \end{array}$$

extremely reactive

CF_3



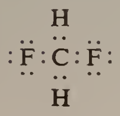
$$\begin{array}{ccccc} & & :\ddot{F}: & & \\ :\underset{\cdot\cdot}{\ddot{F}} & : & \underset{\cdot}{\ddot{C}} & : & \underset{\cdot\cdot}{\ddot{F}}: \end{array}$$

extremely reactive

CHF_3

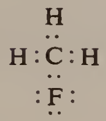
$$\begin{array}{ccccc} & & H & & \\ :\underset{\cdot\cdot}{\ddot{F}} & : & \underset{\cdot\cdot}{\ddot{C}} & : & \underset{\cdot\cdot}{\ddot{F}}: \\ & & :\underset{\cdot\cdot}{F}: & & \end{array}$$

CH_2F_2



$$\begin{array}{ccccc} & & H & & \\ :\underset{\cdot\cdot}{\ddot{F}} & : & \underset{\cdot\cdot}{\ddot{C}} & : & \underset{\cdot\cdot}{\ddot{F}}: \\ & & H & & \end{array}$$

CH_3F

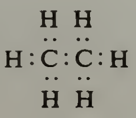


$$\begin{array}{ccccc} & & H & & \\ H & : & \underset{\cdot\cdot}{\ddot{C}} & : & H \\ & & :\underset{\cdot\cdot}{F}: & & \end{array}$$

For atoms in the first three rows of the periodic table, one can expect with confidence that molecules with unused bonding capacity will be extremely reactive (as for CH_3 and CF_3). The reverse is generally, but not always, true; for this reason the student should not be encouraged to believe that a molecule with completely used bonding capacity can be expected to be unreactive. Fluorine, F_2, is a good example of an extremely reactive substance in which all of its bonding capacity is used. Nevertheless, the free radicals are more reactive, as can be verified by observing that no one can prepare a bottle full of CH_3 radicals, whereas F_2, despite its reactivity, is available by the tank-car load. The CH_3 reacts with itself, whereas F_2 does not.

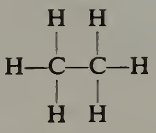
Ex. 16-5. Draw an electron dot and a structural formula for the molecule C_2H_6 (ethane) which forms if two CH_3 molecules are brought together. Explain why C_2H_6 is much less reactive than CH_3.

Answer



$$\begin{array}{ccccccc} & & H & & H & & \\ H & : & \underset{\cdot\cdot}{\ddot{C}} & : & \underset{\cdot\cdot}{\ddot{C}} & : & H \\ & & H & & H & & \end{array}$$

electron dot



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

structural

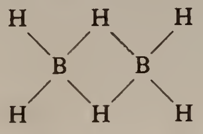
C_2H_6 has no unused bonding capacity, hence can be unreactive. In contrast, CH_3 has one valence orbital containing only one electron. This half-filled orbital is available for bond formation, accounting for the reactivity of CH_3.

Question on p. 285

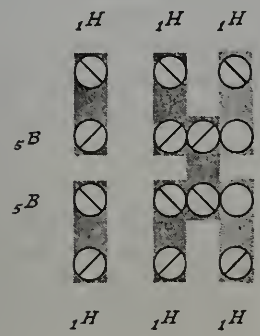
You might wish to predict the structure of diborane (which is now known), but do not be discouraged if you are not able to. Its structure, once elucidated, came as quite a surprise to even the most sophisticated chemists. The explanation of the structure is, even today, composed of a large proportion of words and a small proportion of understanding.

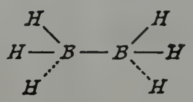
Answer

Diborane, B_2H_6, is known to have a bridged structure. In the diagram, the terminal hydrogens are above and below the plane defined by the boron atoms and the central hydrogen atoms. Diborane has the structure

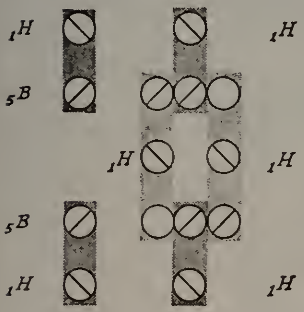


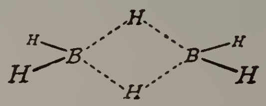
The student may connect the molecular formulas, C_2H_6 and B_2H_6, and hence propose an ethane-like structure. Perhaps he would offer an orbital representation such as that shown below. In this structure, two of the B—H bonds





would be weakened because only one electron is available for each of these bonds. Perhaps such a structure would find some way to share this electron deficiency among all of the B—H bonds. This was the common view prior to the spectroscopic determination of the correct structure. The correct structure cannot be predicted from the bonding rules. *Don't take class time to discuss this structure*, but if individuals show interest, give them time to consider alternate possibilities *after* someone suggests the ethane structure and you tell them it is incorrect.





The current explanation is that one pair of electrons "occupies" three orbitals, including the 1*s* orbital of a hydrogen in the bridge position, as suggested here. This is what is called a "molecular orbital." (See *Background Discussion*.)

Conclude the discussion by asking whether such a molecule, though found to be stable, can be expected to be reactive. (The molecule reacts spontaneously as soon as it is exposed to air, sometimes explosively. This reactivity can be attributed to the deviation from normal bonding.)

Ex. 16-6. From the following bond energy data and the ionization energies given in Table 15-III, calculate the entries in the last two columns of Table 16-III for the compounds LiF and LiBr. The ionization energy, E_1, for bromine atom is 273 kcal/mole.

$$\begin{array}{rl}
Li_2(g) = 2Li(g) & \Delta H = 25 \text{ kcal} \\
F_2(g) = 2F(g) & \Delta H = 36 \text{ kcal} \\
Br_2(g) = 2Br(g) & \Delta H = 45.5 \text{ kcal} \\
LiF(g) = Li(g) + F(g) & \Delta H = 137 \text{ kcal} \\
LiBr(g) = Li(g) + Br(g) & \Delta H = 101 \text{ kcal}
\end{array}$$

Answer

The student is given an opportunity to calculate the values for one of the compounds in Table 16-III (LiF) and for one compound not in the table (LiBr).

$$E_1(\mathrm{F}) - E(\mathrm{Li}) = 401.5 - 124.3 = 277.2 \text{ kcal/mole}$$
$$\Delta H(\mathrm{LiF}) - \tfrac{1}{2}[\Delta H(\mathrm{Li_2}) + \Delta H(\mathrm{F_2})]$$
$$= 137 - \tfrac{1}{2}(25 + 36) = 137 - 30.5 = 106.5 \text{ kcal}$$
$$E_1(\mathrm{Br}) - E(\mathrm{Li}) = 273 - 124 = 149 \text{ kcal/mole}$$
$$\Delta H(\mathrm{LiBr}) - \tfrac{1}{2}[\Delta H(\mathrm{Li_2}) + \Delta H(\mathrm{Br_2})]$$
$$= 101 - \tfrac{1}{2}(25 + 45.5) = 101 - 35 = 66 \text{ kcal}$$

Pr. 1. Which one of the following statements is FALSE as applied to this equation?

$$H_2(g) \rightleftharpoons H(g) + H(g) \qquad \Delta H = 103.4 \text{ kcal}$$

(a) The positive ΔH means the reaction is endothermic.
(b) Two grams of $H(g)$ contain more energy than 2 grams of $H_2(g)$.
(c) Weight for weight, $H(g)$ would be a better fuel than $H_2(g)$.
(d) The spectrum of $H_2(g)$ is the same as the spectrum of $H(g)$.

Answer

(a) True. Since ΔH is defined as H(products) $-H$(reactants) and is positive, H(products) > H(reactants). To obtain this condition, heat must have been added to the system—i.e., the reaction must have been endothermic.

(b) True. Since heat is added to the system, this answer is required by energy conservation. Energy must have been added to the system $H_2(g)$ to break bonds to form $2H(g)$.

(c) True. To act as a fuel, hydrogen must combine with something. Since H_2 has no bond-forming capacity, the bond forming the molecule must be broken. This would consume energy, hence $2H(g)$ is a better fuel than $H_2(g)$.

(d) False. All energy levels of H_2 differ from those of H.

Pr. 2. What are the molecular species present in gaseous neon, argon, krypton, and xenon? Explain.

Answer

Ne, Ar, Kr, and Xe are inert gases for which the gaseous species are single atoms. This is because their valence orbitals are completely filled. Having no partially filled valence orbitals, they have no bonding capacity.

Pr. 3. Determine the number of attractive forces and the number of repulsive forces in LiH.

Answer

A tabulation of the forces:

Repulsion between electrons	6
Repulsion between nuclei	1
Attraction between Li nucleus and electrons	4
Attraction between H nucleus and electron	4

There are 7 repulsive and 8 attractive terms. In discussing these terms, it will be helpful to draw on the blackboard a counterpart to Textbook Figure 16-4 (p. 277), using different colors of chalk to show the various types of interactions. Be sure to show two of the electrons close to the lithium nucleus to suggest that they occupy the 1*s* orbital of lithium.

Pr. 4. What energy condition must exist if a chemical bond is to form between two approaching atoms?

Answer

The energy of the atoms must be lower when they are close together than when they are far apart.

Pr. 5. What valence orbital and valence electron conditions must exist if a chemical bond is to form between two approaching atoms?

Answer

(a) *Valence electrons must be available* in at least one of the atoms.

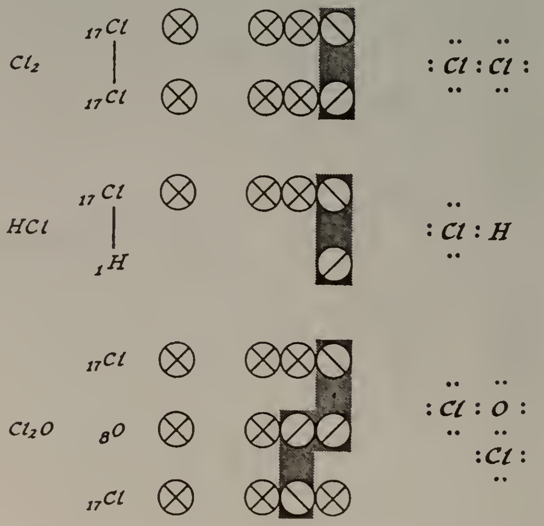
(b) *Partially-filled or vacant valence orbitals must be present* in at least one of the atoms.

The underscored portions of the answer are sufficient, but the complete sentences encompass much more. For example, all of the chemical bonds below are included in the complete answer.

$H + H \longrightarrow H_2$	
$H + H^+ \longrightarrow H_2^+$	(one electron bond)
$BF_3 + NH_3 \longrightarrow F_3BNH_3$	(electron acceptor-electron donor bond, or Lewis acid–base reaction)

Pr. 6. Give the orbital and also the electron dot representations for the bonding in these molecules: Cl_2, HCl, Cl_2O.

Answer



Pr. 7. Using the electron dot representation, show a neutral, a negatively charged, and a positively charged OH group.

Answer

$:\underset{\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}$ neutral

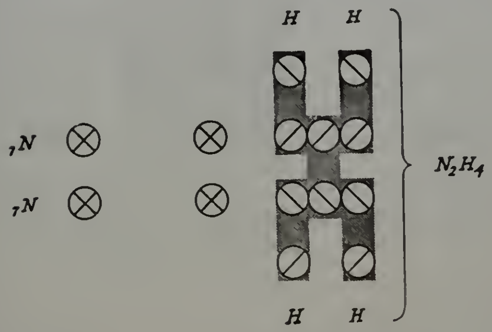
$[:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}]^-$ negatively charged

$[:\ddot{\mathrm{O}}:\mathrm{H}]^+$ positively charged

Contrast the probable reactivities of these species to indicate why OH^- is the more important, chemically.

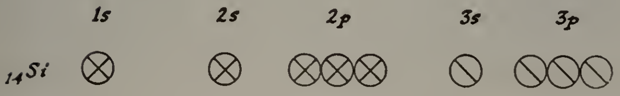
Pr. 8. Draw the orbital representation of the molecule N_2H_4, hydrazine.

Answer



Pr. 9. Knowing the orbitals carbon uses for bonding, use the periodic table to predict the formula of the chloride of silicon. What orbitals does silicon use for bonding?

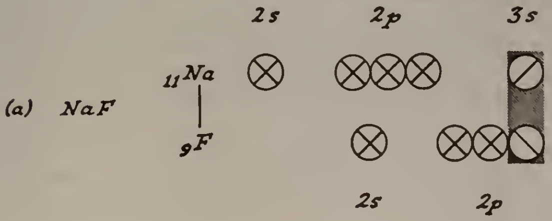
Answer: $SiCl_4$

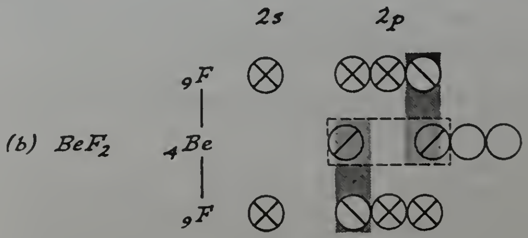


Like carbon, silicon uses sp^3 orbitals for bonding. But the orbitals used have a principal quantum number of 2 for carbon and 3 for silicon.

Pr. 10. Draw the orbital representations of
(a) sodium fluoride,
(b) beryllium fluoride, BeF_2.

Answer





Pr. 11. In general, what conditions cause two atoms to combine to form:
(a) a bond that is mainly covalent;
(b) a bond that is mainly ionic;
(c) a polar molecule?

Answer

In each case, the three conditions stipulated in Problems 4 and 5—lower energy, available valence electrons, and partially filled valence orbitals—are needed. In addition,

(a) the two atoms must have nearly the same ionization energy;
(b) the 2 atoms must have ionization energies that are quite different;
(c) same as b.

Pr. 12. What type of bonding would you expect to find in MgO? Explain.

Answer

The clue as to the type of bonding comes from ionization energy. These can be found on p. 268 of the Textbook.

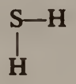
Mg	175.2 kcal/mole
O	313.8

Accordingly, one would expect bonding that is mainly ionic in MgO (the atoms have quite different ionization energies).

Pr. 13. Considering comparable oxygen compounds, predict the shape of H_2S and H_2S_2 molecules. What bonding orbitals are used?

Answer

(a) H_2S should be like H_2O. It has the same relative amount of hydrogen, and sulfur has the same number of valence electrons as oxygen. There should be p^2 bonding around the S atom, and a "bent" molecule should result:



$$\begin{array}{l}S\text{—}H\\ |\\ H\end{array}$$

Note: The HSH angle is somewhat smaller (92.2°) than that in H_2O (104.5°).

Pr. 14. Predict the formula and molecular shape of a hydride of phosphorus.

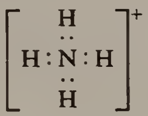
Answer

Phosphorus is in the same column of the periodic table as nitrogen. The outermost electrons of N and P are $2p^3$ and $3p^3$, respectively, and the respective hydrides are NH_3 and PH_3. Each of these molecules uses p^3 bonding, which is associated with pyramidal structures.

Pr. 15. Draw an electron dot representation for the NH_4^+ ion. What shape do you predict this ion will have?

Answer

The expected orbital occupancy of nitrogen produces a trivalent atom. However, the 2*s* orbital has nearly the same energy as the 2*p* and can be used in bonding with a hydrogen atom that is missing its electron. The hydrogen atoms are assumed to be equally bonded. The bonding orbitals would then be equivalent and of the sp^3 type. Such orbitals produce tetrahedral geometry.

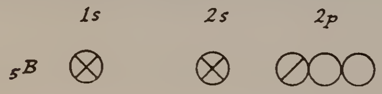


$$\left[\begin{array}{c} H \\ \ddot{} \\ H:N:H \\ \ddot{} \\ H \end{array}\right]^+$$

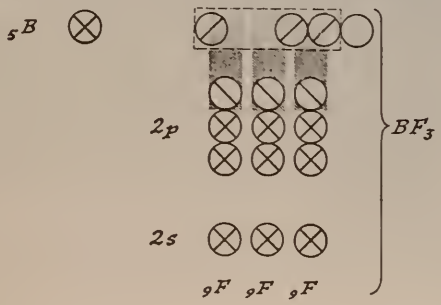
Pr. 16. Predict the type of bonding and the shape of the ion BF_4^-.

Answer

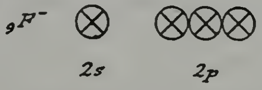
The type of bonding can be revealed through the orbitals available. These are:



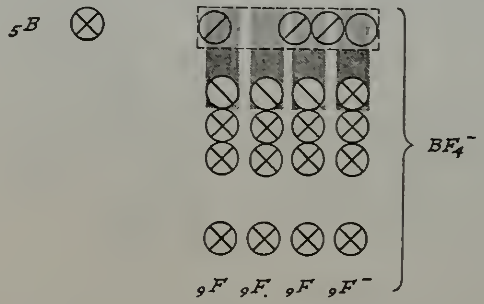
This can be used first to represent BF_3.



Then a F^- ion, represented by



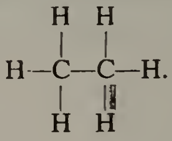
can form a bond by sharing one electron pair with a vacant 2*p* orbital of boron. The result is sp^3 bonding with tetrahedral geometry.



Pr. 17. Consider the two compounds CH_3CH_3 (ethane) and CH_3NH_2 (methylamine). Why does CH_3NH_2 have an electric dipole while CH_3CH_3 does not?

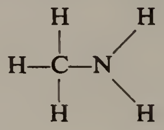
Answer

The symmetry of ethane causes an exact cancellation of all bond dipoles:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H. \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

In methylamine, however,



no such cancellation occurs, since C and N have different nuclear charge. Hence CH_3NH_2 is polar (measured μ is between 1.2 and 1.3 Debyes). (Note that the student may be aided in answering this question by referring him to Textbook Figure 18-1, p. 323.)

Pr. 18. Consider the following series: CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4. In which case(s) will the molecules have electric dipoles? Support your answer by considering the bonding orbitals of carbon, the molecular shape of the molecules, and the resulting symmetry.

Answer

Since atoms with different ionization energies are bonded, one could expect the bonds to have some ionic character. But such bond dipoles result in a molecule with an electrical dipole only if the proper geometry exists. The tetrahedrally oriented bonds of carbon present a geometry in which dipoles will not cancel unless all four attached groups are alike. Such is the case only for CH_4 and CCl_4. The other gaseous molecules have the following dipole moments:

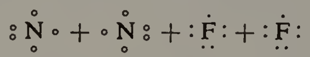
CH_3Cl	chloromethane	1.8 Debye
CH_2Cl_2	dichloromethane	1.6 Debye
$CHCl_3$	chloroform	1.0 Debye

Ball and stick models will be very useful here in showing that the electric dipoles of two C—Cl bonds do not cancel.

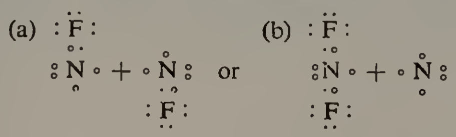
Pr. 19. Predict the structure of the compound N_2F_2 from the electron dot representation of the atoms and the molecule.

Answer

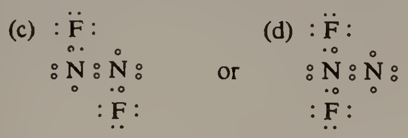
The structure might be approached in a succession of drawings. The atoms are:



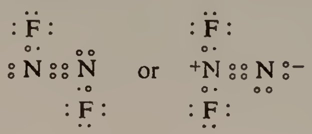
Each fluorine atom can form one bond, but there are two possible arrangements.



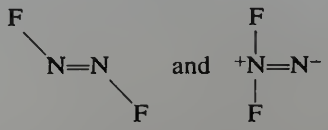
These groups can combine to give



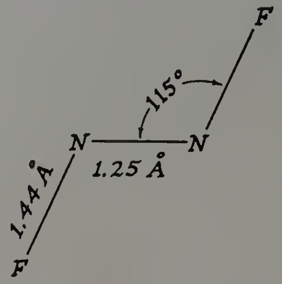
Arrangement (c) can satisfy its bonding capacity by forming a double bond. Structure (c) is favored relative to structure (d), which requires a charge separation:



These correspond to the structures



Both have been postulated, but at present the experiments favor (c), which has the following molecular dimensions.



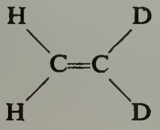
Pr. 20. Which of the isomers of dichloroethylene shown in Figure 16-18 will be polar molecules?

Answer

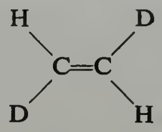
Chlorine has a greater tendency to acquire electrons than does either hydrogen or carbon (as suggested by ionization energies, if the suggested empirical number 200 kcal is used for H). Consequently each carbon-chlorine bond can be expected to have a bond dipole. The symmetries of (*59*) and (*60*) cause a net addition of these bond dipoles, parallel to the C—C bond in (*59*) and perpendicular to it in (*60*). These two isomers are polar. In (*61*), there is an exact cancellation of the bond dipoles, by symmetry, giving a zero electric dipole.

Pr. 21. Draw structural formulas for all the isomers of ethylene (C_2H_4) in which two of the hydrogen atoms have been replaced by deuterium atoms. Label the *cis* and the *trans* isomer.

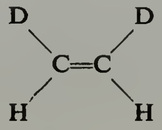
Answer



ethylene-1,1-d_2



ethylene-*trans*-1,2-d_2



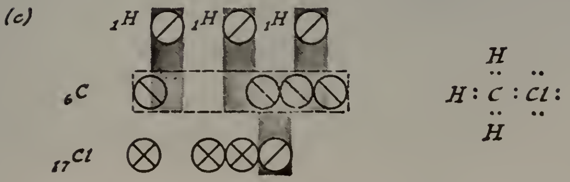
ethylene-*cis*-1,2-d_2

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

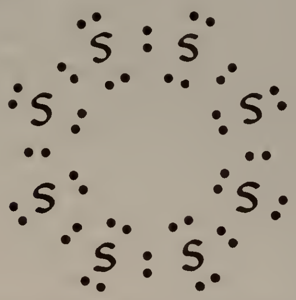
1. Draw orbital and electron dot representations for each of the following molecular substances:
   (a) H_2,
   (b) HCl,
   (c) CH_3Cl.

   Answer



2. Draw the electron dot structure for a sulfur molecule, S_8, in the ring form (see Chapter 20, p. 366).

   Answer



3. Using the electron dot method show a neutral OCl and an OCl^{-1} ion. Which is more reactive? Why?

   Answer

   $\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$ neutral OCl

   $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$ OCl^{-1}

   Neutral OCl is more reactive because it has an empty orbital Some student may ask if the compound Cl—O—O—Cl exists. Although its existence is formally possible, through the sharing of unpaired electrons on two OCl groups, the compound Cl_2O_2 is not stable.

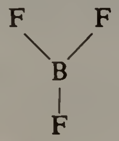
4. Write structural formulas for each of the following compounds, and predict the molecular shape (linear, pyramidal, etc.). Refer to Table 16-IV, p. 293.
   (a) HCl,
   (b) $BeCl_2$,
   (c) BF_3,
   (d) SiF_4,
   (e) AsH_3,
   (f) H_2S.

   Answer

(a) H—Cl diatomic or linear

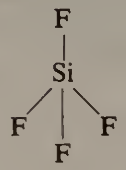
(b) Cl—Be—Cl linear

(c)



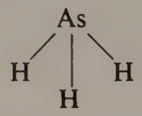
trigonal planar

(d)



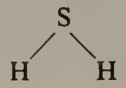
tetrahedral

(e)



pyramidal

(f)



angular or bent

5. On the basis of molecular symmetry, which of the compounds in question 4 would have an electric dipole?

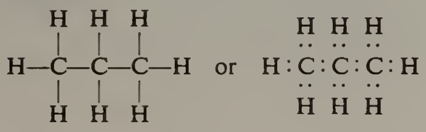
   Answer: (a) HCl; (e) AsH_3; (f) H_2S.

6. Consider the electron dot structure for ethane, C_2H_6, and ethylene, C_2H_4. Which of the two structures would you expect to react more readily with $Cl_2(g)$?

   Answer
   Ethylene, since it can readily share electrons with the chlorine to form $C_2H_4Cl_2$.

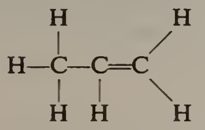
7. Propane is a three-carbon chain, C_3H_8. Draw the structural formula, using either electron pairs or dashes to represent the covalent bonds.

   Answer



8. Propylene, C_3H_6, is a three-carbon chain with a double bond between two adjacent carbons. Draw the structural formula, using dashes to represent the covalent bonds.

   Answer



(*Note*: only one isomer)

9. Which of the combinations (1)–(5) are most likely to form (a) predominantly covalent bonds? (b) Predominantly ionic bonds?
   (1) potassium-chlorine
   (2) oxygen-oxygen
   (3) hydrogen-carbon
   (4) cesium-fluorine
   (5) chlorine-fluorine

   Answer: (a); 2, 3, 5.
   (b); 1, 4.

Use the electron configurations for the following neutral atoms to answer questions 10 and 11:

J	$1s^2, 2s^2, 2p^6, 3s^2$
L	$1s^2, 2s^2, 2p^6, 3s^1$
M	$1s^2, 2s^2, 2p^6$
Q	$1s^2, 2s^2, 2p^5$
R	$1s^2, 2s^2, 2p^1$

10. Write the empirical formula for the stable substance containing the elements
    (1) *L* and *Q*
    (2) *Q* and *R*
    (3) *J* and *Q*
    (4) *M* only
    (5) *Q* only

    Answer
    (1) LQ
    (2) RQ_3
    (3) JQ_2
    (4) M
    (5) Q_2

11. Predict the shape of the molecule in part (2) question 10. Does it have an electric dipole?

    Answer: Trigonal planar. No.

12. What constitutes the chemical bond in a hydrogen molecule? What causes it to form?

    Answer
    The chemical bond in a hydrogen molecule is the sharing of a pair of electrons between two protons. The bond forms because each of the two electrons is attracted to two protons simultaneously. This arrangement is energetically more stable than the separated atoms in which each electron is attracted to only one proton.

CHAPTER

17

THE BONDING IN SOLIDS AND LIQUIDS

Intent and Approach

The basic principles that explain bonding between atoms in gaseous molecules are applied in this chapter to the more complicated situations presented by condensed phases. The simplest situation, in which all atoms are identical, is considered first. Our intent is to show how the ideas of valence orbital occupancy, ionization energy, and electron sharing by nuclei can be used to draw a coherent picture of molecular solids, network solids, and metals. Then the next level of complexity is considered—condensed phases of compounds. This means that unsymmetrical charge separations can occur. The principles presented in Chapter 16 suffice for the discussion of new situations not found for pure elements—e.g., molecular solids of odd-shaped molecules, metallic alloys, ionic solids, and hydrogen-bonded solids. The primary purpose of Chapter 17 is to provide the student with a basis for understanding the properties of the various kinds of condensed phases and a basis for predicting which should be expected for a given chemical substance.

Outline

THE ELEMENTS (17-1)

1. Van der Waals forces are discussed in reference to the condensed phases of the inert gases and of the homonuclear molecules of elements at the right side of the periodic table (17-1.1).
2. Covalent bonding is shown to explain the properties of such network solids as diamond (17-1.2).
3. Metallic bonding is treated in terms of vacant valence orbitals and low ionization energies. The location of metals in the periodic table, and their properties, are explained (17-1.3).

COMPOUNDS (17-2)

4. Van der Waals forces between molecules with symmetrical charge distributions (no molecular dipole) are considered. Number of electrons, molecular size, and molecular shape are examined as factors that influence the melting point and the boiling point (17-2.1).
5. The silicates are cited as examples of network solids formed through covalent bonding (17-2.2).
6. Metallic alloys are briefly treated, with attention to electrical conductivity, hardness, and strength (17-2.3) (reduced type).
7. Ionic solids are treated (17-2.4).
8. The interactions between polar molecules are discussed and used to show why chemists are interested in bond types (17-2.5).
9. Hydrogen bonding is explored. Energy, intermolecular and intramolecular hydrogen bonds, and the significance of hydrogen bonding are all considered (17-2.6).

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
S 17-1/17-1.2 (pp. 301–303)	1	S 17-1/17-1.2	1	1			Van der Waals and Covalent bonding in solids
Expt. 27 Parts I–V	2	Expt. 27 Parts I–V					Packing of spheres of a single size
S 17-1.3 (pp. 303–306)	3	S 17-1.3			2–4	5	Metals and their properties
S 17-2/17-2.3 (pp. 306–311)	4	S 17-2/17-2.3	2		6–8		Molecular solids, Network solids, and alloys (reduced type)
S 17-2.4 (pp. 311–312)	5	S 17-2.4			9–11		Ionic solids
Expt. 27 Parts VI, VII	6	Expt. 27 Parts VI, VII					Packing of spheres of two sizes
S 17-2.5/17-2.6 (pp. 312–317)	7	S 17-2.5/17-2.6		12	13, 16	14, 15	Polar molecules, Hydrogen bonding
	8	Film: CRYSTALS AND THEIR STRUCTURES*					Review: Expt. 27, Bonding in solids
	9	Test on Ch. 14–17					

* Optional here or in Chapter 14. See p. 451 for summary.

New Concepts

1. Neutral, nonpolar molecules (and inert gas atoms) attract each other weakly. The forces are called van der Waals forces.
2. Covalent bonding accounts for the structure and properties of some solids.
3. Atoms with low ionization energy and empty orbitals form metals.
4. Compounds containing atoms with very different ionization energies usually form ionic solids.
5. A hydrogen atom bonded to oxygen, nitrogen, or fluorine can interact strongly with another atom. The interaction is called a hydrogen bond.

Development

INTRODUCTION

The extreme range of properties represented in the condensed phases of pure lithium, pure fluorine, and lithium fluoride is used to encourage consideration of the kinds of bonding found in condensed phases. Emphasize that the principles developed in Chapters 15 (ionization energy) and 16 (valence orbital occupancy, electron sharing, charge separation) will provide a basis for understanding these systems. Notice that this chapter centers primarily on the properties of solids. Liquids are much more complicated.

THE ELEMENTS (17-1)

The pure elements are considered first. This is the simplest situation, since bond dipoles cannot occur if all of the atoms are identical. The bonding types found for the elements are three: van der Waals forces (giving molecular solids), covalent bonds (giving molecular and network solids), and metallic bonding (giving metals).

van der Waals Forces (17-1.1)

The halogens, oxygen, nitrogen, sulfur, and phosphorus form molecules in which all of the bonding capacity is satisfied. Without additional bonding capacity, molecules such as F_2, N_2, P_4, and S_8 behave like inert gas atoms. The intermolecular forces between molecules are very weak—much weaker than the forces holding the atoms together in each molecule. These weak forces are called van der Waals forces.

To explore these forces, let us consider the interaction between two sulfur molecules (formula S_8) (see Textbook Figure 20-3, p. 366). Let's call the two molecules M_1 and M_2. As M_1 is brought close to M_2, electrons attached to the sulfur nuclei in M_1 are simultaneously attracted to the sulfur nuclei of M_2. The case is like that pictured for two helium atoms (Textbook Figure 16-3, p. 276). The electrons of M_1 cannot occupy the valence orbitals of the atoms of M_2 because the valence orbitals of every atom in M_2 are occupied by an electron pair. The same is true for the interaction between the electrons of M_2 and the nuclei of M_1. Since the two molecules cannot approach closely, the attractions are much weaker than they are when electrons simultaneously occupy valence orbitals of each atom. The valence electrons of M_1 can be shared with M_2 only through extra-valence orbitals of M_2 (and vice versa).

Thus the discussion of van der Waals forces is built upon the discussion of the interaction of two helium atoms in Sec. 16-1.2. Notice that this is but one of the contributions to van der Waals forces. Other contributions are present when molecular dipoles are present.

Covalent Bonds and Network Solids (17-1.2)

The normal bonding of a carbon atom gives a tetrahedral bond orientation, as in methane. The spatial arrangement around the carbon would not be expected to change if each of the four hydrogen atoms in methane were replaced by a carbon atom. The central carbon would bond to each of the four adjacent carbons by sharing electrons, just as do the two fluorine atoms in F_2. When four carbons share electrons with a central carbon, four normal covalent bonds result. But the four peripheral carbon atoms have residual bonding capacity. Thus each of these must also have four neighbors, each neighbor requiring three additional carbon atoms to join the aggregate of atoms. This must be continued ad infinitum, building up an infinite network held together by normal, covalent bonds.

Recall that the existence of network solids requires only the repeated application of ideas encountered in Chapter 16. The orbital occupancy, bonding capability, and angular distribution of the bonds determine the molecular structure in the same way for a diatomic molecule such as F_2, for an eight-atom molecule like S_8, and for an "infinite molecule" like a diamond crystal.

Metallic Bonding (17-1.3)

The properties of metals identify a new bonding situation. Yet the existence of metals can also be explained quite simply on the basis of the concepts introduced in Chapters 15 and 16. In metals the electrons are shared among atoms having very low ionization energies and vacant valence orbitals.

Emphasize that most of the elements are metallic. The common properties (electrical conductivity, thermal conductivity, luster, malleability, ductility, etc.) dictate a similar explanation for all. Since metals are characterized by low ionization energies and vacant valence orbitals, a natural model would consist of regularly spaced positive nuclei that have "surrendered" their valence electrons to a communal sharing. The positive nuclei would be immersed in a sea of mobile, free-moving electrons. With such a model, the characteristic properties of metals and the trends shown by their properties are readily explained.

Because the atoms must share the mobile electrons in several valence orbitals, we find that orbital directionality is no longer important in the bonding. Instead the atoms merely seek a packing that places them as close together as possible. Hence the crystal structures can be discussed in terms of the ways in which spherical objects can be packed together. The closest packing arrangements are those found most commonly among metallic crystals. These are explored with models in Expt. 27, Parts I–V.

Expt. 27, THE PACKING OF ATOMS OR IONS IN CRYSTALS,
fits here. See p. 557 for guide.

Part I	Some General Considerations on Packing of Spheres
Part II	Model A—Hexagonal Closest Packing
Part III	Model B—Cubic Closest Packing or Face-centered Cubic Packing
Part IV	Comparison of Hexagonal Closest Packing with Cubic Closest Packing
Part V	Model C—Body-centered Cubic Packing

COMPOUNDS (17-2)

With two or more types of atom present, a new variable enters the discussion of bonding. Unsymmetrical charge separations can now occur. The resulting bond dipoles cause additional interactions, even between molecules whose bonding capability is satisfied. In the extreme cases of ionic bonding in which one of the atoms has vacant valence orbitals, ionic solids occur.

van der Waals Forces and Molecular Substances (17-2.1)

Just because charge separations (bond dipoles) may occur does not mean they must occur. The C—H bond, for example, involves a very small electric bond dipole. Even for molecules involving substantial bond dipoles, molecular symmetry can cause cancellations that result in a zero molecular dipole. Molecules having zero molecular dipoles attract each other with the same weak van der Waals forces that account for liquefaction and solidification of the inert gases and of such elements as F_2, Cl_2, P_4, and S_8. Thus we find an explanation for the properties of such molecular compounds as CF_4, CH_4, CCl_4, C_2Cl_6, BF_3, CO_2, etc. Because the forces between molecules are so weak, many properties of these substances remain virtually unchanged as the molecules pass from gas to liquid to solid state. Therefore, such substances are called molecular solids.

More variety in molecular shape and size is encountered among molecular compounds than among the elements. The way in which the properties relate to the number of electrons (in the peripheral atoms), to molecular size, and to molecular shape is treated in the Textbook.

Covalent Bonds and Network Solid Compounds (17-2.2)

The discussion of the network solids formed by elements is again applicable to compounds, though much greater variety is encountered. The silicates furnish an excellent example; first, because they are so abundant and, second, because the network types are so obviously responsible for an interesting range of macroscopic mineral properties.

Metallic Alloys (17-2.3) (reduced type)

New principles are not needed in discussing metallic alloys. The ease of forming alloys is readily explained within the metallic model we have used. Since the bonding between neighbors is diffuse—through the highly mobile "electron sea"—impurity substitutions can occur without serious disturbance to the crystal bonding. If the impurity atoms tend to form rigid and localized bonds (as does carbon, for example), then metallic properties are sacrificed somewhat. The result is that we have great control over such metallic properties as electrical conductivity, tensile strength, hardness, brittleness, melting point, etc., through alloy formation. Steel, the most important single example, is treated again in Sec. 22-3.6 (Textbook p. 403).

Ionic Solids (17-2.4)

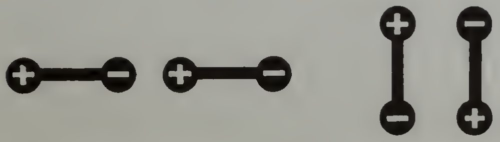
When a compound is formed between two elements with extremely different ionization energy, there tends to be a large charge separation (ionic bonding), and the vacant valence orbitals of the metallic atoms tend to give a nondirectional character to the bonding (as in metals). The result is that the crystals are made up of interlocking arrays of positive and negative ions whose packing is complicated compared to metals because of two new factors: the two kinds of ions may have different size, and they must be placed so as to avoid nearest neighbors of the same electric charge. Once again the packing of spheres readily explains the observed crystal structures, provided attention is given to size and charge.

Expt. 27, THE PACKING OF ATOMS OR IONS IN CRYSTALS,
fits here. See p. 557 for guide.
Part VI The Sodium Chloride Lattice
Part VII The Zinc Sulfide (Wurtzite) Lattice

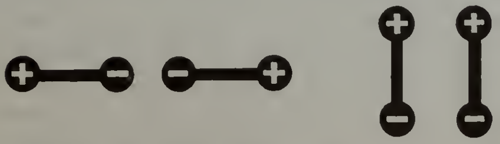
Such an alternating arrangement of positive and negative ions gives crystals having quite distinctive properties. They do not have the electrical conductivity of the metals; the valence electrons remain highly localized near the negatively charged ions. In general, ionic bonds tend to be strong (see the discussion on p. 531) and, since they interlink the entire crystal, ionic solids tend to be high melting, hard, and brittle.

Effects Due to Charge Separations (17-2.5)

Relatively few molecules have sufficient symmetry to give a zero molecular dipole. A molecular dipole causes molecules to interact more strongly with each other than do molecules without dipoles. The molecules tend to be oriented relative to one another so as to give the lowest energy arrangement. The tendency toward randomness opposes this orderly arrangement. If the lowering of energy is sufficient to offset the loss of randomness, then an orderly arrangement will result. The arrangements



have lower energy than the arrangements



There is no doubt that polarity has an influence on solubility. It is not the only factor, however, and, if considered alone, can lead to erroneous statements. One such statement is "like dissolves like." Although this rule of thumb does have some use *for an experienced person*, it is not suitable for a beginner. Much of the beginner's limited experience is in conflict with the rule, which in turn is too limited.

Consider, for example, the ways in which NaCl and AgCl are alike. Yet how different are their solubilities in water! On the other hand, two quite soluble substances, salt and sugar, are decidedly unlike. In none of the three—NaCl, AgCl, or sugar—is there any obvious resemblance to the solvent, water.

Finally, the rule is frequently applied in a circular fashion: "like dissolves like"; like things are those which dissolve in the same solvent. The experimental data in Textbook Table 17-IV are interpreted by a more general consideration of the summation of energy and randomness effects required to break up the interactions between molecules of the two pure compounds and to form the interactions present in the solution. We can show this in terms of the general reaction

$$\begin{array}{lll} \text{Solute } A + \text{Solvent } B & \text{gives} & \text{Solution } AB \\ A\cdots\cdot A \qquad B\cdots\cdot B & & A\cdots\cdot B \end{array}$$

The dotted lines represent the interactions. There are now four possible cases, shown in outline form below.

You will notice the cautious comments about solubility. This is necessary because other factors such as entropy changes and hydrogen bonding might be acting in opposition to the interactions shown. Perhaps a more positive way to put the conclusions in the table is to say, for the first and last examples, that the polar properties are appropriate for good solubility. The reverse is true for examples 2 and 3. The final solubility achieved is the sum of this and other influences.

Solute	Solvent	$A\cdots\cdot A$	$B\cdots\cdot B$	$A\cdots\cdot B$
Nonpolar	nonpolar	weak	weak	weak, not much change for solute or solvent; solubility can be high
Nonpolar	polar	weak	strong	weak, difficult to break up $B\cdots\cdot B$; solubility probably low
Polar	nonpolar	strong	weak	weak, difficult to break up $A\cdots\cdot A$; solubility probably low
Polar	polar	strong	strong	strong, not much change for solute or solvent; solubility can be high

Striking effects of such molecular dipoles appear in the dielectric and solvent properties of liquids. The high dielectric constant of water is attributable to the high molecular dipole of this compact molecule. The most important single consequence is the dissolution of such substances as NaCl and HCl in water during which ions are formed. The great stability of ionic solids is shown by their characteristically high melting points. Yet sodium chloride dissolves readily in water, showing that ions in water are also extremely stable. The explanation is found in the attractive interactions between the molecular dipoles of water and the ionic charges. The arrangement of the water molecules around a positive ion can be represented in terms of dipoles, as shown on Textbook p. 314.

The simplified discussion of energy and randomness effects given on Textbook p. 313 is intended to help the student further understand some of his experimental results (Expt. 12). For most solids that are soluble in water, the various processes are nearly balanced, and only a small effect is noted. For gases that dissolve in liquids, the randomness is very much reduced in solution. Further, the effect is heightened as temperature increases, hence the solubility of almost all gases decreases as the mixture is heated. (There are rare examples of the reverse trend. Hydrogen dissolves more in xylene as the temperature is raised.) The observed effect is always the sum of two or more processes.

Hydrogen Bonds (17-2.6)

The formation of hydrogen bonds can be attributed to molecular dipole effects. This is substantiated by the fact that the strongest hydrogen bonds occur when hydrogen is attached to an atom having high ionization energy, such as oxygen or fluorine. In addition, there seems to be a uniqueness about the effect that is probably associated with the relatively small size of the hydrogen atom. There is some evidence that lithium has similar behavior, but, by and large, the effects of hydrogen bonds distinguish these interactions from others.

Energetically, hydrogen bond interactions are intermediate between the normal chemical bond (usually over 50 kcal/mole) and the weak van der Waals interactions (usually less than 1 kcal/mole). The magnitudes of hydrogen bond energies, 3–7 kcal/mole, account for their special importance. These interactions are sufficiently strong to dominate the usual solvent interactions, yet weak enough such that they do not challenge molecular stability. Most properties of hydrogen bonded systems can be understood in terms of these relative energies. The most dramatic and important examples occur in the biochemical systems, where it is found that hydrogen bonds play a crucial role in fixing molecular configuration, as discussed in Sec. 24-3.3.

Film, CRYSTALS AND THEIR STRUCTURES,
can fit here. See p. 451 for summary.

EXPERIMENT 27 THE PACKING OF ATOMS OR IONS IN CRYSTALS

PURPOSE. To study the ways in which spheres can be packed and to relate these arrangements to common crystal structures found for metallic and ionic solids.

PRELAB DISCUSSION. None. See *Laboratory Hint* section below.

TIMING. Parts I–V mesh with the discussion of metals and should be used with Textbook Sec. 17-1.3. Parts VI and VII relate to the structures of ionic solids and should be used with Sec. 17-2.4.

EQUIPMENT NEEDED (FOR EACH GROUP—OF TWO OR, IF NECESSARY, FOUR)

a box containing the following styrofoam spheres:
36 2-inch spheres (one of these should be colored)
13 1-inch spheres
13 $\frac{3}{4}$-inch spheres
pipe stem cleaners cut into one- to two-inch lengths (about 60 for each set). (Pipe stem cleaners can be cut on a paper cutter.)

TIME REQUIRED. Parts I–V: $\frac{2}{3}$ period. Parts VI and VII: $\frac{1}{2}$ period.

LABORATORY HINT. Some students find these ideas extremely easy to grasp. Many, however, will find them difficult. Plan on being quickly available for those who have difficulty. Splitting the experiment into two parts not only makes for better correspondence with the Textbook, but also enables the student to review the packing of spheres of the same size after he has read more about the structure of solids and before he goes on with a study of ionic crystals.

DISCUSSION

PARTS I–IV (Questions included in *Procedure* are answered below)

Discussion of the experiment should emphasize the idea that "closest packing" is the packing of spheres of uniform size to occupy the smallest volume, hence to bring the atoms as close together as permitted by the repulsive interactions that give the atoms size. In Part I, the student learns that within one plane, the closest packing of spheres of the same size gives each sphere six nearest neighbors, no matter how large the spheres. In II, this packing is extended to three dimensions by using the hexagonal closest packing arrangement. Then in III and IV, the cubic closest packing is demonstrated in two ways, in III to display the cubic arrangement, and in IV to contrast hexagonal and cubic closest packing. Point out that twelve nearest neighbors result from either closest packing arrangement.

PART V

The body-centered cubic packing is not a closest packed arrangement. Each atom has only eight nearest neighbors, and the density is lower than it is in the closest packing arrangements.

PARTS VI AND VII

Two common ionic lattices are contrasted. Emphasize that these lattice types are found for many crystals. Thus all of the alkali halides have NaCl lattices except three, CsCl, CsBr, and CsI. The wurtzite (ZnS) lattice is found in many crystals of composition *AB*, including AlN, GaN, InN, BeO, ZnO, CdS, SiC, CdSe, MgTe, and AgI.

ANSWERS TO QUESTIONS IN PROCEDURE SECTION

PART I

(a) The maximum number of spheres that can be packed around a single sphere in the same plane is six. The number is independent of the size of the spheres if they are all the same size.

(b) The marked sphere has twelve neighbors touching it. Since these neighbors are all at the same distance and closer than any others that can now be added, they are called *nearest neighbors.* The number of nearest neighbors is equal to the coordination number.

PART II

(d) The coordination number is twelve.

PART III

(b) The model is called face-centered cubic because the unit cell cube has a sphere placed in the center of each cube face.

PART IV

(c) No. The coordination number is 12 for each type of closest packing. There is no difference in density when spheres of the same size and weight are involved.

Since most metals are found in closest packing arrangements, closeness of approach rather than fixed direction of bonding dominates the crystal structure. Nevertheless, the fact that some metals are found in cubic, but not hexagonal, packing, whereas others are found in hexagonal, but not cubic, packing could be interpreted to mean that some metals have a directionality that favors one closest packing and that other metals have a directionality that favors the other. A relatively small amount of directionality may be the factor that determines which of the closest packed structures is the more stable. Yet the difference between hexagonal and cubic closest packing could also be attributed to interactions between the first and third layers of atoms rather than to nearest neighbors.

PART V

(b) The alkali metals have many vacant valence orbitals but very few valence electrons. Presumably the shortage of bonding electrons accounts for the fact that the alkali metals are more stable when the arrangement is such that each atom shares valence electrons with only eight nearest neighbors (as in body-centered cubic packing) rather than with twelve nearest neighbors (as in the closest packed structures).

(c) α-ferrite (alpha-ferrite) has coordination number 8.
γ-ferrite (gamma-ferrite) has coordination number 12.
δ-ferrite (delta-ferrite) has coordination number 8.

The effect of raising the temperature could be to excite more and more electrons to act as valence electrons. At low temperatures, perhaps there is a shortage of valence electrons, making the structure having coordination number eight the most stable. As more electrons become mobile, the structure having coordination number twelve becomes the most stable. Explaining the high-temperature transition to the δ form is more difficult. Perhaps the thermal excitation of lattice modes finally favors a less densely packed crystal that gives each atom more space in which to vibrate. The student is asked to "suggest" a reason, so detail is not to be expected. The actual answer is not known.

PART VI

(c) Surrounding each Na$^+$ ion are six Cl$^-$ ions, and around each Cl$^-$ ion are six Na$^+$ ions. The coordination number for each kind of ion is six. Coordination number in ionic solids is determined as for metallic structures, by counting the number of nearest neighbors. In ionic solids, the nearest neighbors have a charge opposite to that of the central atom.

(d) $0.95\ \text{Å}/1.81\ \text{Å} = 1/1.91 = 0.525$

The stability of this type of packing can be attributed to the proximity of ions of opposite charge.

PART VII

(c) The coordination number for Zn^{+2} is four.

(d) $0.70/1.90 = 1/2.71 = 0.368$

QUESTIONS AND ANSWERS (AT THE END OF THE EXPERIMENT)

1. Write a brief description of each type of packing of metallic crystals that you studied.

Answer: The student's description should include hexagonal closest packing, cubic closest packing, and body-centered cubic packing.

2. Answer all questions raised in the *Procedure* sections. Label them by Parts and Sections, for example, Q.I-a.

Answer: See *Answers to Questions in Procedure Section* (previous page).

3. In one of the types of cubic packing, the spheres occupy about two-thirds of the space, and in the other they fill about three-fourths of the space available. Identify which type is which. Which is more dense? Which has the larger number of bonds?

Answer: In the body-centered cubic packing, about two-thirds of the space is occupied by the spheres. Three-fourths of the space available is occupied by the spheres in cubic closest packing. Cubic closest packing is the more dense of the two, and has the larger number of bonds.

4. From your consideration of the models constructed in Parts VI and VII, what relation can you deduce concerning the radius ratio of ions and the coordination number in crystals? In which case is the number of interionic attractions the greater around any given ion?

Answer: In NaCl the ratio is about 1/2 for the radii of the ions, and the coordination number of each ion is six. In ZnS the ratio of the radii is about $\frac{3}{4}/2$, and the coordination number of zinc is four. One may deduce that the coordination number will tend to be smaller in crystals having a greater difference between their ionic radii. Conversely, the smaller the difference between ionic radii, the larger the coordination number. Note that for metallic crystals in which the atoms have the same radii, the common coordination numbers are eight and twelve.

5. Suppose you have a crystal XY with the sodium chloride packing in which each of the ions is the same size as the Na^+ and Cl^- respectively, but each is doubly charged X^{+2} and Y^{-2}. Would XY have a higher or lower melting point than NaCl? Suggest a real pair of crystals which meet the above criteria and look up their melting points to check your prediction.

Answer: Crystal XY would have a higher melting point, due to the stronger attractions between the ionic charges (for example, NaCl, m.p. = 801°C; CaO, m.p. = 2850°C).

Of course, not all $X^{+2}Y^{-2}$ crystals have the NaCl structure (e.g., ZnS). The student can find tables that list the crystal structures in most handbooks under the index entry "X-ray crystallographic data"; for example, in the *Handbook of Chemistry and Physics*, 41st ed., such a table is found on pp. 2678–2710. Some examples of NaCl-type crystals are MgO, MgS, CaO, CaS, SrO, SrS, BaO, BaS, MnO, FeO, PbS.

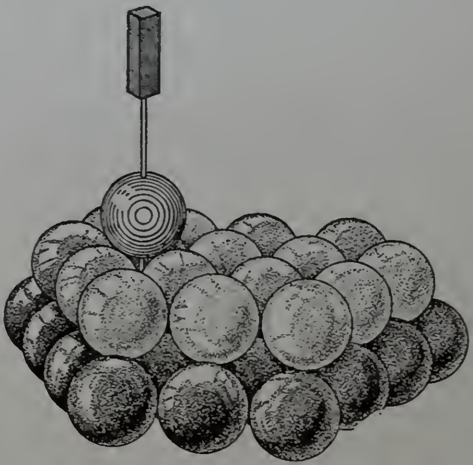
6. Suppose you have a crystal AB with the sodium chloride packing in which each of the ions has the same charge A^+ and B^-, as Na^+ and Cl^-, but the radii of A and B are proportionately larger. Would AB have a higher or lower melting point than NaCl? Suggest a real pair of crystals which meets the above criteria, and look up their melting points to check your prediction.

Answer: The larger the ions, the farther the charges are separated, hence the weaker will be the crystal. It would be desirable to compare salts with constant radius ratio. This isn't possible, but the trend is nevertheless detectable in the following data.

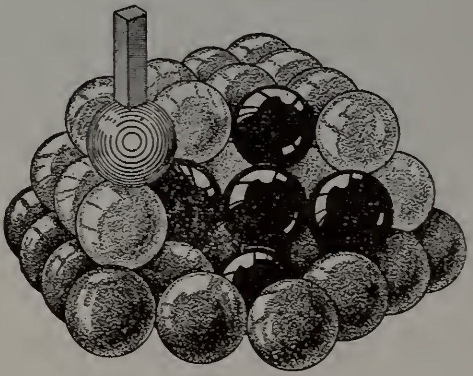
Salt	Radii (A) M^+	Radii (A) X^-	$\frac{\text{Radius } X^-}{\text{Radius } M^+}$	m.p.
LiF	0.60	1.36	2.27	870°C
NaCl	0.95	1.81	1.91	801°C
KBr	1.33	1.95	1.47	730°C
KI	1.33	2.16	1.62	723°C

POSTLAB DISCUSSION. The difference between hexagonal and face-centered cubic close packing is not easy to demonstrate. The following apparatus, which you can make, will help. Glue 20–25 blue balls onto a board in a hexagonal arrangement. Then have a separate second layer (maybe 10–15) painted white and a third layer painted red. These two layers should be removable. Finally, you need a "gauge" stick made from a piece of ¼ inch dowel three times as long as the diameter of the sphere used, plus one inch for mounting a handle. Glue a handle at one end, and insert the dowel through a hole bored along a diameter of a sphere.

When using the apparatus, first show the bottom layer, then place the second one on it, and use the gauge to show that there are two possible positions for the third layer. In one position the dowel will fall down to the base board, and the movable ball will slide up near the handle, showing that the third layer is over a hole in the bottom layer. This face-centered cubic arrangement is sometimes labeled *ABC* because the three layers are different. In the other position, the dowel will only go down to the top of the bottom layer, and the movable ball will be about one sphere diameter below the handle. In this position the third layer is directly over the first layer. This arrangement is called hexagonal closest packing, and is labeled *ABA*. There are only two different layers of atoms. The diagram on the opposite page shows how the apparatus is used.



You can also use this demonstration apparatus to show how a side of a face-centered cubic (f.c.c.) unit cell occurs in the layers of the *ABC* structure. For this you need a segment of the cell, as shown on the left below.



One ball of the first (blue) layer must be removable. The side of a f.c.c. unit cell will fit where the blue ball is removed if it is tilted to the proper angle. This is not possible if the layers are ordered *ABAB* ⋯ . With the model in front of you, the arrangement is clear.

Supplementary Material

Articles

1. R. A. Lefever, "An introduction to the electron theory of metals," *J. Chem. Education*, 30, 486 (1953).* A brief treatment suitable for the interested student.
2. R. A. Lefever, "A summary of semiconductor and transistor theory," *J. Chem. Education*, 30, 554 (1953).* A brief treatment suitable for the interested student.
3. T. R. P. Gibb and A. Winnermann, "Crystal geometry—application to salts," *J. Chem. Education*, 36, 46 (1959);* 36, 160 (1959).* Suitable reading for the interested student; includes discussion of the Born-Haber cycle.
4. R. W. Taft and H. H. Sisler, "Hydrogen bonding and some observations on the physical properties of the hydrogen compounds of the elements of groups 4a, 5a, 6a, and 7a," *J. Chem. Education*, 24, 175 (1947).* Suitable reading for the interested student; elementary estimates of the thermodynamics of hydrogen bond formation, including entropy.
5. G. H. Wannier, "The nature of solids," *Scientific American*, December 1952† (Offprint No. 249).** Good, nonmathematical discussion for the interested student and teacher. Distinguishes metallic and semiconductor solids.
6. J. A. Campbell, "Some simple solid state models," *J. Chem. Education*, 34, 210 (1957).‡ Suitable reading to supplement Expt. 27.
7. L. N. Ferguson, "Hydrogen bonding and physical properties of substances," *J. Chem. Education*, 33, 267 (1956). Qualitative review of the effects of hydrogen bonding. Suitable for the interested student.

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* Included in "Supplementary Readings for Chemical Bond Approach," reprints from *J. Chem. Education*.

† Included in "Supplementary Readings for Chemical Bond Approach," reprints from *Scientific American*.

** Available from W. H. Freeman and Co., San Francisco. Order by number.

‡ Included in "Selected Readings in General Chemistry," compiled by W. F. Kieffer and R. K. Fitzgerel, published by Div. of Chem. Ed., ACS, Easton, Pennsylvania; reprints from *Journal of Chemical Education*.

Books

1. M. J. Sienko and R. A. Plane, *Chemistry*, McGraw-Hill, New York (1961). Chapter 8 provides a discussion of solids that is suitable for the above-average student.
2. L. A. Hiller and R. H. Herber, *Chemistry*, McGraw-Hill, New York (1960). Chapters 6 and 9 give a discussion of solids (Chapter 6) and metals (Chapter 9) suitable for the above-average student.
3. W. J. Moore, *Physical Chemistry*, Prentice-Hall, Englewood Cliffs (1955 . Chapter 13, "Crystals," and Chapter 14, "Liquids," contain excellent background reading for the teacher.
4. L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, New York (1960). Chapter 11, "The Metallic Bond," Chapter 12, "The Hydrofgen Bond," and Chapter 13, "The Sizes of Ions and the Structure of Ionic Crystals," are excellent background reading for the teacher.
5. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco (1960). A complete and nonmathematical treatment of hydrogen bonding, suitable for the interested student or as background reading for the teacher.

Films

"Film Strips on Molecular Models," J. A. Campbell, Encyclopaedia Britannica Series (seven film strips available), 1960.

Encyclopaedia Britannica Films
1150 Wilmette Avenue
Wilmette, Illinois

CRYSTALS AND THEIR STRUCTURES

A CHEM Study film
Running Time: 22 minutes

See page 451 for summary.

Background Discussion

INTRODUCTION

In the present discussion, we attempt to present a brief systematic view of the interactions that hold matter in condensed phases. This topic is a very large one, and our discussion cannot be complete. We shall indicate the directions in which are found useful explanations for each of the various types of interaction, but we shall not be able to follow any of these paths very far.

In the development of chemistry, it has become convenient to identify the following types of interactions in solids and liquids:

(1) covalent bonding,
(2) van der Waals interactions,
(3) metallic bonding,
(4) ionic bonding,
(5) hydrogen bonding.

All these interactions are ultimately accounted for by the simultaneous movement of electrons near two or more nuclei. In spite of this common cause, these interactions are distinguished because the properties of a system are influenced markedly by orbital occupancy, ionization energy, and charge distribution. We shall see how these three factors provide a coherent picture of the five types of interactions we have listed.

SOLIDS AND LIQUIDS DISTINGUISHED

Before we consider in detail how the condensed states of matter are held together, it will be useful to distinguish between solids and liquids, on both a macroscopic and a microscopic scale. On a macroscopic scale such a distinction is easy and familiar. *A solid retains its shape regardless of the shape of the container, whereas a liquid tends to assume—at least to the extent that its volume allows—the shape of the confining volume.*

On a microscopic scale there are two distinctions that can be considered. The first relates to mobility of the constituent particles (atoms or molecules), and the second relates to order.

*In solids the nearest neighbor particles (atoms or molecules) tend to remain in fixed relative positions over long time periods.** *In liquids, the nearest neighbor particles are constantly changing.* A given atom (or molecule) may migrate from one location to another while the number of nearest neighbors to a given atom (or molecule) remains constant, on the average, due to compensating migration of other atoms or molecules.

Another way in which solids and liquids can be contrasted on a microscopic scale is in relation to long distance order. Long distance order or repetitious spatial arrangement is not present in liquids. In some solids, called crystals, it is present; in others, called glasses, it is not. Let us consider crystals first.

A crystalline solid can be described as an orderly array of repeating units in space. The entire crystal can be "generated" merely by specifying the positions of a small number of atoms and some rules by which this unit is moved through space in regular increments. This small number of atoms is called a unit cell. In some crystals the rules for moving the unit cell are merely to slide (translate) it along the three Cartesian coordinate axes. In other crystals, the axes must be taken at angles other than 90°. In some crystals, the unit cell must be translated and turned. But in all cases, the unit cell is repeated again and again throughout the macroscopic dimensions of the crystal. A crystalline solid consists of an arrangement of atoms with this type of long range order. In contrast, a glass lacks this definite repeating order. It meets the macroscopic criterion of solids—it maintains shape—as well as the diffusion criterion—diffusion is often negligible in a glass. Nevertheless, the spatial arrangements are disordered, like those in liquid. In fact, a reasonable argument can be made for defining a glass as a limiting case of a liquid of very high vis-

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* Diffusion within a solid is encompassed in this statement through the arbitrary specification "*long time periods.*" For our purposes, we mean that diffusional movement can normally be neglected during experimentally significant time intervals (seconds, minutes, hours).

cosity. The viscosity of glycerine, for example, increases as temperature is lowered. The temperature at which it is considered to become a glass is difficult to ascertain and is, in fact, rather arbitrary. Ultimately, the classification of a glass as a "solid without long range order" or as a "liquid with extremely high viscosity" is a matter of convenience, and need not divert us further. Henceforth, we shall ignore the glassy state and shall interpret a solid as a condensed phase of matter possessing long range order, and a liquid as a condensed phase of matter without long range order.

COVALENT BONDING IN NETWORK SOLIDS

Whether a chunk of a covalently bonded crystal be called a network solid or a molecule is a matter of semantics dictated by convenience. Apparently the interactions that hold the carbon atoms together in diamond are the same as those that hold the four carbon atoms to the central carbon atom in a highly branched hydrocarbon such as $C(CH_3)_4$ (neopentane), in terms of both energy and bond orientation. The requirement that a molecule contain only a limited number of atoms is purely a matter of convenience (readily abandoned when desired, as it is in discussing the so-called "macromolecules," such as proteins). The important thing to stress is that the ideas already developed for gaseous molecules—the nature of chemical bonds, the number per atom, and their spatial arrangements—suffice for an understanding of the existence of network solids.

VAN DER WAALS INTERACTIONS

The principles we have developed to explain chemical bonding also aid us in seeing the origin of van der Waals interactions between atoms not held together by a chemical bond. The very general explanation of bonding explains that these forces, too, must arise because electrons are simultaneously near two nuclei. However, each valence orbital can hold but two electrons. If these valence orbitals are all fully occupied, then the nuclei of nonbonded atoms must remain at relatively large separations and the interactions will be weak. In terms of orbitals, only extra-valence orbitals are accessible for electron sharing, hence the binding of an electron in an extra-valence orbital is quite weak.

With this general view of why atoms or molecules that have no empty bonding orbitals still display residual but very weak attractions, we can proceed to examine more closely the classifications that are convenient among van der Waals interactions. We shall consider only two types, London and dipole–dipole interactions.

London Interactions

The forces that hold inert gas atoms together in the liquid and solid states (as well as symmetrical molecules like methane, CH_4) were explained by F. London. The London theory recognizes that the electron–electron repulsion between, for example, two helium atoms can be lessened if the electron movements correlate so as to keep the electrons apart. The electrons on one atom apparently spend as much time as possible between the two nuclei when the electrons of the second atom happen to be in some other region of space.

Mathematically, this situation can be likened to the interaction of two dipoles. An electron and the nucleus of the first atom are thought of as an "instantaneous electric dipole"; an electron and the nucleus of the second atom as another "instantaneous electric dipole." Energetically, these two dipoles seek an alignment in which opposite charges are close together. The result is as pictured in Figure 17-1; the electrons move with preference to energetically favorable arrangements like 1 and 2, while discriminating against unfavorable arrangements like 3 and 4. In each picture, the dominant intermolecular interaction is shown by broken lines. The London scheme permits a formulation of the statistical average of the net interaction. It is found to be attractive, and depends upon the internuclear distance as r^{-6}.

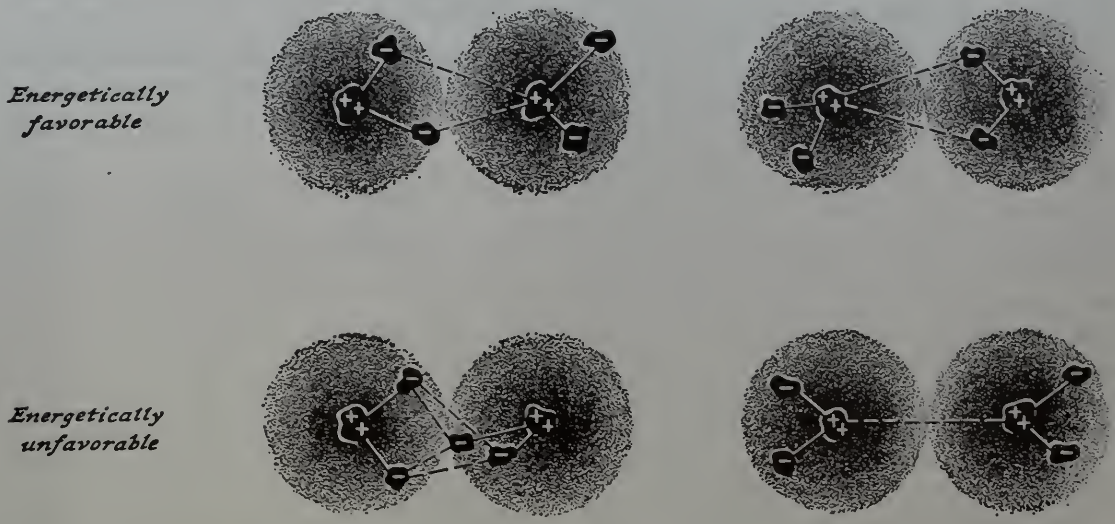


Fig. 17-1. **Favorable and unfavorable positions of electrons** *as helium atoms approach.*

Dipole-dipole Interactions

Molecules possessing nonzero electric dipoles interact more strongly than is accounted for by the London treatment. In certain ways, the problem is analogous to the "instantaneous dipole" interaction just described. This additional interaction also depends upon the distance as r^{-6}. Its magnitude depends upon the dipole moment very sensitively—as μ^4 for identical molecules—and can be quite large if μ is appreciable! (For different molecules, A and B, the dependence is $\mu_A{}^2\mu_B{}^2$.) Table 17-I shows the calculated interactions due to dipole-dipole interactions and London interactions for a series of molecular species, all considered at 5.0 Å separation to provide a common basis. The trend in the results parallels that shown by the heats of vaporization.

METALLIC BONDING

Metallic properties are found for the condensed phases of elements having the following properties:

low ionization energies;
vacant valence orbitals;
few valence electrons (relative to the number of valence orbitals).

Table 17-I. **Calculated Intermolecular Interactions (All Calculations at 5.0 Å)**

Molecule	Dipole Strength (Debyes)	Calculated Energy Due To London Forces	Calculated Energy Due To Dipole-dipole	Sum	$\Delta H_{\text{vap'n}}$ (kcal/mole)
He	0	0.7	0	0.7	0.02
Ar	0	42	0	42	1.6
CO	0.12	66	0.003	66	1.4
HCl*	1.03	112	17	129	3.9
NH_3*	1.5	81	75	156	5.6
H_2O*	1.84	38	172	210	9.4

* Hydrogen bonding present.

We explain the existence of metals in terms of these three factors as follows. Under these conditions, the atoms cluster together as closely as possible so as to completely occupy the empty valence orbitals with the few valence electrons available. The combination of low ionization energy and many available orbitals yields an environment in which valence electrons are not localized in a particular region between two atoms, and thus do not form a single specific bond. Instead, they move freely about the central atom within the many available orbitals in such a way that they contribute to the bonding of several nearest neighbors. This free movement of the valence electrons accounts for the high electrical and thermal conductivities of metals.

There seems little question that low ionization energy plays a role in fixing metallic properties. For example, it is an empirical fact that all of the elements with distinctly metallic properties have first ionization energies below 250 kcal/mole. That the first ionization energy is by no means the only factor fixing metallic properties is readily seen by comparing electrical conductivities (the most characteristic metallic property) to ionization energy.* Table 17-II lists the fifteen elements having highest electrical conductivity in order of decreasing conductivity. The fourth column lists the first ionization energies. The absence of correlation is obvious. The lowest ionization energy among these elements is that of potassium (100 kcal/mole), which is next to last in electrical conductivity. Gold, which has one of the highest ionization energies, is the third best conductor among all the elements.

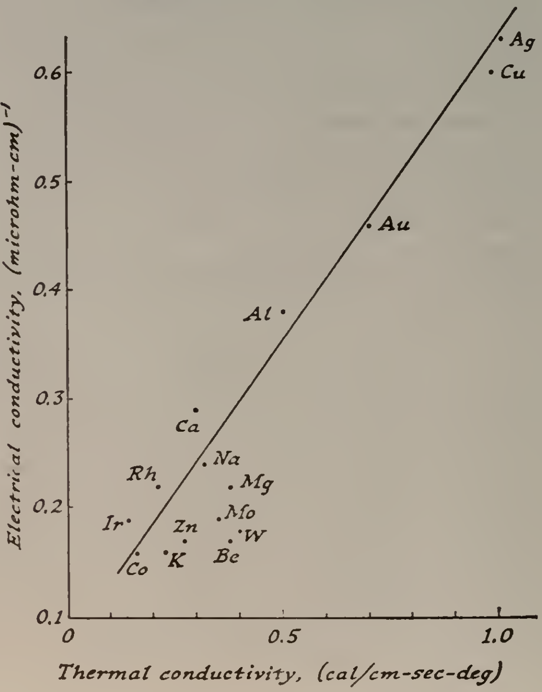
On the other hand, Table 17-II suggests that whatever does cause high electrical conductivity also causes high thermal conductivity. Figure 17-2 shows a plot of these data. The correlation is clear at the higher values, and it is explained in terms of the contribution by the mobile electrons (which cause high electrical conductivity) to the thermal conductivity. Of course, a significant amount of the thermal conductivity that

Table 17-II

First Ionization Energy, Electrical and Thermal Conductivity of the Fifteen "Most Metallic" Elements

Element	Electrical Conductivity (microohm-cm)$^{-1}$	Thermal Conductivity (cal/cm-sec-deg)	First Ionization Energy (kcal/mole)
Ag	0.63	1.01	175
Cu	0.60	0.99	178
Au	0.46	0.70	213
Al	0.38	0.50	138
Ca	0.29	0.3	141
Na	0.24	0.32	118
Mg	0.22	0.38	176
Rh	0.22	0.21	177
Mo	0.19	0.35	170
Ir	0.19	0.14	212
W	0.18	0.4	184
Be	0.17	0.38	215
Zn	0.17	0.27	216
K	0.16	0.23	100
Co	0.16	0.16	182

Fig. 17-2. **Relation between electrical and thermal conductivity.**



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* The ionization energy *does* correlate with chemical properties of the metallic elements when they are *not* in the metallic state (e.g., acid–base properties).

exists in certain solids (for example, sulfur) does *not* depend upon mobile electrons.

The Fermi Gas Model of Metals

The most elementary theory of metallic properties is based upon the calculated properties of a gas consisting of electrons confined within the crystal but free to move without restraint. It is assumed that these electrons do not interact either with the nuclei or with each other. Surprisingly, this simple model, called the Fermi Gas model, is remarkably successful in explaining many properties of metals. For example, classical theories of the heat capacity of metals predicted that the conduction electrons, if completely free, should contribute much more to the heat capacity than is found experimentally. Yet the Fermi Gas model explains the high conductivity without requiring a large contribution to the heat capacity by the electrons. There are other successes, too, such as the agreement between the model and experiment in predicting that the electromotive force generated by a thermocouple should depend upon the square of the temperature of the bimetallic junction.

How this model gives rise to these predictions can be indicated only qualitatively here. The model gives the electrons only kinetic energy, since all potential energy interactions are ignored. A set of energy levels is generated, as in the hydrogen atom, but they are almost continuous in their spacing. Each energy level corresponds to a particular electron velocity in a particular direction. Corresponding to each energy level that designates electron movement in, for instance, a north-to-south direction in the crystal, there is another energy level that designates electron movement in the opposite direction, south-to-north. The Pauli Principle is assumed to apply, therefore only two electrons can occupy a given energy state. An enormous number of states is needed to accommodate all the valence electrons in a macroscopic crystal. For example, if the crystal contains one mole of sodium atoms, it contains 6×10^{23} valence electrons. Thus at absolute zero, 3×10^{23} energy states would be occupied.

Let us first examine how this model explains electrical conductivity. With no external electric field, electrons occupy as many of the north-to-south levels as they do the south-to-north levels. No net electron movement results. When an appropriate electric field is applied, however, the north-to-south moving electrons are moving "downhill" energetically, and the south-to-north moving electrons are moving "uphill." That is, all the north-to-south levels are lowered slightly, and the others are raised slightly. Some of the electrons spill over from the south-to-north levels into the lower-energy north-to-south levels. With more electrons having kinetic energy carrying them toward the south than there are electrons moving toward the north, conductivity results. The ease of obtaining this type of conductivity arises because the levels in this model are so closely spaced that only a small electric field is needed to get a net current. Since the model neglects all interactions with the atoms, the moving electrons cannot transfer energy to the lattice, and the model predicts zero electrical resistance.

The Band Theory: Bloch's Model

Felix Bloch made a significant improvement on the Fermi Gas model by introducing a periodic potential function to represent the effect of the positive nuclei in the crystal lattice. The Bloch model retained the desirable features of the Fermi Gas model and added a new facet. The addition of the periodic potential causes the practically continuous set of energy levels to break up into separate sets of practically continuous energy levels *with forbidden energies between the sets*. Thus arose the band theory of the energy levels of solids. The beauty of this new feature is that it provides an explanation for semiconductor behavior as well as metallic behavior. If the number of electrons in an element is such that one of the sets of energy levels is only partially filled, then the uppermost electrons behave as do electrons in a Fermi Gas. Metallic properties result But if the number of electrons per atom is such that one of the sets of energy levels is exactly filled, right up to the top level of a band (e.g., for Si or Ge), then the next unoccupied levels are separated by a forbidden energy zone. A nonconductor (dielectric) results. Then the electrical properties are not at all like those of metals. In fact the electrical conductivities can be completely dominated by the electron occupancy of "perturbed" energy levels, the perturbations being caused by minute concentrations of impurities. This is the type of phenomenon that gives rise to transistor action. The language used in the Textbook—"an array of positive ions ⋯ immersed in a 'sea' of mobile electrons" (p. 304)—is intended to suggest the Bloch model of solids.

IONIC BONDING

When atoms of very different electronegativity are bound together, asymmetric charge distributions result. We have already seen that the presence of such a charge separation implies that the bond formed is somewhat stronger than a covalent bond between the two atoms (see pp. 531–534). Hence we can expect the bonding in ionic solids to be quite strong.

This strong bonding in ionic solids is not the unique feature that gives ionic solids their high melting points, however. After all, diamond has an extremely high melting point without ionic bonding. The high melting point of diamond is due to the interlinked nature of the three-dimensional network structure. Metals, too, tend to have high melting points, also without ionic bonding. In metals, the high melting point has to do with the continuous, three-dimensional linking of each atom to a number of neighbors. The same factor—three dimensional linkage—accounts for the high melting point and extreme stability of ionic solids, just as it does in network solids and in most metals.

The possibility of such a three-dimensional linkage can be attributed to the existence of vacant valence orbitals on the metal atom. This can be seen by comparing the energy necessary to disrupt a gaseous lithium chloride molecule (115 kcal/mole) to that required to disrupt a gaseous chlorine molecule (57 kcal/mole). The bond in gaseous lithium chloride is much more stable, yet LiCl condenses to a solid at room temperature, whereas Cl_2 remains a gas. The lithium atom in LiCl has residual bonding capacity through its empty valence orbitals that makes it energetically favorable for the LiCl molecules to aggregate into a crystalline arrangement.

The crystal arrangement obtained is dictated by the same kinds of considerations as for metals, but with the added complication that the charge distribution between lithium and chlorine must be taken into account. Just as in lithium metal, the lithium atom favors having as many nearest neighbors as possible (so as to make use of its valence orbitals), but these neighbors must be chlorine atoms. Clearly, the lattice is most stable if the positive lithium ions are surrounded by the negative chloride ions. Conversely, the chloride ions ought to be contacted solely by lithium ions.

The type of packing obtained with this restriction depends upon the relative size of the positive and negative ions. We can explore this restriction by considering the structures of ionic crystals with composition AB. If the two ions A^{+n} and B^{-n} are about the same size, the body-centered cubic packing tends to be favored. This structure gives each atom eight nearest neighbors of opposite charge. But if the positive ion is systematically reduced in size, the negative ions will eventually come into contact with each other, and they will then tend to hold each other away from the positive ions. Just when this will occur depends generally upon the relative sizes of the ions—that is, upon the ratio of the two radii. When the radius ratio becomes too small, a new packing tends to be favored, with fewer nearest neighbors, the sodium chloride lattice. In this lattice, in which each atom has only six nearest neighbors, the negative ions are farther apart, and ions of opposite charge are again in contact. If the radius ratio is reduced even further, negative ion contacts again occur. Once again, there is a tendency for the substance to seek a packing in which each atom has still fewer nearest neighbors. If we adopt the model that defines ions as spheres with fixed radii, it is easy to calculate the radius ratios at which

Table 17-III

Expected Types of Packing for *AB* Ionic Crystals Based on Radius Ratio

Radius Ratio $\left(\frac{\text{positive ion } A}{\text{negative ion } B}\right)$	Number of Nearest Neighbors (coordination number)	Ion Symmetry
1.00 –0.732	8	cubic (body-centered)
0.732–0.414	6	octahedral (NaCl structure)
0.414–0.225	4	tetrahedral
0.225–0.155	3	triangular

these changes in packing are to be expected. They are given in Table 17-III.

Experimentally, we find that the crystal structures of the alkali halides reflect the expected influence of the radius ratio, but only in a rough correlation. Table 17-IV lists twenty alkali halides, five alkaline earth oxides and eleven sulfides. The predicted coordination number is in agreement with the experimental one for 20 of the 36 cases.

The many failures in this correlation stimulate a closer look at the factors that fix the size of an atom, whether it be charged or not. The existence of a finite separation between two nuclei at equilibrium implies that the energy is a minimum at that separation. The energy rises if the nuclei are moved away from this position,

Table 17-IV. **Comparison of Predicted and Experimental Coordination Numbers for *AB* Ionic Crystals***

Compound	Radius Ratio	Coordination Number		Compound	Radius Ratio	Coordination Number	
		Predicted	Found			Predicted	Found
LiI	0.28	4	6	BeO	0.22	3 or 4	4
LiBr	0.31	4	6	MgO	0.46	6	6
LiCl	0.33	4	6	CaO	0.7	6	6
	(0.414)			SrO	0.81	8	6
LiF	0.44	6	6	BaO	0.96	8	6
NaI	0.44	6	6				
NaBr	0.49	6	6	BeS	0.17	4	4
NaCl	0.52	6	6	MgS	0.35	4	6
KI	0.62	6	6	CoS	0.39	4	6†
KBr	0.68	6	6	ZnS	0.40	4	4
RbI	0.69	6	6				
NaF	0.70	6	6	FeS	0.41	6	6†
	(0.732)			MnS	0.43	6	4
KCl	0.73	8	6	CdS	0.53	6	4
RbBr	0.76	8	6	CaS	0.54	6	6
CsI	0.78	8	8	HgS	0.60	6	4
RbCl	0.82	8	6	SrS	0.61	6	6
CsBr	0.87	8	8				
CsCl	0.93	8	8	BaS	0.73	8	6
KF	0.98	8	6				
RbF	1.09	8	6				
CsF	1.24	8	6				

* Ionic radii are taken from A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford (1962), p. 71.

† This structure is peculiar in that three metal atoms are close enough together to be considered to be bonded to each other. It is the NiAs structure.

Table 17-V. **Experimental *M*—*X* Distances for Alkali Halides in the Gaseous and Crystalline States**

Alkali Halide	Bond Length, Gas (A)	Nearest Neighbor Distance, Crystal (A)	Difference (A)	% Increase Over Gas Value
LiF	1.51	2.01	0.50	33
LiI	2.39	3.00	0.61	26
NaCl	2.36	2.81	0.45	19
NaBr	2.50	2.98	0.48	19
NaI	2.71	3.23	0.52	19
KCl	2.67	3.14	0.47	18
KBr	2.82	3.29	0.47	17
KI	3.05	3.53	0.48	16
CsF	2.35	3.00	0.65	28
CsI	3.32	3.95	0.63	19

either closer together or farther apart. At the equilibrium distance, a balance exists between attractive forces and repulsive forces. All attractions contribute (electrons simultaneously near two nuclei), and all repulsions contribute (electron–electron and nucleus–nucleus repulsions) toward determining this balance. Small wonder that it does not occur at the same apparent size for a given ion in different environments. This is dramatically displayed in Table 17-V, which lists the experimental bond lengths in certain gaseous alkali halides and the nearest neighbor distances in the crystal. Most gaseous alkali halides are considered to be quite ionic in their bonding, yet the balance between attraction and repulsion uniformly occurs when the internuclear distance in gaseous molecules is about half an angstrom less than that found in the crystal. This increase is reasonably attributed to the repulsions among the halogen ions, and it cannot be considered surprising that the crystal bond length is a complicated, not a simple, function of the choice of ions. Some workers take cognizance of this by supposing that each ion has a different effective radius for each coordination number.

Aqueous Solutions of Ionic Substances

One of the most important properties of ionic substances is their formation of conducting solutions in water. The importance of the electric dipole of water in explaining the stability of the aquated ions should be stressed. It is *not* correct to say that the ease of formation of ions in the aqueous solution can be attributed to the fact that the ions were "already formed" in the solid. The high melting points of ionic crystals show that the crystals are quite stable, and this stability works against the solubility. Furthermore, some crystals thought to be quite ionic have extremely low solubilities (e.g., CaF_2, BaF_2), whereas some substances that form molecular crystals (e.g., HCl, HBr, HI) are quite soluble in water, forming ions. Hydrofluoric acid, which should be more ionic than any of the substances HCl, HBr, or HI, is the least ionized acid in water. Finally, we must observe that the energy necessary to pull a gaseous lithium fluoride molecule apart to form $Li^+(g) + F^-(g)$ is higher than the energy necessary to pull it apart to form neutral atoms, $Li(g) + F(g)$. The formation of ions in an aqueous salt solution must be attributed to the very great stability of both positive and negative ions when surrounded by water molecules properly oriented, not to the parentage of the ion in an ionic crystal. Conversely, one can hardly cite the electrolyte properties of an aqueous salt solution as compelling evidence that the salt forms an ionic crystal.

The orientation of water molecules around ions is called hydration of the ions, and this process is a dominant one in aqueous chemistry. The effect of this high degree of order is seen in the heat of hydration. For instance, the heat of hydration of Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2} and Ba^{+2} ions is −570, −460, −395, −355, and −305 kcal/mole, respectively. In general, ionic heats of hydration are large negative numbers, indicating that the combination of an ion with water dramatically abets the search for minimum energy. As a result, ions are hydrated in water solution.

Let us contrast the overall heat and entropy effects when gaseous, nonpolar substances as one class, and ionic solids as another, dissolve in water. For nonpolar gases, such as Ar, O_2, C_2H_6, Cl_2, we have negative ΔH and negative ΔS of solution, see Table 17-VI. The negative ΔH means heat is evolved, a result of new interactions forming in solution. The values of ΔS are so high that, for the substances mentioned, ΔF is positive, hence the solution of these substances is not favored. For ionic solids, however, ΔS is observed to be either positive or negative. The case of negative ΔS is like that above. For ΔF to be negative, ΔH *must* be negative—i.e., heat must be evolved during solution. When ΔS is positive, then ΔH can have either positive or negative sign, depending upon the relative magnitude of ΔF and $T\Delta S$. Thus a spontaneous dissolving ($-\Delta F$) can absorb energy ($+\Delta H$) if there is sufficient gain in randomness ($T\Delta S > \Delta H$). Thus the dissolving of $NH_4Cl(s)$ proceeds, even though it absorbs energy, because there is a large enough entropy change to offset ΔH. For the student who recalls Expt. 12, where this cooling effect was observed, you can now say "the trend toward maximum randomness offsets the trend away from minimum energy."

Table 17-IV

Some Entropy and Heat Effects on Dissolving

Substance	ΔH (kcal/mole)	ΔS (e.u.)*
Ar	−2.7	−22
O_2	−3.0	−23
C_2H_6	−4.4	−27
Cl_2	−6.0	−25

* Entropy unit = cal-mole⁻¹ degree⁻¹.

HYDROGEN BONDING

When a hydrogen atom is attached to an oxygen, nitrogen, or fluorine atom, the hydrogen atom retains the capability of additional bond formation. The second bond forms most readily between an H atom and an electronegative atom, such as an oxygen atom in another molecule. The second attachment is called a hydrogen bond, and its energy is only about one-tenth to one-twentieth as large as that of a normal chemical bond. Nevertheless, hydrogen bonds are quite important. Many properties are noticeably affected by hydrogen bond formation. In particular, the so-called physical properties of hydrogen bonded substances are obviously discordant when compared with those of substances that are similar except for a lack of hydrogen bonding capability. Some of the effects in hydrogen bonded substances are:

1. Boiling points tend to be high.
2. Freezing points tend to be high.
3. Solubilities are drastically affected. Hydrogen bonding substances tend to dissolve each other. Hence hydrogen bonding acids (that is, proton donors such as R—O—H) tend to dissolve hydrogen bonding bases (such as ketones) readily. Substances like alcohols tend to be poor solvents for non-hydrogen bonding substances (such as hydrocarbons) because the entrance of the hydrocarbon into the alcohol medium would require the separation of alcohol molecules, breaking hydrogen bonds.
4. Crystal structures are strongly influenced by hydrogen bonding capability (the reason melting points tend to be high). It is almost an axiom that a molecular solid with capacity for hydrogen bond formation will have a structure that takes maximum advantage of this possibility. Notice that the helical structures of macromolecules such as protein represent a special case of this general tendency.

5. The dielectric constants of hydrogen bonded liquids are distinctively high. Some examples are H_2O, H_2O_2, HF, and HCN, which have dielectric constants of 78.5 (25°C), 73 (20°C), 83.6 (0°C), and 158 (0°C), respectively. Typical values for liquids without hydrogen bonds are those for dioxane, benzene, heptane, and diethyl ether, respectively 2.2, 2.3, 1.9, and 4.3.
6. Densities of hydrogen bonded substances tend to be high due to the attraction provided by the hydrogen bonding.
7. Viscosities tend to be high as a result of the intermolecular linkages.
8. Hydrogen bonding in the gas phase causes large deviations from perfect gas behavior.
9. The thermodynamic properties of a substance are affected. Heats of mixing, fusion, and vaporization are affected. Sometimes even more significant are the entropy effects, since the hydrogen bond interaction implies a high degree of order.
10. Spectroscopic changes are observed when hydrogen bonds form. Most characteristic are those that are found in the vibrational spectrum. The absorptions characteristic of the stretching vibration of an *A*—H bond are very much altered when this group is joined by a hydrogen bond to some base, *B*.
11. Other properties that show measureable influence by hydrogen bonding are apparent molecular weight, acoustic conductivity, compressibility, surface tension, diamagnetic susceptibility, optical rotation, nuclear magnetic resonance, and thermal conductivity.

The traditional explanation for the existence of hydrogen bonding is based on "electrostatic" interaction. Because the hydrogen atom is attached to another atom *A* in an ionic bond, *A*—H, there is the possibility of an additional energetically favorable interaction with an electron donor. This can be compared to the interactions among polar molecules, as discussed in Sec. 17-2.5, with emphasis upon the unique feature of the hydrogen atom in possessing no electrons except its valence electron.

This explanation provides an acceptable starting point for discussion of hydrogen bond formation, but it does not span all aspects of the phenomenon. For example, one finds no correlation between the heat of formation of a hydrogen bond for a particular acid, *A*—H, and the electric dipole of a number of bases.

Hydrogen bonding can be discussed usefully in terms of the Lewis or electron transfer acid–base concept. The proton in *A*—H is a particularly good electron acceptor, and consequently it interacts strongly with a good electron donor (i.e., a Lewis base). A reliable and self-consistent classification of base strength can be set up if hydrogen bonding is used as a criterion.

The most dramatic effects of hydrogen bonds are surely those found in biochemical systems. It is well established now that hydrogen bonding plays a crucial role in fixing the molecular configurations of such biological substances as proteins and nucleic acids. This important topic receives more specific attention in Chapter 24.

Answers to Exercises and Problems

Ex. 17-1. Gaseous phosphorus is made up of P_4 molecules with four phosphorus atoms arranged at the corners of a regular tetrahedron. In such a geometry, each phosphorus atom is bound to three other phosphorus atoms. Would you expect this gas to condense to a solid with a low or high melting point? After making a prediction on the basis of the valence orbital occupancy, check the melting point of phosphorus in Table 6-VIII, p. 101.

Answer

Phosphorus, like nitrogen, has an orbital occupancy that gives it the capacity to form three bonds. Since each phosphorus is bonded to three other atoms in the P_4 molecule, each atom has completely used its bonding capacity. Without residual valence orbital bonding capacity, only weak interactions will exist between two molecules. A low-melting solid will result. The melting point of white phosphorus, given on Textbook p. 101, is 44.2°C.

Ex. 17-2. Use Figure 17-11 to estimate the resistivities of two metal samples, one made of pure copper and the other of a copper-manganese alloy containing one atom of manganese for every one hundred copper atoms. Calculate the ratio of the cost due to power loss from wire of the impure material to the cost due to the power loss from wire of the pure material.

Answer

A concentration of one atom-percent manganese corresponds to 0.86 weight-percent.

$$\text{wt-percent Mn} = \frac{\text{wt Mn}}{\text{wt Mn} + \text{wt Cu}} \times 100$$

$$= \frac{54.9}{54.9 + 100(63.5)} \times 100$$

$$= 0.857\%$$

From Figure 17-11, p. 311, we read the following resistivities:

pure copper; resistivity = 2 micro-ohm cm
0.86% Mn; resistivity = 4 micro-ohm cm

Cost due to power loss is proportional to resistivity, hence the ratio of power loss for the impure copper wire to that for pure copper wire is 4/2 = 2. The cost is doubled if the impure copper is used.

Pr. 1. Make a table that contrasts the melting points and boiling points of LiF, Li, and F_2, expressing the temperatures on the Centigrade scale.

Answer

This problem simply involves relating phenomena expressed as phase changes to the terms melting point and boiling point. All data are given in the first paragraph of Textbook p. 300. A class can do this problem at the first of the period following the day the reading was assigned.

	LiF	Li	F_2
m.p. (°C)	870	186	−223
b.p. (°C)	1676	1336	−188

Note the stability gained when the atoms combine to form the ionic substance, LiF.

Pr. 2. Without looking in your Textbook, do the following.

(a) Draw an outline of the periodic table, indicating the rows but not the individual elements.
(b) Place a number at the left of each row indicating the number of elements in that row.
(c) Fill in the symbols for as many of the first 18 elements as you can (leave blank any that you forget).
(d) Draw two diagonal lines across the table to separate it into three regions. Write in each region one of the words "metals," "nonmetals," "covalent solids."
(e) Now compare your diagram to Figure 17-4.

Answer

The diagram should be close to Figure 17-4, but do not demand that the intermediate region between metals and nonmetals be exactly defined. There are no clear-cut boundaries—different chemical properties lead to some ambiguity in the placement of some of the elements.

Pr. 3. Sulfur exists in a number of forms, depending upon the temperature and, sometimes, upon the past history of the sample. Three of the forms are described below. *A* is the room temperature form, and it changes to *B* above the melting point of *A*, 113°C. *B* changes to *C* on heating above 160°C.

A		*B*		*C*
Crystalline solid		Liquid		Liquid
Yellow color, no metallic luster		Clear, straw color		Dark color
m.p. = 113°C	$\xrightarrow{113^\circ\text{C}}$	Viscosity (fluidity) about the same as water	$\xrightarrow{\sim 200^\circ\text{C}}$	Very viscous (syrupy)
Dissolves in CS_2, not in water				
Electrical insulator		Electrical insulator		Electrical insulator

Which of the following structures would be most likely to account for the observed properties of each of the three forms described above?

(a) a metallic crystal of sulfur atoms;
(b) a network solid of sulfur atoms;
(c) an ionic solid of S^+ and S^- ions;
(d) a molecular crystal of S_8 molecules;
(e) a metallic liquid like mercury;
(f) a molecular liquid of S_8 molecules;
(g) a molecular liquid of S_n chains, with n = a very large number;
(h) an ionic liquid of S^+ and S^- ions.

Answer

Form *A* is known to be (d), consistent with all properties.

(a) is ruled out by electrical resistivity.
(b) and (c) are ruled out by low melting point.

Form *B* is known to be (f), consistent with the low viscosity and absence of electrical conductivity.

(e) is ruled out by transparency, absence of conductivity.
(g) is ruled out by viscosity.
(h) is ruled out by absence of conductivity.

Form *C* is known to be (g), consistent with high viscosity.

Pr. 4. Contrast the bonds between atoms in metals, in van der Waals solids, and in network solids in regard to:

(a) bond strength;
(b) orientation in space;
(c) number of orbitals available for bonding.

Answer

(a) Van der Waals bonds form between atoms or molecules without residual bonding capacity. They are characteristically quite weak—of the order of a few kcal/mole—as shown by low melting points and low heats of vaporization. Metallic and covalent bonds are of the order of 30–150 kcal, much stronger than van der Waals forces, as shown by high melting points and high heats of vaporization.

(b) Bonds in van der Waals solids and metallic solids are not directional. This is shown in the softness of van der Waals solids and in the malleability of metals. Network solids have directional bonds linking the lattice, hence form hard crystals.

(c) Metallic solids are formed by atoms that have an abundance of empty or partially filled valence orbitals. Van der Waals solids are formed by atoms or molecules in which all valence orbitals are filled. Network solids result when atoms form highly directed bonds. These bonds use all the bonding capacity of each atom.

Pr. 5. Aluminum, silicon, and sulfur are close together in the same row of the periodic table, yet their electrical conductivities are widely different. Aluminum is a metal, silicon has much lower conductivity and is called a semiconductor; sulfur has such low conductivity it is called an insulator. Explain these differences in terms of valence orbital occupancy.

Answer

This comparison shows the importance of orbital occupancy in fixing conduction properties. The orbital occupancies are:

	1s	*2s*	*2p*	*3s*	*3p*
Al	⊗	⊗	⊗⊗⊗	⊘	⊘⊘○
Si	⊗	⊗	⊗⊗⊗	⊘	⊘⊘⊘
S	⊗	⊗	⊗⊗⊗	⊗	⊗⊘⊘

Aluminum is the only one of these elements that has fewer valence electrons than valence orbitals, hence it is the only metal of the three. Silicon, which has four valence orbitals and four valence electrons, can form a three-dimensional network, with the result that every atom can obtain an inert gas arrangement by sharing pairs of electrons with adjacent atoms. Under these bonding circumstances the conductivity is low. Sulfur, which has six valence electrons and four orbitals, can fill its valence orbitals by forming a molecule. Hence the interactions that hold the sulfur crystal together are the weak van der Waals forces. Under these bonding circumstances, the conductivity is almost negligible, hence a substance like sulfur can be used as an insulator.

Pr. 6. Sulfur is made up of S_8 molecules; each molecule has a cyclic (crown) structure. Phosphorus contains P_4 molecules; each molecule has a tetrahedral structure. On the basis of molecular size and shape, which would you expect to have the higher melting point?

Answer

The building blocks are S_8 and P_4. Since melting these substances involves the overcoming of van der Waals forces between adjacent molecules, we must decide among which of these two types of molecules this force is greater. The magnitude of van der Waals forces varies directly with molecular size (perimeter) and depends upon molecular geometry. Both of these factors are more favorable for a strong interaction among sulfur molecules, hence the melting point of sulfur is expected to be higher. (Melting points are: for sulfur, rhombic, 113°C; monoclinic, 119°C; for phosphorus, 44°C.) Notice that the masses of the particles are not a major factor.

Pr. 7. Discuss the conduction of heat by copper (a metal) and by glass (a network solid) in terms of the valence orbital occupancy and electron mobility.

Answer

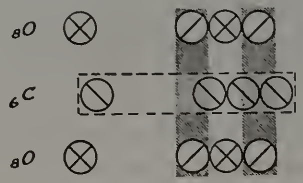
Copper is a better conductor than glass because the bonding electrons in copper are much more mobile than are those in glass. Metals are characterized as having few valence electrons, low ionization energies, and many orbitals available for occupancy. As a result of these factors, the bonding electrons are highly mobile, and they are not localized.

Network solids occur when all of the valence orbitals can become occupied through normal bonding in an interlinked, extensive structure. In normal bonds, the electrons are rather localized in space, and lack the mobility necessary for conductivity.

Pr. 8. The elements carbon and silicon form oxides with similar empirical formulas: CO_2 and SiO_2. The former sublimes at −78.5°C, and the latter melts at about 1700°C and boils at about 2200°C. From this large difference, propose the types of solids involved. Draw an electron dot or orbital representation of the bonding in CO_2 that is consistent with your answer.

Answer

The melting points show that SiO_2 must be a network solid and that CO_2 must be a molecular solid.



Pr. 9. How do you account for the following properties in terms of the structures of the solids?

(a) Graphite and diamond both contain carbon. Both are high melting, yet the diamond is very hard while graphite is a soft, greasy solid.
(b) When sodium chloride crystals are shattered, plane surfaces are produced on the fragments.
(c) Silicon carbide (carborundum) is a very high-melting, hard substance, used as an abrasive.

Answer

The Textbook shows the structures of graphite and diamond in Figure 17-2 and that of sodium chloride in Figure 5-10. Through class discussion, the silicon carbide structure can be predicted readily from the similar bonding capacities of silicon and carbon.

(a) The high melting points of diamond and graphite are accounted for by the interlinked nature of the crystal structures. The diamond lattice has a three-dimensional, interlinked structure. The graphite lattice has two-dimensional, interlinked planes, successive planes being held together weakly. The two-dimensional, infinite network is sufficient to give a high melting point (as is true for the micas, shown in Textbook Figure 17-9, p. 310). The hardness of diamond is related to the fact that any cleavage plane in diamond is crossed by many bonds. Graphite, with its two-dimensional structure, has planes that exert only weak forces toward other such planes or other substances. These weak forces give graphite its softness and the property that makes it act as a lubricant in some circumstances.

(b) Sodium chloride is an ionic solid whose crystal is made up of a lattice of evenly spaced sodium ions surrounded by regularly spaced chloride ions. The plane surfaces produced on cleavage are related to this regularity. Cleavage occurs most readily between neutral planes (same number of sodium and chlorine atoms).

(c) Crystals of SiC consist of silicon and carbon atoms bound together by strong chemical bonds that form a three-dimensional network solid having the usual accompanying properties—hardness and high melting point.

Pr. 10. If you were given a sample of a white solid, describe some simple experiments that you would perform to help you decide whether or not the bonding involved primarily covalent bonds, ionic bonds, or van der Waals forces.

Answer

It is difficult to decide the nature of the bonding in a solid through simple measurements. Nevertheless, certain significant correlations provide valuable clues. Finally, *the answer must be based upon a general pattern of self-consistency among several properties, since none is decisive.*

(a) *Behavior on warming.* In general, ionic solids and network solids tend to have high melting points, whereas molecular solids (van der Waals solids) tend to have low melting points. Hence an initial sorting of molecular solids can be based upon what happens when the solid is heated to a few hundred degrees centigrade.

(b) *Solubility in water and electrolyte behavior.* The solubility in water provides a further basis for classification. Though it is by no means true that all ionic solids have high solubility in water, many of them have detectable solubility. Furthermore, the substances that are commonly known to form ionic solids form conducting solutions. Hence the combination of solubility in water and ionic conductivity of the resulting solution provides a reasonable basis for assuming an ionic solid. Much reservation is attached to this statement, however, since many molecular substances have measurable solubility in water, and some of these form conducting solutions (e.g., HCl, H_3PO_4, acetic acid, benzoic acid, ammonia).

(c) *Hardness.* Ionic solids and network solids are often hard; molecular solids tend to be soft.

(d) *Conductivity of melt.* Well-recognized ionic solids conduct electricity when melted. Hence electrical conductivity in the pure liquid suggests that it will form an ionic solid.

Pr. 11. If elements A, D, E, and J have atomic numbers, respectively, of 6, 9, 10, and 11, write the formula for a substance you would expect to form between the following:

(a) D and J;
(b) A and D;
(c) D and D;
(d) E and E;
(e) J and J.

In each case describe the forces involved between the building blocks in the solid state.

Answer

First note that:

A has atomic no. 6 and 4 valence electrons;
D has atomic no. 9 and 7 valence electrons;
E has atomic no. 10 and 0 valence electrons;
J has atomic no. 11 and 1 valence electron.

(a) D and J would form a compound, JD, which would involve ionic bonding and have an ionic crystal lattice.

(b) *A* and *D* would probably form a compound, AD_4, a covalently bonded, nonpolar compound. Atoms that have half-filled valence orbitals tend to form covalently bonded compounds with other atoms. The solid would likely be molecular, van der Waals forces holding adjacent molecules together.

(c) *D* and *D* would tend to form a molecule having formula D_2. Since this molecule would have no unused bonding capacity, it would likely form a molecular solid, held together by the very weak van der Waals forces.

(d) *E* and *E* would not combine, since these atoms have no orbitals available for bonding. This same situation is found in the inert gases. The elements Ne, Ar, Kr, and Xe crystallize with the cubic close packed structure. Helium forms a solid only under pressure (25 atm minimum). The structure is probably hexagonal close packed. Radon has not been studied in the solid state.

(e) *J* and *J* would form a metallic solid because there is but one valence electron per atom and four available valence orbitals.

Pr. 12. Consider each of the following in the solid state: sodium, germanium, methane, neon, potassium chloride, water. Which would be an example of

(a) a solid held together by van der Waals forces that melts far below room temperature;
(b) a solid with a high degree of electrical conductivity that melts near 100°C;
(c) a high melting, network solid involving covalently bonded atoms;
(d) a nonconducting solid which becomes a good conductor upon melting;
(e) a substance in which hydrogen bonding is pronounced?

Answer

(a) neon;
(b) sodium;
(c) germanium;
(d) KCl;
(e) H_2O.

Pr. 13. Predict the order of increasing melting point of these substances containing chlorine: HCl, Cl_2, NaCl, CCl_4. Explain the basis of your prediction.

Answer

Melting involves the overcoming of forces between the units of which the solid is made. Three of the given substances, HCl, Cl_2, and CCl_4, would be expected to form molecular solids (no unused bonding capacity, and similar ionization energies); the other, NaCl, would be expected to form an ionic solid (great difference in ionization energies). The coulombic forces holding an ionic solid together are strong, hence NaCl would be expected to have a high melting point.

The van der Waals forces holding the molecular solids together are weak. Of the three, CCl_4, owing to its large and complex surface, should have the highest melting point. The size of the Cl_2 molecule should be greater than that of HCl and, on this basis, its melting point should be higher. The possibility of hydrogen bond formation among HCl molecules works the other way, making a positive prediction difficult. The observed melting points are: HCl, −114°C; Cl_2, −101°C; CCl_4, −22.8°C; NaCl, 801°C.

Pr. 14. Identify all the types of bonds you would expect to find in each of the following crystals:

(a) argon,
(b) water,
(c) methane,
(d) carbon monoxide,
(e) Si,
(f) Al,
(g) $CaCl_2$,
(h) $KClO_3$,
(i) NaCl,
(j) HCN.

Answer

v = van der Waals
c = covalent
i = ionic
h = hydrogen bonding
m = metallic

(a) *v*
(b) *c* within molecule; *v*, *h* between molecules
(c) *c* within molecule; *v* between molecules
(d) *c* within molecule; *v* between molecules
(e) *c* (f) *m* (g) *i*
(h) *i*, *c* within ClO_3^- ion
(i) *i*
(j) *c* within molecule; *v*, *h* between molecules

Pr. 15. Each of three bottles on the chemical shelf contains a colorless liquid. The labels have fallen off the bottles. They read as follows.

Label No. 1	*Label No. 2*	*Label No. 3*
n-butanol	*n*-pentane	diethyl ether
$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2OCH_2CH_3$
mol wt = 74.12	mol wt = 72.15	mol wt = 74.12

The three bottles are marked *A*, *B*, and *C*, and a series of measurements were made on the three liquids to permit identification, as follows.

	m.p.	b.p.	Density	$\Delta H_{\text{vap'n}}$	Solubility in Water
Liquid *A*	−131.5°C	36.2°C	0.63 g/cc	85 cal/g	0.036 g/100 ml
Liquid *B*	−116	34.6	0.71	89.3	7.5
Liquid *C*	−89.2	117.7	0.81	141	7.9

Which liquid should be given Label No. 1? Label No. 2? Label No. 3? Explain how each type of measurement influenced your choices.

Answer

Label 1 is correct for liquid *C*, Label 2 for *A*, and Label 3 for *B*.

Little chance for initial discrimination is offered by the melting points. They do not differ sufficiently. Since the boiling point of substance *C* is so much higher than the other two, there is some chance for discrimination. The three different molecules exhibit essentially covalent bonding, and hence probably form molecular solids. Only *n*-butanol can form hydrogen bonds. These bonds would make it difficult to separate the molecules from each other and would explain the high boiling point and $\Delta H_{\text{vap'n}}$ of *C*. Hydrogen bond formation is also consistent, liquid *C* having the highest density (tightest packing) and the highest solubility in water. Liquid *C* is No. 1.

The density varies so little that it is best used to confirm, not predict.

The $\Delta H_{\text{vap'n}}$ is also best used for confirming predictions, not making them.

The knowledge that the solubility of *A* is so much lower than the others is a useful bit of data. The *n*-pentane has none of the characteristics commonly possessed by water-soluble molecules. It is nonpolar, can form no hydrogen bonds, and is not ionic. These factors are also consistent with these facts: it has the lowest melting point, boiling point, $\Delta H_{\text{vap'n}}$, and density, due to the very small forces that exist between adjacent molecules. Liquid *A* is probably No. 2.

This leaves *B* for No. 3. Diethyl ether is a bent molecule (p^2 bonding on the oxygen) which is polar. This would explain some weak attractions between molecules, hence the low melting point. The low boiling point and $\Delta H_{\text{vap'n}}$ could be explained by assuming that the kinetic energy at these temperatures is sufficient to break the weak attractions caused by polar molecules. The high solubility in water is consistent with the fact that water molecules may be hydrogen bonded to the oxygen, and also with the expected polar nature of the molecule.

Pr. 16. Maleic and fumaric acids are *cis* and *trans* isomers having two carboxyl groups

$$HOOC—CH{=}CH—COOH$$

Maleic acid gives up its first proton more readily than does fumaric acid. However, the opposite is the case for the second proton. Account for this in terms of structure.

Answer

Maleic acid can form an intramolecular hydrogen bond, and fumaric acid cannot. After the first proton is released from maleic acid, the negative charge left on one end of the molecule makes this intramolecular hydrogen bond especially strong in the negative ion. This special stability of the once-ionized maleic acid tends to favor its formation through release of the first proton and tends to work against its loss through release of the second proton. Hence the first dissociation constant is abnormally high; and the second, abnormally low.

It is also possible that the formation of the intramolecular hydrogen bond in maleic acid draws electrons away from the second O—H group, weakening its bond and making release of the first proton occur more readily. This effect would also act to lower the first ionization constant.

Suggested Quiz Questions

These suggested questions are designed for a one-period open book test. There are more than enough, hence some selection is required.

Nitrogen is a gas at temperatures above 126°K (−147°C). Very little energy is required to change nitrogen from solid to liquid to gas. Nevertheless, kinetic energies corresponding to thousands of degrees Kelvin cannot cause appreciable decomposition of the N_2 molecules.

1. What are the forces acting to hold the nitrogen molecules, N_2, together in the liquid phase? Describe briefly the nature of these forces.

   Answer
   Van der Waals forces. Van der Waals forces are electrical forces due to the interaction between electrons of one atom and the nucleus of a second atom, but from a relatively long distance, because the valence orbitals are all filled.

2. What is the nature of the chemical bond between the two nitrogen atoms in the N_2 molecule?

   Answer
   The chemical bond in an N_2 molecule is composed of three pairs of electrons shared between the two nitrogen atoms.

   :N⋮⋮N:

   This produces a very strong covalent bond.

Questions 3–8 use information in the following table.

Substance	m.p. (°K)	b.p. (°K)
(1) Helium	3.3	4.1
(2) Sodium chloride	1073.4	1686
(3) Carbon tetrachloride	250	349.8
(4) Carbon dioxide	—	sublimes at 194.5
(5) Silicon dioxide	about 2000	about 2500
(6) Diamond	above 3800	about 4500
(7) Methane	89	111
(8) Water	273	373

3. In which of the substances, if any, is the intermolecular force of attraction mainly due to van der Waals forces?

   Answer: 1, 3, 4, 7.

4. Which of the above substances, if any, forms a molecular solid made up of polar molecules?

   Answer: 8.

5. In which of the substances, if any, does hydrogen bonding occur?

   Answer: 8.

6. According to the data given, in which of the solid substances do the weakest bonds exist?

   Answer: 1.

7. Which of the solid substances, if any, forms due to bonds that are predominantly ionic?

   Answer: 2.

8. Explain the differences in melting points and boiling points between carbon dioxide and silicon dioxide in terms of the types of bonding involved.

   Answer
   The low sublimation temperature for carbon dioxide indicates the presence of weak intermolecular van der Waals forces and small molecules. Carbon in CO_2 satisfies its bonding capability by forming two double bonds to two oxygen atoms. These CO_2 molecules are then held together by weak van der Waals interactions. On the other hand, the extremely high melting point and boiling point for silicon dioxide indicate the presence of strong bonds. This occurs because silicon forms four single bonds to four oxygen atoms, giving a network solid.

9. By way of generalization, as the number of electrons in a molecule increases the

van der Waals forces between molecules (increase or decrease).

Answer: Increase.

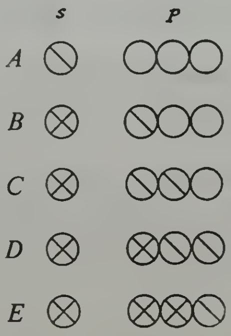
10. How does adding traces of other elements to metals, such as adding carbon to iron, often make the resulting alloy harder and more brittle? Explain in terms of bonding.

Answer
Metallic bonds form when there are several empty bonding orbitals available to the valence electrons. This permits the valence electrons freedom of movement between the positive ions in the metal. The addition of an element having the property of forming more directed bonds (having valence orbitals more completely filled) utilizes some of the freely moving electrons in forming more directed covalent-type bonds. These directed bonds give, locally, the character of a network solid, contributing to strength and brittleness.

11. Explain why aluminum is a good conductor of heat and electricity whereas pure silicon is not.

Answer
Aluminum has three valence electrons and four valence orbitals. Although the metallic bonding that occurs in aluminum is more directed than it is in some of the other metals which have even more available empty bonding orbitals, the electrons are still relatively free to move about between the positive aluminum ions. Silicon, however, has four valence electrons (as does carbon) and has four valence orbitals. This makes an ideal situation for the formation of four directed covalent bonds that utilize all the available electrons and valence orbitals. Having no free electrons, silicon is a poor conductor of electricity and heat.

To answer Questions 12–17, consider the orbital representation of the valence electrons for the following elements.



12. Which of the elements given, if any, could be expected to form metallic bonds?

Answer: *A* and *B* (unless *B* is boron).

13. Which, if any, could be expected to form a network solid?

Answer: *C* (and *B* if it is boron).

14. Which, if any, could form a covalent bond with like atoms in the solid state?

Answer: *C*, *D*, and *E* (and *B* if it is boron).

15. What combinations of two elements could form an ionic solid?

Answer
AE, A_2D, BE_3, and possibly A_2D_2.

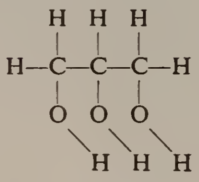
16. Write the empirical formula for a compound formed by the combination of *C* and *D*.

Answer: CD_2.

17. Write the empirical formula for a compound formed by combining *D* and *E*.

Answer: DE_2.

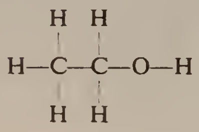
18. Glycerine,



$$\mathrm{H{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}H}$$

[or $C_3H_5(OH)_3$]

is far more viscous than ethyl alcohol,



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H}$$

[or C_2H_5OH]

Why?

Answer

Glycerine, having three times as many OH groups per mole, can form many more hydrogen bonds per molecule. This increases the net attraction between all the molecules, and hence increases resistance to flow.

CHAPTER

18

THE CHEMISTRY OF CARBON COMPOUNDS

Intent and Approach

It should be made very clear that the chemical principles that govern the behavior of organic compounds are in no way unique; that we are not dealing with a new "kind" of chemistry. The classification of organic chemistry as a definite area of study is primarily one of convenience, because the number of carbon compounds is enormous and because their typical behavior is not what is ordinarily found for inorganic compounds, whose chemistry deals more with ionic substances than with nonionized, covalent molecules. Part of this philosophy is to show the applicability of the chemical principles already studied. This thread runs through the remaining seven chapters.

A central idea is the importance of structure as contrasted with composition alone. Up to this point in the course, the student has not encountered many instances in which a given formula can represent more than one compound. Isomerism is not an essential idea in a beginning study of inorganic chemistry.

Coupled with the central idea of the importance of structure and the related concept of isomerism is the great versatility of carbon in using its four valence orbitals to form compounds. The three-dimensional possibilities of bond formation to a tetravalent atom can give rise to great structural complexity.

The purely descriptive aspects of organic chemistry (the uses of esters as flavors and perfumes, the structures of common polymers, the structures of complex compounds such as drugs, dyes, etc.) should be minimized. Biochemistry is to be postponed to Chapter 24.

The aims of a chapter on the chemistry of carbon compounds are chiefly three: (1) to show the importance of structural arrangement of the atoms of which compounds are composed; (2) to introduce the chemistry of bond-breaking and bond-making in compounds in which the bonds are essentially covalent in nature; and (3) to show how large numbers of individual compounds can be grouped into classes according to the similarities in their behavior caused by functional groups.

Outline

The earlier material related to this chapter includes:

Combustion of hydrocarbons (Expts. 1 and 4)
Acids and bases—acetic acid (Chapter 11)
Covalent bonds
Molecular architecture } (Chapters
Double bonds and isomerism } 16, 17)

1. The sources of carbon compounds are the first topic (18-1).
2. Section 18-2.1 considers composition and structure by means of various kinds of formulas (empirical, molecular, structural). How they are determined is discussed in Sec. 18-2.2. Ethanol is used as an example.
3. The properties of ethanol bring out the ethyl group (18-2.3) as an entity.
4. Reactions of bromides (18-3.1) and oxidation of carbon compounds (18-3.2) lead to functional groups (18-3.3).

5. Amines (18-3.4) and two acid derivatives (esters and amides) are discussed (18-3.5).
6. Nomenclature is covered briefly (18-4).
7. Hydrocarbons of several classes are described—saturated (18-5.1), unsaturated (18-5.2), benzene and its derivatives (18-5.3).
8. Types of polymerization are treated (18-6.1), then nylons (18-6.2) and proteins (18-6.3) are discussed.

New Concepts

1. The importance of structure in determining chemical behavior.
2. The use of *functional* groups to describe a general type of behavior.
3. The substitution (or replacement) reaction. Formation of a new bond as an old one is broken.

Development

SOURCES OF CARBON COMPOUNDS (18-1)

This section serves to set the stage for the diversity of carbon-containing substances. This is not the appropriate time to discuss the various ways these compounds are obtained from coal or oil. The student cannot understand them without knowledge of functional groups or reactions.

MOLECULAR STRUCTURES OF CARBON COMPOUNDS (18-2)

The Composition and Structure of Carbon Compounds (18-2.1)

This section gives a brief account of three kinds of formulas. Be sure the student understands these, or the remaining sections will be confusing.

Experimental Determination of Molecular Structure (18-2.2)

Determining the Empirical Formula. Before starting to describe the various formulas and how they are found, it is worthwhile reminding the student that this is not an idle exercise. Every compound must be carried through this process before it can be called "known."

Earlier in the course, we usually encountered empirical formulas in situations where *only* that kind of formula can be found. There is no molecular formula for SiO_2 or NaCl. The student may need some help in this new area, where empirical formulas occur much more frequently. Emphasize *isomers*, which he has not had to use much before, and make it clear that they arise because there are many ways to connect the same atoms. Be sure to use the mole method, not weight-percent, in calculating empirical formulas.

Determining the Molecular Formula. This reduces to a molecular weight determination. Several are described. See also Textbook p. 324.

Determining the Structural Formula. The Textbook adequately describes the use of reaction differences to decide between possible isomers. There are other methods, however, one of which consists in synthesizing the compound in a way that furnishes final proof of the structure. When only two possible structural formulas need to be considered *either* may be synthesized.

The spectroscopic methods described in Chapter 14 can also be used. Infrared spectroscopy is probably the most useful, and is easy and fast. Each functional group has fairly typical vibration frequencies that can be used for identifica-

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
S 18-1/18-2.3 (pp. 321–325)	1	S 18-1/18-2.3	1–3	1–3	4–6	**7**,[*] 8	Molecular structure, Ethyl group
S 18-2.3/18-3.1 (pp. 325–332)	2	S 18-2.3/18-3.1	4, 5	9			
Expt. 28	3	Expt. 28					
S 18-3.2/18-3.5 (pp. 332–339)	4	S 18-3.2/18-3.5 Film: MECHANISM OF AN ORGANIC REACTION (see *Note*) Film: SYNTHESIS OF AN ORGANIC COMPOUND	6–10	10, 14, 15–17	11	12, 13, 18, 19	Reactions, Oxidation
Expt. 29	5, 6	Expt. 29					
S 18-4/18-5.2 (pp. 339–343)	7	S 18-4/18-5.2	11–14	20			Nomenclature, Hydrocarbons
S 18-5.3 (pp. 343–346)	8	S 18-5.3			21	22	Benzene derivatives
S 18-6 (pp. 346–349)	9	S 18-6	15				Polymers
Expt. 29a	(optional)						
Review	10						

Note: Scheduling after Expt. 29 is flexible, depending upon time and interest. Either of the films described on p. 613 may be shown either before or after performing Expt. 29.

[*] Boldface indicates problems whose answers are given in the Textbook.

tion. Nuclear magnetic resonance tests are more time-consuming, and not so universally applicable; but for many problems they offer good answers. X-Ray diffraction is, relatively, the most difficult, but can give a reliable answer for crystalline solids.

Ethanol is one of many examples of hydrogen bonded organic compounds. Acids, amines, and amides are other examples. Most associated materials are organic substances. The similarity in the chemical behavior of ethanol and water should be stressed. Furthermore, the properties of ethanol that depend upon the OH group are characteristic of homologous alcohols. The reaction

$$CH_3CH_2OH + HBr \rightleftharpoons CH_3CH_2Br + H_2O$$

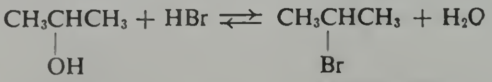
is characteristic of *alcohols* in general; 1-propanol, 2-propanol, 1-butanol, and many other alcohols react in the same way:

$$CH_3CH_2CH_2OH + HBr \rightleftharpoons CH_3CH_2CH_2Br + H_2O$$

1-propanol 1-bromopropane

$$CH_3CH_2CH_2CH_2OH + HBr \rightleftharpoons CH_3CH_2CH_2CH_2Br + H_2O$$

1-butanol 1-bromobutane



$$\underset{\text{OH}}{CH_3\underset{|}{C}HCH_3} + HBr \rightleftharpoons \underset{\text{Br}}{CH_3\underset{|}{C}HCH_3} + H_2O$$

2-propanol 2-bromopropane

The Ethyl Group (18-2.3)

The concept of the *group* of atoms that retains its original structural integrity is well exemplified in the chemical behavior of ethanol and ethyl bromide. In the replacement of OH by Br and of Br by OH, OCH_2CH_3, or NH_2, the ethyl group remains unchanged.

Emphasize that the ethyl group (and other "groups" in organic compounds) is not a substance, with independent existence, but only a structural entity, a component part of a compound. Although a group such as the ethyl group may retain its integrity through a series of reactions, the group can be altered. For example, if ethyl alcohol is oxidized through the stages described in Sec. 18-3.2, the ethyl group is changed by the conversions

$$CH_3CH_2OH \longrightarrow CH_3CHO \longrightarrow CH_3COOH$$

In this oxidation series it is the *methyl* group that is unchanged.

SOME CHEMISTRY OF ORGANIC COMPOUNDS (18-3)

Chemical Behavior of Ethyl and Methyl Bromide (18-3.1)

The reaction of methyl bromide and ethyl bromide with sodium hydroxide,

$$CH_3Br + OH^-(aq) \rightleftharpoons CH_3OH + Br^-(aq)$$
$$CH_3CH_2Br + OH^-(aq) \rightleftharpoons CH_3CH_2OH + Br^-(aq)$$

is quite unlike the reaction of aqueous HBr with aqueous NaOH. Aqueous HBr is not HBr, but a solution of hydrated protons and bromide ions:

$$HBr + H_2O \rightleftharpoons H^+(aq) + Br^-(aq)$$

Aqueous HBr reacts with aqueous NaOH in a very fast reaction in which the proton is transferred to $OH^-(aq)$

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O$$

Methyl bromide, however, is *not* ionized in aqueous solution. Aqueous methyl bromide (actually, methyl bromide is only slightly soluble in water) is a solution of CH_3Br, not of CH_3^+ and Br^-.

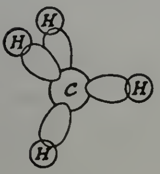
Hence, when OH^- reacts with CH_3Br, the reaction is one between an ion (OH^-) and a neutral, covalent molecule. It is a slower reaction than that between OH^- and H^+, requiring appreciable activation energy (p. 331).

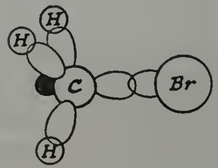
To the student, the most puzzling feature of the reaction

$$CH_3Br + OH^- \rightleftharpoons CH_3OH + Br^-$$

is this: if CH_3Br does not undergo a preliminary ionization into CH_3^+ and Br^-, how can OH^- react to form a carbon-oxygen bond? Since all four of the available orbitals of carbon are filled in CH_3Br, how can OH^- form a bond to carbon before the carbon-bromine bond breaks?

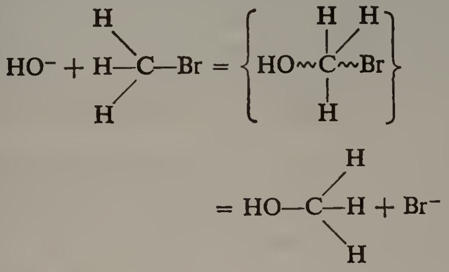
The answer to this question is: in CH_3Br, the carbon-bromine bond has a certain degree of "ionic character"—that is, the electron-pair between C and Br is drawn closer to Br by virtue of the greater electronegativity of the halogen atom. This withdrawal of the electron-pair from carbon is equivalent to incomplete occupancy of one of carbon's four orbitals and permits the electron-pair of OH^- to take part in forming a weak bond to carbon. In methane, C—H bonds are of such a character that no electron deficiency exists on carbon, thus there are no "unoccupied" orbitals. These molecules are illustrated below.





Since one carbon orbital in CH_3Br is not fully occupied, electrons of an approaching reagent can overlap at the side of the carbon atom opposite the direction of the C—Br bond. Thus the reaction with HO^- can be pictured as in Figure 18-1.

A consequence of the reaction according to this scheme is that the attacking reagent becomes attached to the side of the carbon atom opposite that at which the displaced group was attached. The configuration of the groups around the carbon atom becomes inverted in the process:



$$HO^- + H{-}\overset{H}{\underset{H}{C}}{-}Br = \left\{HO\sim\overset{H\ \ H}{\underset{H}{C}}\sim Br\right\}$$

$$= HO{-}\overset{H}{\underset{H}{C}}{-}H + Br^-$$

(*Note:* Compare Textbook Figure 18-4, p. 331, with these sketches.)

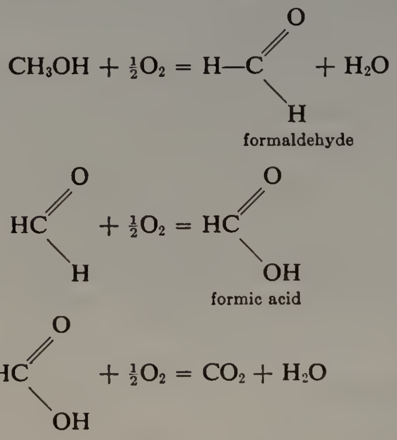
There is a further discussion of this reaction in the article by J. D. Roberts, "Organic chemical reactions," *Scientific American*, November 1957, p. 117.

Expt. 28, SOME REACTIONS OF HYDROCARBONS AND OF ALCOHOLS,
fits here. See p. 597 for guide.

Oxidation of Organic Compounds (18-3.2)

The most highly oxidized condition of a single carbon atom is CO_2. The most reduced condition of a simple carbon atom is methane, CH_4. Between these extremes lie three other levels of oxidation, and the whole series of reactions can be carried out to give the compounds shown in the following equations:

$$CH_4 + \tfrac{1}{2}O_2 = \underset{\text{methanol}}{CH_3OH}$$

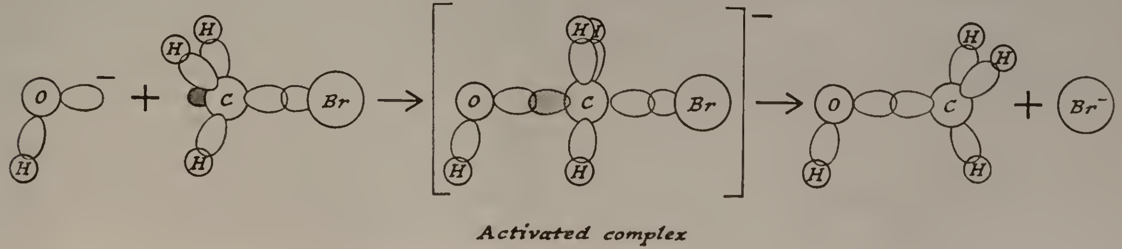


$$CH_3OH + \tfrac{1}{2}O_2 = \underset{\text{formaldehyde}}{H{-}\overset{O}{\underset{H}{C}}} + H_2O$$

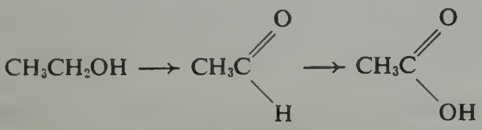
$$H\overset{O}{\underset{H}{C}} + \tfrac{1}{2}O_2 = \underset{\text{formic acid}}{H\overset{O}{\underset{OH}{C}}}$$

$$H\overset{O}{\underset{OH}{C}} + \tfrac{1}{2}O_2 = CO_2 + H_2O$$

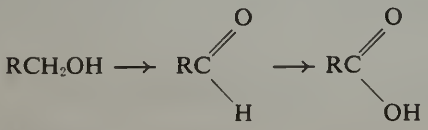
Fig. 18-1. **Schematic mechanism of the reaction** $CH_3Br + OH^- \rightleftharpoons CH_3OH + Br^-$



Oxidation of Higher Homologues. Ethanol can be oxidized to an aldehyde, and this, in turn, to an acid, in exactly the same way as methanol:


acetaldehyde acetic acid

Homologous primary alcohols can be oxidized in the same way:

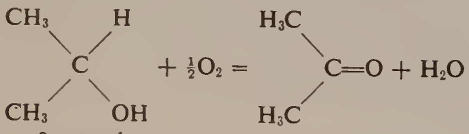

a primary alcohol an aldehyde an acid

The first step in these series, starting from the alkane, can be written

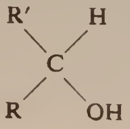
$$\underset{\text{an alkane}}{RCH_3} \longrightarrow \underset{\text{a primary alcohol}}{RCH_2OH}$$

but this process cannot be carried out to give good yields of a single product; mixtures of oxidation products are formed. The oxidation of methane to methanol, on the other hand, is actually a feasible process.

Oxidations of Other Kinds. One of the advantages of writing equations in a partial form, shown earlier for formaldehyde, is that it permits us to make reasonable predictions about the way in which related compounds will behave. For example, what would we predict to be the immediate (i.e., two-electron change) oxidation product of 2-propanol, $CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCH_3$? We would write

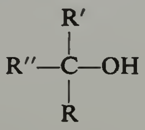

2-propanol acetone (a ketone)

Secondary alcohols, of which 2-propanol is an example, have the generalized structure



where R and R′ are alkyl groups (methyl, ethyl, propyl, etc.). These alcohols oxidize to *ketones.*

It may be pointed out to the students that there is a third class of alcohols—tertiary alcohols—in which the C—OH grouping carries three alkyl groups:



$$R''-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-OH$$

They can be oxidized only by very strong reagents, in which case smaller fragments (containing fewer carbon atoms) are formed. This is a subject that cannot be profitably discussed in the time available and should be explored further only by those students who wish to consult textbooks of organic chemistry.

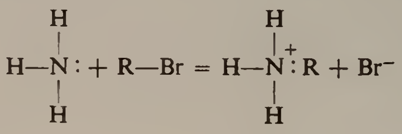
The Functional Group (18-3.3)

These groups serve as the organizing points, since they determine, in a gross way, the reactions which will occur. They are also the basis for naming compounds.

Amines (18-3.4)

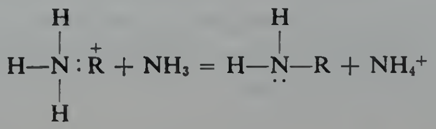
Amines are the typical organic bases. As bases they have about the same strength as ammonia. (*Note:* It would be reasonable to expect that, in RNH_2, the strength of the amine as a base—that is, its dissociation constant—would vary as the nature of R varied. This is true, but a detailed discussion of the relationship between base strength and the structure of the group R would be too involved for this course.)

The formation of an amine by the reaction of ammonia with an alkyl halide (using here an alkyl bromide as the example) proceeds according to equation (*20*), p. 336 of the Textbook:



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}: + R-Br = H-\overset{\overset{\displaystyle H}{|_+}}{\underset{\underset{\displaystyle H}{|}}{N}}:R + Br^-$$

In the presence of a large excess of ammonia, simple proton exchange between RNH_3^+ and NH_3 in the acid-base equilibrium

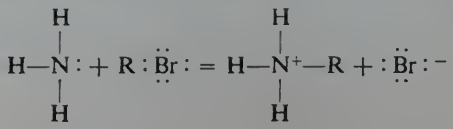


$$\mathrm{H{-}\overset{H}{\underset{H}{N}}{:}\overset{+}{R} + NH_3 = H{-}\overset{H}{\underset{..}{N}}{-}R + NH_4^+}$$

will result in the formation of the free amine, RNH_2.

Special attention should be paid to the resemblance between ammonia plus an alkyl halide and the reaction of an alkyl halide with hydroxide ion:

$$\mathrm{H{-}O{:}^- + R{:}\underset{..}{\overset{..}{Br}}{:} = H{-}O{:}R + {:}\underset{..}{\overset{..}{Br}}{:}^-}$$



$$\mathrm{H{-}\overset{H}{\underset{H}{N}}{:} + R{:}\underset{..}{\overset{..}{Br}}{:} = H{-}\overset{H}{\underset{H}{N^+}}{-}R + {:}\underset{..}{\overset{..}{Br}}{:}^-}$$

Acid Derivatives: Esters and Amides (18-3.5)

These two types of functional groups are introduced to allow discussion of some important classes of polymers.

Expt. 29, THE PREPARATION OF SOME DERIVATIVES OF ORGANIC ACIDS, fits here. See p. 603 for guide.

NOMENCLATURE (18-4)

It often appears to a beginning student that the naming of organic compounds is completely without system. This is not true, and this section is intended to make that point. Do not drill on the subject. While teaching names, comment on their pronunciation.

HYDROCARBONS (18-5)

Saturated Hydrocarbons (18-5.1)

This class of compounds is of minor importance because saturated hydrocarbons take part, in one sense, in relatively few reactions. On the other hand, since petroleum is a complex mixture of saturated hydrocarbons, they are quite important as the starting point for a variety of materials. The *Background Discussion* tells how some of these materials are made.

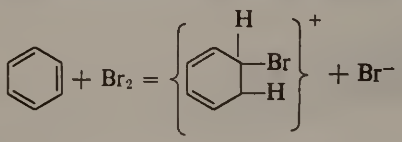
Unsaturated Hydrocarbons (18-5.2)

This type of carbon compound contains the multiple carbon–carbon bonds described in Chapter 16 (p. 296). Use this opportunity to show the applicability of previously studied principles to carbon chemistry. The compounds with double bonds are called alkenes, and the names end in -ene. Compounds with triple bonds are alkynes (acetylene is a nonsystematic name).

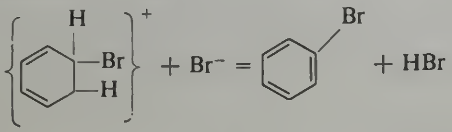
Benzene and Its Derivatives (18-5.3)

An important thing to fix in the student's mind is *what the structure of benzene represents.* We do not have a satisfactory representation, but we do know the properties. Analysis and molecular weight tell us that benzene is C_6H_6. X-Ray and electron diffraction tell us that the six carbons are in a flat ring, with a regular, hexagonal shape. All the carbon–carbon bonds are the same length, and all the C—H bonds are the same. We are forced to use a symbol which can be misleading if taken literally. More than is usually true, the student must keep in mind that this is not a complete picture of benzene.

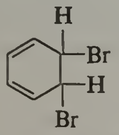
The resulting "aromatic" arrangement has its own chemistry—somewhat between that of saturated and unsaturated hydrocarbons. The substitution reaction with Br_2 is a good example. Ethylene adds Br_2 to give 1,2-dibromoethylene. Ethane does not react. Benzene "substitutes" one Br atom for one H atom to give bromobenzene. The reaction is believed to go through the following steps. First an intermediate forms



which then loses the proton (on the same carbon as Br) to give

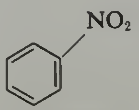


The great stability of the benzene ring, with its six electrons uniformly disposed over the ring, accounts for this result. The recovery of the aromatic structure shown in the last equation is quite exothermic; bromobenzene is much more stable than the other possible final product formed by adding the second bromine.

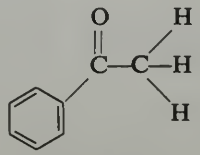


1,2-dibromo-3,5-cyclohexadiene

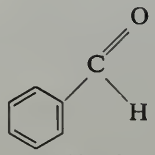
The aromatic substitution reaction produces an enormous number of benzene derivatives such as the following



nitrobenzene



acetophenone



benzaldehyde

By altering the introduced groups, a host of compounds can be made. These reactions, however, are beyond the scope of discussion you will have time for.

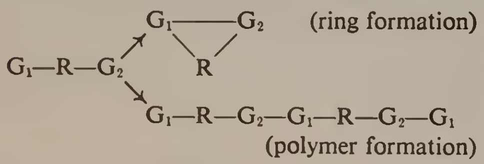
POLYMERS (18-6)

Types of Polymerization (18-6.1)

"Nylon," a Polymeric Amide (18-6.2)

Protein, Another Polymeric Amide (18-6.3)

These sections deal with several kinds of polymers. The important thing is to clarify the polymerization process. One kind of molecule which can take part in polymerization is that which has two points (or groups) within one molecule which can react with each other. Let us designate the two functional groups, G_1 and G_2, and the starting compound (monomer) as $G_1—R—G_2$. Then we have two possibilities:



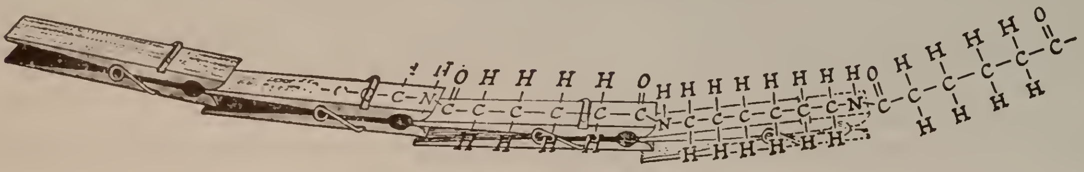
Although of interest, ring formation does not lead to polymers, hence will not be discussed.

You can use the following simple illustration to explain polymerization. Have available eight or ten spring-type clothespins, all alike. Describe one as a molecule with two different groups (the jaws, and one of the thin tail pieces). It is a monomer.

Show "dimer formulation," and compare the structure with that of the monomer. The dimer

still has the same two groups available for reaction. Then continue the "chain" as shown below. Finally, relate this model to a specific reaction, and write the formulas on the board.

Next point out that the different classes of



polymers arise when the functional groups are varied, giving polyamides, polyethylene, etc. Variations within the class come from changes in the other (nonfunctional) part of the monomer.

Expt. 29a, THE PREPARATION OF SOME POLYMERS (Optional), fits here. See p. 608 for guide.

EXPERIMENT 28 SOME REACTIONS OF HYDROCARBONS AND OF ALCOHOLS

PURPOSE. To gain familiarity with some organic molecules. To provide illustrations of saturated, unsaturated, and ring compounds and of one functional group.

PRELAB DISCUSSION. Have ball and stick models available, if possible, so that students may study them. Point out that the four hydrocarbons are selected as representatives of the classes of compounds. The reactions studied in this experiment help define these classes (saturated, unsaturated, and aromatic). Mention also that the reactions of the alcohols are characteristic and may be used to identify the functional group —OH.

TIMING. Assign this experiment anytime during the study of Chapter 18. Oxidation reactions for alcohols are discussed on Textbook p. 332. Reactions of unsaturated compounds are found on p. 342; reactions of cyclic compounds, especially benzene, are found on p. 343. But since these discussions are not necessary to the experiment, it could precede them.

EQUIPMENT NEEDED (FOR EACH STUDENT OR GROUP)

minimum of 6 13 × 100 mm test tubes
(9 would be highly desirable)
test tube rack
cork stoppers for test tubes

beaker for water bath (100 ml or 250 ml)
wax pencil or labels
burner, ring stand, ring, wire gauze

The following should be available in dropper bottles:

1 ml cyclohexane (see lab hint 1)
1 ml cyclohexene
1 ml benzene
1 ml toluene
2 ml methanol
1 ml ethanol
4 ml each of primary, secondary, and tertiary butanol
0.02 ml sodium metal (about 0.02 g) (see lab hint 3)

15 ml 12 M HCl (conc. reagent)
14 ml 0.01 M $KMnO_4$, neutral (1.6 g $KMnO_4$/liter)
5 ml 0.1 M bromine in carbon tetrachloride (5 ml $Br_2(l)$/995 ml CCl_4) (see lab hint 2)
2 ml 6 M H_2SO_4 (340 ml conc. reagent/liter)
4 ml 6 M NaOH (24 g/100 ml)
20 cm B and S #22 copper wire

For Part II b (optional or demonstration):

penny or small piece of copper sheet
20 cm copper wire (B and S #16 is satisfactory)

glass stirring rod
100 ml beaker

PRECAUTIONS. Place hydrocarbons and alcohols in small containers, and remind students that all are flammable. You should supervise the use and disposal of Na. See lab hint 3.

TIME REQUIRED. The student will need one period if chemicals and reagents are supplied to each 3 or 4 students and if the optional parts are not done. A convenient stopping point occurs after Part I (approx. 20 min).

LABORATORY HINTS

1. Other hydrocarbons may be substituted or added. Note that many products have impurities and that it is especially difficult to avoid contamination by unsaturated hydrocarbons. With

the quantities suggested, however, there will be a significant difference between the behavior of unsaturated compounds and that of liquids containing some unsaturated molecules as impurities. Avoid extremely volatile substances (about 75°C is the minimum safe boiling point).

2. A solution of 5 ml Br_2 in 995 ml CCl_4 is satisfactory (approx. 1% by weight), or dissolve in 150 ml CCl_4 the bromine produced from 0.03 mole of NaBr (mol wt 103) or KBr (mol wt 119) oxidized by MnO_2 and H_2SO_4. This amount is sufficient for a class of 30.
3. Trim the oxide deposits from a small piece of Na that has been dried by blotting with a paper towel. Give each student three tiny slivers. After an hour there will likely be some Na unreacted. To avoid the possibility of fire, have all tubes dumped into a clean waste container half full of ethanol.

EXPECTED RESULTS

PART I

The results of mixing alkaline $KMnO_4$ with some hydrocarbons are shown below.

	Cyclohexane	Cyclohexene	Benzene	Toluene
After addition and mixing	purple (no change)	green (MnO_4^{-2})	purple (no change)	purple (no change)
After 5 minutes	grey-purple (possibly some MnO_4^{-2})	brown ppt (MnO_2)	grey-purple (possibly some MnO_4^{-2})	grey (some MnO_4^{-2})
bromine (See Note) After agitating	no change	becomes colorless; continues to decolorize additional Br_2	no change	some slight loss of color

Note: Cyclohexene will remove the color of more bromine than will the other compounds. Their loss of or decrease in color is probably due to some unsaturated impurity in the compounds being furnished. But bromination of saturated compounds may be brought about when energy from sunlight is absorbed.

PART II

(a) Ethanol with:	Basic $KMnO_4$	Neutral $KMnO_4$	Acid $KMnO_4$
after 10 seconds	green (MnO_4^{-2})	no change	red rather than purple
after 5 minutes	yellow-brown	no change or somewhat more red than purple	very light red or pink

(b) The wire becomes shiny and copper-colored again. The odor is very different from the original alcohol, and students who have had biology may identify it as formaldehyde.

Optional: The copper (wire or penny) remains hot and is alternately red-hot or black (oxide with possibly some carbon coating). The alternating reaction described here indicates oxidation-reduction; the Cu undoubtedly serves as a catalyst. Carbon dioxide and H_2O are produced plus some formic acid as well as formaldehyde. It is also interesting to try silver here; it works quite well.

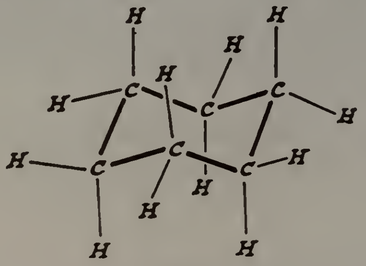
(c) The results of mixing alcohols with various reagents are shown in the following table. In the $KMnO_4$ test, add 1 ml H_2O per 0.5 ml alcohol to speed reaction.

Reagent	Primary alcohol 1-butanol	Secondary alcohol 2-butanol	Tertiary alcohol 2-methyl-2-propanol
Sodium	bubbles of gas evident	fewer bubbles of gas than primary alcohol. Later, some white solid forms (sodium butoxide)	fewer bubbles of gas than primary alcohol. Later, considerable white solid forms (sodium methyl propoxide)
Concentrated HCl	no reaction evident	no reaction evident	milky emulsion produced
Neutral $KMnO_4$ after first shaking	decided color change (deep red)	some color change (red)	some color change (to red)
After 5 minutes	brown ppt separates; liquid forms two layers, both clear	liquid in two layers; upper one is pink, lower one is brown-red with some ppt	single layer. A slight amount of brown ppt settles

QUESTIONS

1. Examine the ball-and-stick models of the various hydrocarbons you tested. Which contain double bonds? Which of the models is (are) planar, which nonplanar? Is there an alternate structure for cyclohexane?

   Answer: All but cyclohexane contain double bonds. Benzene and toluene are planar. Cyclohexane may be either "chair" (shown) or "boat" form.



2. (a) Which of the hydrocarbons were readily oxidized by the alkaline solution of $KMnO_4$?
   (b) Which was reactive with the bromine solution?
   (c) What is the relationship between the reactivity noted in (a) and (b) and the structure of the hydrocarbons?

   Answer: (a) Cyclohexene was most readily oxidized.
   (b) Cyclohexene was most reactive.
   This is the only one that is expected to react, but some unsaturated compounds are nearly always present as impurity in the supposedly saturated samples. The benzene ring compounds do react with bromine, not as addition of bromine, but as a substitution for a hydrogen atom. This, however, does not take place under ordinary conditions unless a catalyst is present. There is no reason why reaction would be more likely with toluene than with benzene, hence if a reaction is observed, it probably reflects the lack of purity in the substances used.

(c) These reactions show that an isolated double bond (as in cyclohexene) is not the same as an aromatic ring (as in benzene and toluene). Many other results reinforce this conclusion. The bonding is different, as hinted at in the Textbook discussion (p. 343) about the symbol for benzene.

3. Write the balanced equation for the reaction in which methanol was oxidized by the hot copper oxide.

Answer: $CH_3OH + CuO \rightleftharpoons H_2O + HCHO$ (formaldehyde) $+ Cu$

4. What differences were noted when C_2H_5OH reduced the neutral, acidic, and basic solutions of $KMnO_4$? Assuming that C_2H_5OH was oxidized to acetic acid, CH_3COOH, in each case, write balanced equations for each reaction. Be sure to use the reduction half-reaction which involves the reduction product of manganese which you observed.

Answer: The general comment that manganese has several oxidation states accounts for the differences noted. The rates of these reactions are strongly affected by H^+ and are very slow in neutral solutions.

In strong acid solution,

$$12H^+ + 4MnO_4^- + 5C_2H_5OH \rightleftharpoons \underset{\substack{\text{clear or}\\ \text{light pink}}}{4Mn^{+2}} + 5CH_3COOH + 11H_2O$$

In basic solution

$$4OH^- + 4MnO_4^- + C_2H_5OH \rightleftharpoons \underset{\text{green}}{4MnO_4^{-2}} + CH_3COOH + 3H_2O$$

and finally

$$4MnO_4^- + 3C_2H_5OH \rightleftharpoons 4MnO_2 + 3CH_3COOH + 4OH^- + H_2O$$

In neutral solution, the student will have observed very little reaction, hence should probably not write an equation. It may be, however, that the distilled water is slightly acid and that some Mn^{+2} is produced. If alkaline tap water is used, some brown MnO_2 may have resulted.

5. In the reactions involving the three isomeric alcohols with the formula C_4H_9OH, what did each of the following tests show about the functional group —OH and its position in each alcohol?

(a) The test with metallic sodium;
(b) The test with concentrated hydrochloric acid;
(c) The test with neutral potassium permanganate.

Answer: (a) $Na + ROH = \frac{1}{2}H_2 + RONa$

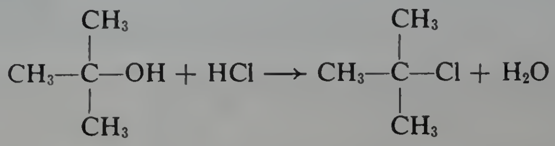
All the alcohols showed the same reaction, but the primary alcohol was more reactive, and the product, RONa, from the tertiary was least soluble. The RONa compounds are called sodium alkoxides, in this case butoxides.

(b) For 2-methyl-2-propanol a reaction occurs, producing a product of low solubility. The others showed no reaction. This indicates a less strong bond between the C and the OH in the compound where the carbon is bonded to three other carbons.

(c) The primary and secondary alcohols were more easily oxidized. Aldehydes and acids were produced from the primary alcohol and a ketone from the secondary alcohol (shown also in the film SYNTHESIS OF AN ORGANIC COMPOUND).

6. Write a balanced equation for each case in Question 5 (a), (b), and (c) where a reaction occurred.

Answer: (a) $C_4H_9OH + Na \longrightarrow C_4H_9ONa + \frac{1}{2}H_2$

(b) 

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-OH + HCl \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-Cl + H_2O$$

(c) Using the half reaction method, we write C_4H_9OH gives C_4H_8O. To account for the conservation of hydrogen atoms we add $2H^+$ to the right and then also add $2e^-$ to the right to give electrical balance.

$$C_4H_9OH \longrightarrow C_4H_8O + 2H^+ + 2e^-$$

The reduction of permanganate is shown by

$$MnO_4^-(aq) + 4H^+(aq) + 3e^- \longrightarrow MnO_2(s) + 2H_2O$$

Taking 3 times the first equation and twice the second gives, with algebraic cancelling

$$3C_4H_9OH + 2MnO_4^-(aq) + 2H^+(aq) \longrightarrow 3C_4H_8O + 2MnO_2(s) + 4H_2O$$

Using the oxidation number system we see that the carbon to which oxygen is attached goes from +2 to 0, while manganese goes from +7 to +4. Hence three molecules of alcohol must react for each two MnO_4^- ions:

$$3C_4H_9OH + 2MnO_4^- \longrightarrow 3C_4H_8O + 2MnO_2(s)$$

Using H^+ and H_2O to balance gives

$$3C_4H_9OH + 2MnO_4^- + 2H^+ = 3C_4H_8O + 2MnO_2(s) + 4H_2O$$

7. Examine the ball-and-stick models of the three isomeric alcohols with the formula C_4H_9OH. Note especially any difference in the nature of the carbon to which the functional group —OH is attached. Discuss the relation of your results as summarized in Question 5 to the structure of the three alcohols.

Answer: In each location the O—H bond was broken in reaction with Na, but this seems to occur most easily when the —OH is attached to a carbon atom which is bonded to only one carbon. Only when the —OH was on a carbon bonded to three other carbons was the Cl substituted for the —OH. A carbon atom bonded to three other carbons was least susceptible to oxidation, whereas that on an end carbon was most susceptible.

8. *Optional:* Note the physical properties of the three alcohols summarized in the following table:

Alcohol	m.p. (°C)	b.p. (°C)	Solubility (g/100 g H_2O)
1-Butanol	−89	117.7	7.9
2-Butanol	−89	100	12.5
2-Methyl-2-propanol	25.5	82.8	infinitely soluble

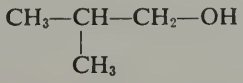
Using principles discussed in Chapter 17 of the Textbook, *The Bonding in Solids and Liquids*, discuss the relationship of the structure of the three alcohols and the trends and differences in the physical properties tabulated.

Answer: The difference in melting point of the tertiary alcohol may be due to the closer packing possible with this more symmetrical molecule. The greater van der Waals forces between the longer hydrocarbon chain accounts for the trend in boiling point. This same factor also accounts for the solubility trend with the longer chain less soluble.

9. *Optional:* There is a fourth alcohol with the formula C_4H_9OH. Draw a structural formula for it, and name it. How would you predict that it would react with

(a) metallic sodium;
(b) 12 *M* HCl;
(c) neutral 0.01 *M* $KMnO_4$?

Answer: The fourth isomer, 2-methyl-1-propanol, is



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH$$

It would be expected to react as the primary alcohol did—with Na and with $KMnO_4$, but not with HCl.

POSTLAB DISCUSSION. Emphasize the relation between differences in reaction and differences in structure. Mention particularly the ease with which the double bond is oxidized and the differences in reactivity for various positions of the —OH group.

EXPERIMENT 29 THE PREPARATION OF SOME DERIVATIVES OF ORGANIC ACIDS

PURPOSE. To illustrate some organic molecules and their reactions. To demonstrate the skeletal integrity of a hydrocarbon group.

PRELAB DISCUSSION. Have ball and stick or other models available. Emphasize the integrity of the hydrocarbon radical during changes of functional group. The reactions are characteristic of the functional groups rather than of the entire molecule.

TIMING. To allow for a full understanding, assign this experiment after the class has read Textbook p. 338.

EQUIPMENT NEEDED (FOR EACH STUDENT OR GROUP)

1 test tube (25×200 mm) or 50 ml Erlenmeyer flask with a 1 hole stopper and a 2 foot length of 8–10 mm glass tubing
1 glass bend (6 mm)
6 test tubes (13×100 mm)
1 test tube (18×150 mm)
250 ml beaker
hot plate and/or ring stand, clamp, burner
small condenser (see lab hint 2)
separatory funnel (see lab hint 4)
litmus paper
boiling chips
melting-point apparatus as described in Expt. 26 (Laboratory Manual p. 70)
safety glasses

CHEMICALS NEEDED

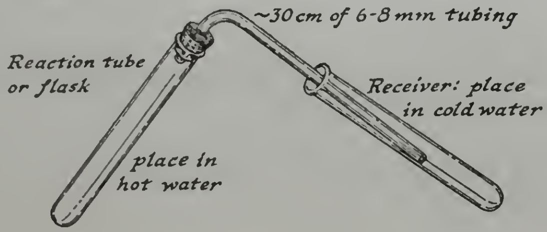
5 ml ethanol
16 ml glacial acetic acid
0.5 ml 18 M H_2SO_4 (for safety in dispensing see p. 216, lab hint 4, Expt. 12)
2 ml sodium carbonate solution (saturated; about 20 g $Na_2CO_3 \cdot H_2O$/100 g water)
0.5 g anhydrous calcium chloride (see lab hint 5)
4 g ammonium carbonate
15 ml acetone (if Part II d is to be done)

PRECAUTIONS. Ethanol, ethyl acetate, and especially acetone are flammable, therefore heating must be done very carefully. Electric hot plates are preferred. Be sure to caution students about the use of concentrated H_2SO_4. (See p. 216 for convenient dispenser.) Safety glasses should be worn.

TIME REQUIRED. Two periods will be needed. A convenient stopping place is available after Part I. If less than a full period is available for Part I, stop after I c (25 minutes).

LABORATORY HINTS

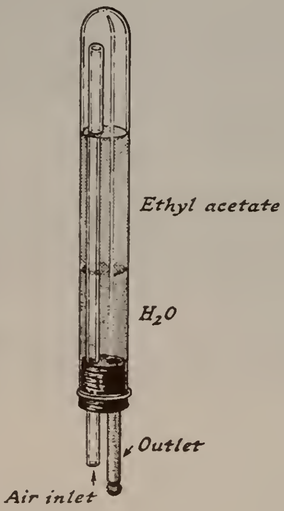
1. A cork is better than a rubber stopper because of the greater ease of boring a suitable hole for 8–10 mm tubing. If rubber is used, see lab hint 3. If cork is used, wrap the lower part in aluminum foil so that vapors will not be absorbed.
2. A small water-cooled condenser is desirable for Part I, but if such is not available, a right-angle bend may be used as follows:



In Part II, an air condenser is satisfactory, although some vapors will escape into the room; and if small water-cooled condensers are used in Part I, they may as well be used in Part II also. But when the water and excess acetic acid have been collected, the water for the condenser should be shut off to allow the temperature to exceed 200°C so that the acetamide can be collected in the test tube rather than in the condenser.

Use thermometers reading to 250°C if they are available. Fit a two-hole stopper with a thermometer (see lab hint 3) and a glass bend leading to the condenser. The distillate boiling below 200°C may be collected in a single tube. When 200°C is reached, a second tube should be used to collect the acetamide (b.p. = 220°C).

3. The following is a safe technique for putting a thermometer through a rubber stopper. Select a cork borer of a size that the thermometer will just slide through. After moistening the hole in the stopper with a drop or two of glycerol, work the cork borer into the stopper hole from the bottom. When it is through, slide the thermometer in from the top until it extends the desired distance. Hold the stopper and thermometer, and work the cork borer out. At first the thermometer will need to be held in position, but as soon as the cork borer is a little way out, the rubber will grip it. The thermometer may be removed in a similar fashion by working the borer down around it. This works even for thermometers welded to the rubber.
4. If small separatory funnels are not available and you wish to introduce separation of liquids, a substitute may be made as follows:



Remove the stopper, and place the liquid in the tube. Invert the tube, keeping a finger over the outlet (or provide other means of closure). When the liquids have formed layers, control the outflow of heavier liquid by finger pressure on the air inlet tube.

5. In place of anhydrous calcium chloride, either anhydrous magnesium sulfate or Drierite may be used.

DISCUSSION

PART I

(a) See lab hint 1 above.

(b) $CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$

	Acetic Acid		Ethanol
Wt of 1 mole	60 g	wt of 1 mole	46 g
Density	1.05 g/ml	density	0.79 g/ml
Wt of 6 ml	6.30 g	wt of 5 ml	3.95 g
Moles in 6 ml	0.105 mole	moles in 5 ml	0.0859 mole

The acetic acid is therefore in excess, since ethanol and acetic acid react 1 mole to 1 mole.

(c) Since the mixture boils well below the boiling point of water, it is best to heat it just enough to make it boil. At higher temperatures, both ethanol and the product are lost in spite of the reflux tube.

Optional

(d) With the water bath kept at 90°C, about 7–8 ml evaporate and are condensed. It is assumed that what is left behind is the unreacted acetic acid, water, and sulfuric acid. Along with the ethyl acetate will be some unreacted ethanol, since this boils at 79°C and the ethyl acetate at 77°C. The boiling point of the acetic acid is 118°C.

(e) The ethyl acetate has a solubility of 8.6 g/100 g water at 20°C, but with saturated sodium carbonate the separation is fairly good. Less than two milliliters of Na_2CO_3 solution will be needed if the temperature has been kept as suggested in Part d. The water layer will be below the ethyl acetate, since the density of the latter is 0.9 g/ml.

(f) It is unlikely that the student will have more than 5 or 6 milliliters at this point (5 ml of product, if all ethyl acetate, would be 0.05 mole or about 60% yield), and there is not much need to dry it or further distill it. The most noticeable property is the odor. A sample of ethyl acetate should be put out for comparison. Its slight solubility in water should be noted (the student will consider it immiscible). This compound is a good insecticide and is, in fact, used instead of cyanide in insect-killing jars for entomological collecting. The student could investigate its effectiveness by comparing it with ethanol.

DISCUSSION

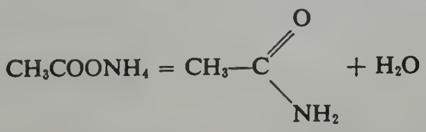
PART II

(a) The equation is

$$2CH_3COOH + (NH_4)_2CO_3 = 2CH_3COONH_4 + H_2O + CO_2$$

Since 10 ml equals 0.175 mole of acetic acid, and since 4 grams of ammonium carbonate are 4/96 = 0.042 mole, there is considerable excess of the acetic acid.

(b) This drives off more of the CO_2, shifting the equilibrium in the direction to give more ammonium acetate. The heat also causes the decomposition to acetamide:



$$CH_3COONH_4 = CH_3{-}C(=O)NH_2 + H_2O$$

(c) Excess acetic acid and water will distill off, allowing about 7 ml of acetamide to be collected. If a thermometer is being used, the first portions may be collected in a single tube. After most of the water and acetic acid is driven off, the temperature will rise rapidly; it is following this rise that the acetamide will be collected. Its melting point is 81°C; its boiling point, 220°C. The test tube or flask will become dry as the acetamide distills over and solidifies as a white, crystalline solid. A 100% yield would be 5.0 grams. An expected yield would be about 40% or 2.0 grams.

If thermometers are not being used, save the 1–2 ml samples until cool. Solidification may not take place immediately, therefore the early samples should not be discarded at once.

Optional

(d) For purification, add as little acetone (about 10 ml) as needed to dissolve the solid. Pour the solution into a watch glass, and allow the acetone to evaporate over warm water. The crystals that form along the edges will be purer than those formed in the center, and may be separated for melting point determination.

(e) It is difficult to get the acetamide completely dry (it is deliquescent) unless it is kept in a desiccator overnight. The determination of melting point will not be satisfactory unless it is thoroughly dry. The student may compare the compound he has produced with ammonium carbonate in order to establish its different properties. Their solubility in water, acetone, and chloroform could be compared, as well as their odor and the conductivity of their solution.

QUESTIONS AND EXERCISES

1. (a) Calculate the number of moles of each reactant, C_2H_5OH and CH_3COOH, which were used in the preparation of $CH_3COOC_2H_5$.

Data: 1 ml of C_2H_5OH weighs 0.79 g;
1 ml of CH_3COOH weighs 1.05 g.

(b) Which reactant is present in excess?

(c) If all of one of the reactants were consumed, how many moles of ethyl acetate could be produced? How many grams of $CH_3COOC_2H_5$ is this?

(d) What is the role of the sulfuric acid in the reaction?

Answer: (a) See the discussion of Part I b. Five ml of ethanol is 0.0859 mole; 6 ml of acetic acid is 0.105 mole.

(b) The acetic acid is present in excess.

(c) If all the ethanol (the reactant not in excess) were used, 0.0859 mole of ethyl acetate could be produced. This would be 0.0859 mole × 88.0 g/mole, or 7.56 grams. Since its density is 0.9 g/ml, this will be 8.4 ml.

(d) H_2SO_4, or any of several other strong acids, acts as a catalyst. It helps speed the attainment of equilibrium, probably by donating a proton and later regaining it.

2. (a) Write the equation for the reaction of acetic acid with ammonium carbonate.

(b) How many moles of each reactant, CH_3COOH and $(NH_4)_2CO_3$, are involved in this reaction? If all of the $(NH_4)_2CO_3$ is converted to CH_3COONH_4 and then to CH_3CONH_2, how many moles and grams of acetamide would be expected?

(c) How does the removal of water during the distillation in Part II c affect the yield of acetamide?

Answer: (a) See the discussion of Part II a.

(b) See the discussion of Part II a. The reaction used 0.175 mole of acetic acid and 0.042 mole of ammonium carbonate. Even though the reaction requires 2 moles of acetic acid to one of the ammonium carbonate, the former is in excess. From 0.042 mole of ammonium carbonate, 0.084 mole of CH_3CONH_2 could be produced. This is 0.084 mole × 59 g/mole, or 5 grams of acetamide.

(c) The removal of water (a product of the reaction) will shift the equilibrium in favor of the products, and should increase the yield.

POSTLAB DISCUSSION. This is an appropriate time to discuss ways of purifying organic compounds—distillation, crystallization, use of differential solvents. It is also good to comment on the use of equilibrium considerations in organic reactions.

EXPERIMENT 29a THE PREPARATION OF SOME POLYMERS (Optional)

It seems unlikely that many classes will include all parts of this experiment; for this reason the equipment and discussion sections are given separately for each part. The questions for all parts are given at the end of Part III.

PURPOSE. To give examples of some simple polymerizations.

PRELAB DISCUSSION. This will depend on the section to be used. Since polymers are introduced in the Textbook, no formal prelab discussion is necessary.

TIMING. This experiment, if assigned, should come late in Chapter 18.

Part I—The Preparation of a Glyptal Resin

EQUIPMENT NEEDED (PER INDIVIDUAL OR PAIR)

2 g glycerol (see lab hint 1)
3 g powdered phthalic anhydride
50 ml beaker or small (baby food size)
  tin can (see lab hint 2)
watch glass
stirring rod
electric hot plate or burner, ring,
  ring stand, gauze
mortar and pestle
solvent (methylethylketone, ethyl
  acetate, or acetone)

TIME REQUIRED. This part requires 20–30 minutes.

PRECAUTIONS. The resin is flammable, therefore care must be taken if an open flame is used. The solvents are also flammable and are quite volatile. When these are being used, there should be no open flames on the lab desk. Good ventilation is necessary.

LABORATORY HINTS

1. The density of glycerol is 1.26 g/ml, thus 2 g occupies 1.6 ml. If the liquid is warmed slightly it becomes very much less viscous and much easier to measure.
2. The use of tin cans eliminates clean-up problems.

DISCUSSION OF PROCEDURE. When phthalic anhydride is heated it sublimes, hence a watch glass is used to cover the can or beaker. Sometimes the resin does not "puff up," but after some bubbling as the phthalic anhydride is mixed and melts, the mixture may reach its boiling point (about 290°C) and boil gently. If this happens, boil the mixture for 10–15 minutes until it is quite viscous, and then pour the material out onto a piece of glass or into a watch glass. After cooling, it may be chipped off and ground as directed. The resin is used as a protective coating for wood and metal and also for cementing surfaces of fibrous materials, glass, metals, etc.

Part II—The Preparation of an Amine-aldehyde-type Polymer

EQUIPMENT NEEDED (PER INDIVIDUAL OR PAIR)

10 ml 40% formaldehyde solution (Formalin)
10 ml saturated aniline hydrochloride
  (see lab hint 3)
2 18 × 150 mm test tubes
small beaker or small tin can

TIME REQUIRED. This part requires 15–20 minutes.

PRECAUTIONS. Caution students to keep reagents off their skin and to wash carefully in case of an accident. Good ventilation is necessary.

LABORATORY HINT. At about 20°C, 75 ml of aniline added to 100 ml of 8 *M* HCl will yield a saturated solution of aniline hydrochloride. But the solution does not need to be saturated; 55 ml of aniline added to 100 ml of 6 *M* HCl is quite sufficient. This solution will be warm, and should be cooled before use. The solubility of aniline hydrochloride in 100 ml of H_2O is 88 g at 15°C and 107 g at 25°C.

DISCUSSION OF PROCEDURE. Ten ml of 40% formaldehyde is about 0.12 mole. Ten milliliters of aniline hydrochloride will be 0.06 to 0.08 mole. The heat of polymerization is quite large, producing a temperature rise of 40–50°C. The resin is deep red and rubbery. Although quite soft when first formed, it becomes hard when dry. It is not soluble in water. A convenient way to observe this polymer is to pour the solution immediately after mixing into a funnel in which a cone of polyethylene film has been folded like filter paper.

Part III—The Depolymerization of a Methyl Methacrylate Polymer and Subsequent Polymerization of the Monomer (to be done *only* if excellent equipment is available)

EQUIPMENT NEEDED

(a) (per class)

distillation apparatus, including flask, condenser, and receiver with ground glass connections (see lab hint 1)

25 g "Lucite" or "Plexiglas" pellets or chips (see lab hint 2)

heating mantle or hot plate

(b) (per individual or pair)

10 g methyl methacrylate monomer (10 ml, since the density is 1 g/ml) (see lab hint 3)

0.02 g benzoyl peroxide. **HAZARD.** See p. 611

baby food jar or expendable glass container

250 ml beaker

burner or hot plate

stirring rod

aluminum foil and rubber band

TIME REQUIRED. Parts (a) and (b) require $1\frac{1}{2}$–2 periods; Part (b) takes about 35 minutes.

PRECAUTIONS. If possible, the distillation should be done in a hood, because the monomer is unpleasant and toxic. Good ventilation is a minimum requirement. This is true also for the heating in Part (b), although the stopper should prevent excessive escape of vapor.

LABORATORY HINTS

1. If depolymerization is to be done, it should be a group or class project. A two-necked flask is convenient for "reloading" with the polymer, but a large single-necked flask makes this unnecessary. Since rubber is affected, the joints should be ground glass. A heating mantle is a better heat source than a burner flame.
2. If the school has a craft shop, waste polymer will probably be abundant. It can easily be ground or broken into small pieces.
3. If repolymerization is to be carried out within a few days, the redistilled monomer may be kept in a tightly stoppered flask without the addition of inhibitor. It may be kept very much longer (several months at least) if kept refrigerated. Hydroquinone (about 0.5 g/100 ml of monomer) may be used as an inhibitor, but any excess is difficult to remove. See p. 146 (22–51s) *Tested Demonstrations*, H. N. Alyea and F. B. Dutton, published by *J. Chem. Education*, 1960, for a procedure used in removing inhibitor.

DISCUSSION OF PROCEDURE

(a) The depolymerization procedure works well if the polymer is heated slowly until it melts and then decomposes. The first condensate will probably be yellow and somewhat viscous, but after redistillation the monomer is colorless and very much like water in viscosity and density as well as boiling point.

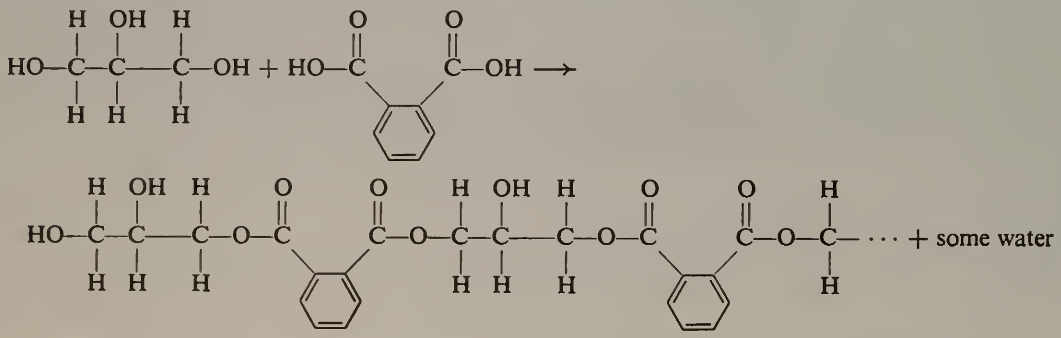
It is convenient to collect the first condensate in a distilling flask so that it need not be transferred. The flask in which the polymer was heated should be rinsed first with methylethylketone and then left filled with sulfuric acid-dichromate cleaning solution (see handbook for recipe) for several days.

(b) A small baby food jar is a convenient container for this polymerization. The polymer is difficult to remove and slow to dissolve. Some students may wish to break the jaw to remove the resin. When polymerization is carried out at or just below 100°C the solution bubbles and forms a porous resin. You can carry out the polymerization at a lower temperature to avoid the formation of bubbles. To do so, use tightly covered jars with aluminum liners in the jar caps. Place the jars in an oven at 45–50°C until polymerization is complete—from 1 to 2 days.

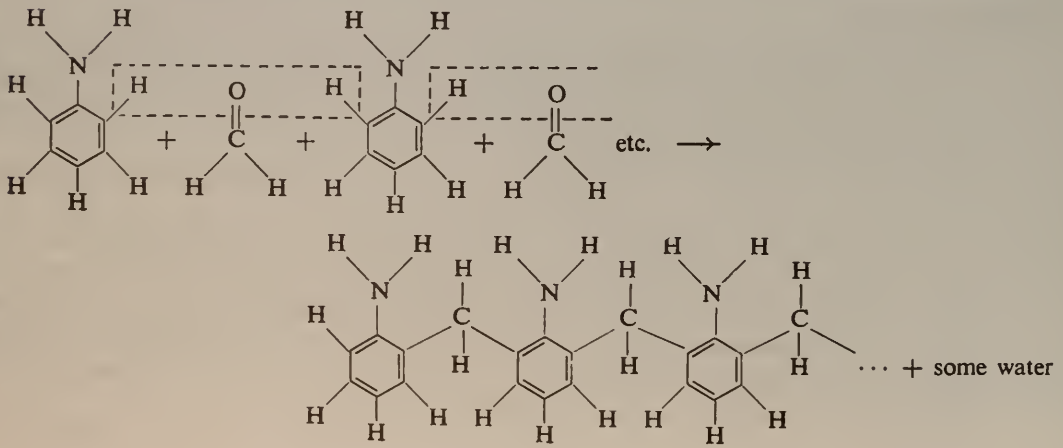
QUESTIONS (FOR PARTS 1-3)

1. Write equations for the reactions involved in each preparation you performed, using structural formulas for the monomers and polymers involved.

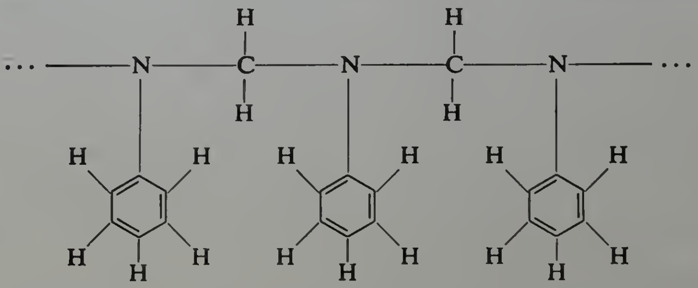
Answer: (a)



(b)



This reaction is what the student will write from the phenol example given. It does occur in strongly acidic solution. At neutral or slightly acid conditions the amino hydrogens condense, and the product can be written as



The student is not expected to know these variations with conditions.

(c) See the structure in the Laboratory Manual.

2. Which of the preparations involve condensation reactions?

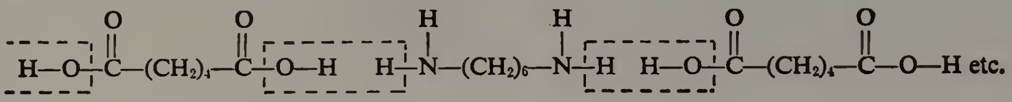
   Answer: Glyptal resin and the aniline-formaldehyde resin involve condensation reactions.

3. Which are addition reactions?

   Answer: The formation of methyl methacrylate polymer is an addition reaction. (The benzoyl peroxide serves as an initiator and forms the ends of long polymeric chains.)

4. "Nylon" is a generic name for polymeric amides, including those formed by the reaction of adipic acid, $HOOC{-}(CH_2)_4{-}COOH$ and 1,6-diaminohexane, $H_2N{-}(CH_2)_6{-}NH_2$. Show how these polyfunctional molecules can condense and form a long-chain polymer.

   Answer:



$$\mathrm{H{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}O{-}H\quad H{-}\overset{H}{\overset{|}{N}}{-}(CH_2)_6{-}\overset{H}{\overset{|}{N}}{-}H\quad H{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}O{-}H\ etc.}$$

Or see p. 348 of the Textbook.

SAFETY NOTE

Do not use solid benzoyl peroxide. It is a dangerous chemical, particularly when jars or cans of the solid become slightly moist. It should not be kept in a high school laboratory.

Benzoyl peroxide is available in the form of pastes in which it is mixed with an ester oil, such as diethyl, or with butyl benzyl phthalate. These pastes are very much safer than the pure compound, and are effective in the reaction. Specific substances for this use and their sources are:

BZQ-45 from U. S. Peroxygen, 850 Morton Ave., Richmond, Calif.

Luperco ATC from Ram Chemical Co., P. O. Box 192, Gardena, Calif.

Supplementary Material

Articles

1. S. Williams, "Synthetic fibers," *Scientific American*, July 1951, pp. 37–45.
2. J. J. Parsons, "Natural gas," *Scientific American*, November 1951, pp. 17–21.
3. L. P. Lessing, "Coal as chemical raw material," *Scientific American*, July 1955, pp. 58–67.
4. J. D. Roberts, "Organic chemical reactions," *Scientific American*, November 1957, pp. 117–126 (Offprint No. 85).*

Book

W. Herz, *The Shape of Carbon Compounds*, Benjamin, New York (1963). Good supplementary reading for teachers and able students.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

1. SYNTHESIS OF AN ORGANIC COMPOUND

A CHEM Study film

Running Time: 22 minutes

This film was produced with the collaboration of Professor T. A. Geissman, an outstanding chemist specializing in organic synthesis. The film gives the student an opportunity to view some typical laboratory operations and equipment of organic chemistry. Thus it provides a partial substitute for the student laboratory experience made inaccessible by the expense of equipment and fire hazards. Using the dichromate oxidation of an alcohol to a ketone (as discussed on Textbook p. 335), the following laboratory operations are demonstrated:

(a) refluxing a reaction mixture with temperature control and stirring;
(b) a liquid-liquid extraction by means of a separatory funnel;
(c) drying an organic liquid with an anhydrous salt;
(d) distillation;
(e) identification by derivative formation;
(f) melting point determination;
(g) identification by infrared spectrum.

2. MECHANISM OF AN ORGANIC REACTION

A CHEM Study film

Running Time: 20 minutes

Prof. H. Rapoport collaborated in making this film study of the hydrolysis of an organic ester. It shows determination of the chemical equation, the structures of reactants and products, the fate of each atom of the reactants, and the structure of intermediate molecules. Mass spectographic detection of an oxygen isotope, ^{18}O, is a critical part of the unraveling story.

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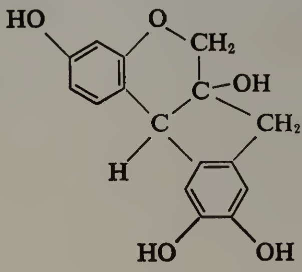
* Available from W. H. Freeman and Co., San Francisco. Order by number.

Background Discussion

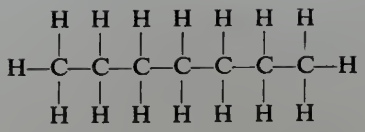
It is not reasonable to expect anything like "thorough coverage" in this chapter. Concentrate on showing that no new principles are needed for organic chemistry. You might expect the student to learn what data are needed for getting at the structure of a molecular compound and to learn the concept of skeletal integrity. He can also be expected to understand a few reactions of the simple functional groups.

Brazilin, the compound mentioned in the quotation at the beginning of the chapter, is a red dye known since ancient times. It was first obtained from East Indian woods called brazilwoods because of their color (Pg *brasa*, glowing coals). Similar dyewoods were found in South America; Brazil is said to have been named from these dye-woods, since they are abundant there. The formula of brazilin is



THE LARGE NUMBER OF CARBON COMPOUNDS

One question that can lead to a discussion of value is: Why do so many compounds of carbon and hydrogen exist, whereas not nearly so many exist for any other pair of elements? The answer would have the following main features. As a result of its electron structure, carbon forms four equivalent bonds joining it to other atoms. These can be other carbon atoms, hydrogen atoms, oxygen, nitrogen, or halogen atoms (and others which are beyond the purpose of our discussion). This means that not only can long chains of carbon atoms be formed,



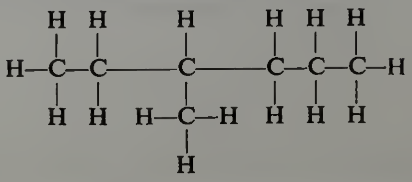
$$\begin{array}{ccccccccc} & H & H & H & H & H & H & H & \\ & | & | & | & | & | & | & | & \\ H- & C- & C- & C- & C- & C- & C- & C- & H \\ & | & | & | & | & | & | & | & \\ & H & H & H & H & H & H & H & \end{array}$$

or

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

heptane

but branching of the chain can occur,

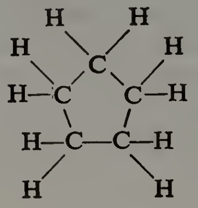


or

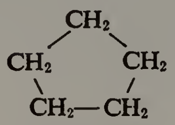
$CH_3CH_2CH(CH_3)CH_2CH_2CH_3$

3-methylhexane

and rings of carbon atoms can exist,

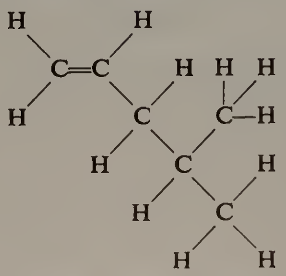


or



cyclopentane

Furthermore, *double bonds* occur in many organic compounds;



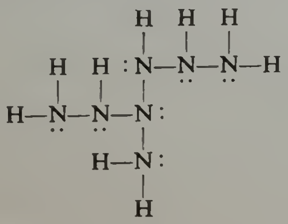
or

$$\begin{array}{l} CH_2{=}CHCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 \end{array}$$

2-methyl-4-pentene

Note that only relatively small molecules are discussed. Remind the student that molecules containing up to twenty carbon atoms are common and that there are many still larger ones.

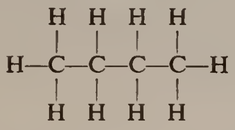
From this start you can lead into the more difficult question: "Why doesn't nitrogen form long chains and branched chains, such as



or, why doesn't silicon form compounds that are the exact counterparts of the carbon compounds?"

The answers to these reasonable questions are difficult, because such compounds *can* exist but do not because of their great instability. In the complex nitrogen compound shown above, each nitrogen atom contains an unshared pair of electrons (shown as the dots on the N atoms). These are points of attack by electron-seeking reagents (such as acids, which can provide H^+), and, consequently, reactions that lead to the rupture of such chains take place very readily.

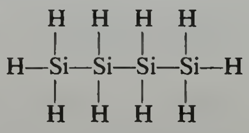
On the other hand, in the long-chain carbon compounds each carbon atom has used all of its valence electrons in bond formation and has a complete (filled) 2-shell ($2s^2$, $2p^6$). Thus the only way for a compound such as butane,



$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

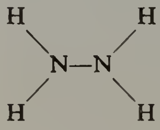
to react is for one of the C—C bonds or one of the C—H bonds to break first. This actually can and does take place; but because of the high energy required to break C—C and C—H bonds these reactions take place either very slowly or at high temperatures (as in the cracking of petroleum).

Why, then, doesn't silicon form stable molecules such as

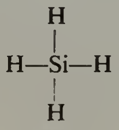


$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{Si} & - & \mathrm{Si} & - & \mathrm{Si} & - & \mathrm{Si} & - & \mathrm{H} \\ & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Silicon does indeed form such compounds, but they are very unstable; silicon (in the third row) has available $3d$ orbitals, and even though in SiH_4, for example, the $3s$ and $3p$ orbitals are completely used in bond formation, reagents that have unshared electrons (such as H_2O) can form a fifth bond to the silicon atom, and reactions that give other products can then occur. It should be pointed out that the simple analogs of carbon compounds are well known for nitrogen and silicon:

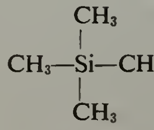


hydrazine



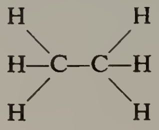
$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{Si} & - & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

silane

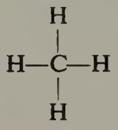


$$\begin{array}{ccccc} & & \mathrm{CH_3} & & \\ & & | & & \\ \mathrm{CH_3} & - & \mathrm{Si} & - & \mathrm{CH_3} \\ & & | & & \\ & & \mathrm{CH_3} & & \end{array}$$

tetramethyl silane

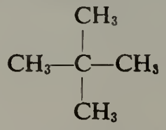


ethane



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

methane



$$\begin{array}{ccccc} & & \mathrm{CH_3} & & \\ & & | & & \\ \mathrm{CH_3} & - & \mathrm{C} & - & \mathrm{CH_3} \\ & & | & & \\ & & \mathrm{CH_3} & & \end{array}$$

2,2-dimethylpropane or neopentane

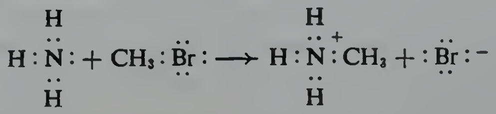
Displacement Reactions (18-3.1)

Section 18-3.1 discusses the reaction of methyl bromide with hydroxide ion. This is a displacement reaction, although the name is not used there. It is worthwhile telling the student that this is an example of one general type of organic reaction. You can briefly expand the topic by showing that the important character of the "incoming" group lies in its possession of unshared electron pairs. The ability of both OH^- and ammonia to accept a proton attests to the existence of these unshared electrons.

The reaction of OH^- with methyl bromide also results in the use of one of these unshared electron pairs in bond formation:

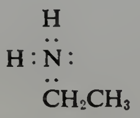
$$\mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:^{-} + \mathrm{CH_3}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Br}}}: \longrightarrow \mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:\mathrm{CH_3} + :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Br}}}:^{-}$$

The reaction of ammonia and an alkyl halide (shown in the Textbook on p. 336) is of the same kind:



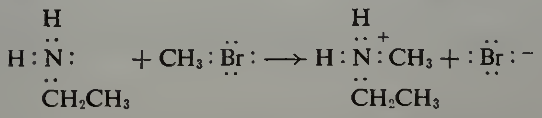
$$\begin{array}{l}\mathrm{H}\\ \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\\ \mathrm{H}\end{array} + \mathrm{CH_3}:\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}: \longrightarrow \begin{array}{l}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot\,+}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{CH_3}\\ \mathrm{H}\end{array} + :\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:^-$$

Ethylamine possesses the same structural feature as ammonia—an unshared electron pair on nitrogen:



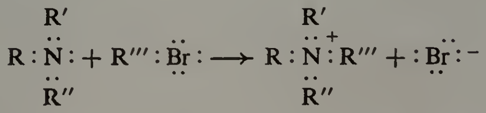
$$\begin{array}{l}\mathrm{H}\\ \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\\ \mathrm{CH_2CH_3}\end{array}$$

Hence it reacts with methyl bromide in the same way:



$$\begin{array}{l}\mathrm{H}\\ \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\\ \mathrm{CH_2CH_3}\end{array} + \mathrm{CH_3}:\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}: \longrightarrow \begin{array}{l}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot\,+}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{CH_3}\\ \mathrm{CH_2CH_3}\end{array} + :\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:^-$$

We can write a *general* expression for the reaction of ammonia or an amine with an alkyl halide:



$$\begin{array}{l}\mathrm{R'}\\ \mathrm{R}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\\ \mathrm{R''}\end{array} + \mathrm{R'''}:\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}: \longrightarrow \begin{array}{l}\mathrm{R'}\\ \mathrm{R}:\overset{\cdot\cdot\,+}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{R'''}\\ \mathrm{R''}\end{array} + :\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:^-$$

For ammonia, $R = R' = R'' = H$. For a primary amine, R is an alkyl group, $R' = R'' = H$. Other groups, for example, cyano (CN^-), methoxy (CH_3O^-) and mercaptan (HS^-), have available electron pairs, and all of them can act in the same way as that shown above for the bases OH^-, NH_3, and $CH_3CH_2NH_2$:

$$:\mathrm{N{\equiv}C}:^- + \mathrm{CH_3}:\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}: \longrightarrow :\mathrm{N{\equiv}C}:\mathrm{CH_3} + :\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:^-$$

$$\mathrm{CH_3}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:^- + \mathrm{CH_3}:\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}: \longrightarrow \mathrm{CH_3}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{CH_3} + :\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:^-$$

$$\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:^- + \mathrm{CH_3}:\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}: \longrightarrow \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:\mathrm{CH_3} + :\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:^-$$

These reactions are all examples of a widely applied, familiar reaction known as the *nucleophilic displacement reaction.* The word nucleophilic is used to denote that reagents of the kind shown above are all capable of forming a bond with one of the four orbitals that surround the carbon nucleus, and thus become attached to the carbon nucleus.

CHARACTER OF THE ETHYLENE DOUBLE BOND

Ethylene acts as an electron donor or proton acceptor to an attacking group that can accept electrons. One closely related kind of behavior that will make this point clear is that of a base such as H_2O, HO^-, or NH_3. As the student knows, these are bases in the general meaning of the term. The reaction of HBr with, for example, OH^- or NH_3, shows these bases accepting protons:

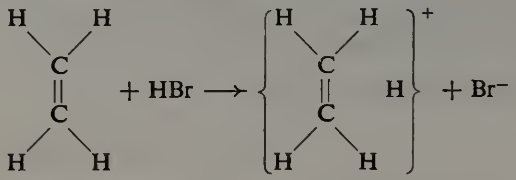
$$OH^- + HBr \longrightarrow HOH + Br^-$$
$$NH_3 + HBr \longrightarrow NH_4^+ + Br^-$$

Ethylene, too, reacts with HBr in an aqueous medium; this reaction proceeds in two steps:

(1) a proton transfer, just as in the above equations; and

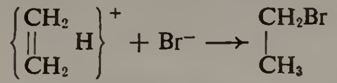
(2) a second reaction in which the protonated ethylene reacts with Br^-.

The first step is represented as follows:



The unusual structure shown for $(CH_2CH_2{\cdot}H)^+$ can be written in other ways, but they all have the same ultimate interpretation: the electron-deficient species (in this case, H^+) is held by a bond formed by its acceptance of one of the electron pairs of the double bond.

The ionic intermediate, $CH_3CH_2^+$, can now react with an anion (in this case, Br^-) to give the final product:



$$\left\{\begin{array}{ll}\mathrm{CH_2} & \\ \| & \mathrm{H}\\ \mathrm{CH_2} & \end{array}\right\}^+ + Br^- \longrightarrow \begin{array}{c}\mathrm{CH_2Br}\\ |\\ \mathrm{CH_3}\end{array}$$

The total reaction is the addition of HBr to $CH_2{=}CH_2$:

$$CH_2{=}CH_2 + HBr \longrightarrow CH_3CH_2Br$$

It is important to analyze this process in the two steps shown here. Otherwise, the student may get the false impression that some reaction such as the following takes place:

$$\begin{array}{lcl} H & \cdots\cdots & CH_2 \\ \vdots & & \| \\ Br & \cdots\cdots & CH_2 \end{array}$$

in which the two fragments H and Br add simultaneously. Remind the student that this kind of a reaction implies the breaking of the H—Br bond simultaneously with an uncoupling of one of the electron pairs in the C═C bond. The activation energy that would be expected for this process is high, in contrast with the low activation energy for the actual reaction of HBr with an olefin.

A good illustration of the two-step nature of addition to ethylene is found in the following experimental facts:

1. The addition of bromine to ethylene gives 1,2-dibromoethane:

$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$

2. However, if this reaction is carried out in an aqueous solution of NaCl, an additional product is formed—this is 1-bromo-2-chloroethane

$$CH_2{=}CH_2 + Br_2 \xrightarrow[NaCl]{aqueous} BrCH_2CH_2Br + BrCH_2CH_2Cl$$

The reason for this is simply that the first step of the reaction between bromine and ethylene to give $(CH_2CH_2Br)^+ + Br^-$ can be followed by reaction with Br^- or Cl^-.

The students can now be asked to predict

(a) What other product might also be found in this reaction?

Answer: Some $HOCH_2CH_2Br$ might be found, from the reaction of $(CH_2CH_2Br)^+$ with the OH^- ions from water.

(b) What would be formed if ethylene were brominated in an aqueous solution of sodium nitrite?

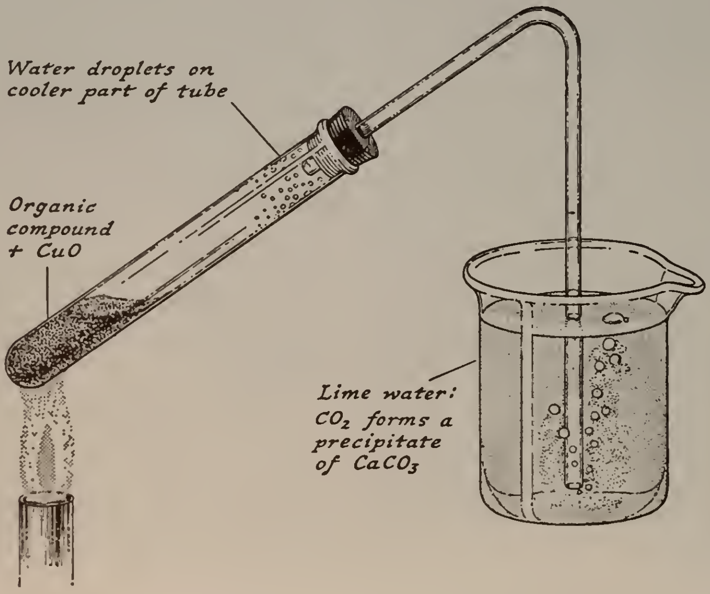
Answer: Some $BrCH_2CH_2NO_2$ would form.

DETERMINING THE COMPOSITION

Some students may be interested in how the composition is determined. These qualitative tests can be described or done by some students.

The first step (sometimes so obvious as to be unnecessary) is to establish the organic nature of the compound. A test for carbon is conclusive and can be quickly (and qualitatively) done by the CuO method (Figure 18-2). When an organic

Fig. 18-2. **The CuO test** *for carbon and hydrogen.*



compound is mixed with copper oxide (CuO) and strongly heated, CO_2 and water are formed and can be detected (identified) by conventional tests such as the student has performed (Expt. 4).

After establishing that the substance does contain carbon (and hydrogen), it becomes interesting to know what other elements it contains. Oxygen, sulfur, nitrogen, and the halogens are most frequently found. For many inorganic compounds qualitative analysis consists of tests for the anions (e.g., Cl^-, SO_4^{-2}, NO_3^-, $H_2PO_4^-$, etc.) and cations (e.g., Na^+, Mg^{+2}, Fe^{+2}, Al^{+3}, Cr^{+3}, etc.) of which they are composed. In most organic compounds that contain a halogen, nitrogen, and sulfur, these elements are present in covalent combination and do not dissociate as separate ions when the compound is dissolved in a solvent. Thus a test for Br^- that will be successful for sodium bromide will not give a positive result for a compound such as bromobenzene, C_6H_5Br, which is a liquid compound of negligible solubility in water.

Since at this stage in the investigation we are not concerned with *how* a bromine, nitrogen, or sulfur atom is bonded to the other atoms of our unknown compound, but only with the presence or absence of these in the compound, the experimental method used consists in subjecting the compound to drastic treatment with a reagent that will free the elements in question from their organic combination and permit us to apply the usual tests to detect their presence.

The usual procedure is to heat the compound strongly (up to a red heat) with metallic sodium. Extensive decomposition occurs, and halogens, nitrogen, and sulfur are converted into halide ions, sulfide ions, and (with the carbon that is present) cyanide ions. The analysis is completed by testing a water solution for these ions. These tests can be found in any text on experimental organic chemistry. Figure 18-3 shows the procedure.

Be sure to use the mole method in all calculations (see Textbook p. 225).

SOURCES OF CARBON COMPOUNDS (18-1)

The following explains the main routes for the chemical use of coal and oil. We usually regard coal, oil, wood, and natural gas as fuels. This is, of course, their chief use; but they serve as the source of the carbon in organic compounds of all kinds.

How is the carbon of coal or petroleum converted into the compounds that serve as starting materials for chemical synthesis? Let us take coal as an example and see how it is used. Initially, coal is heated to produce coal tar (and other fractions) and coke.

Coal tar is a mixture of many compounds; among the industrially important ones are benzene, naphthalene, phenol, and toluene.

Coke is used as a source of carbon in at least two routes to synthetic carbon compounds.

1. Water gas is prepared by the reaction of coke with steam at a high temperature (recall the use of this reaction in Chapter 7).

$$C + H_2O \xrightarrow{1200°C} CO + H_2 \qquad \Delta H = +31\text{ kcal}$$

   In the Fischer-Tropsch process for the manufacture of fuels, water gas is transformed (with high temperature, high pressure, and a catalyst) into a mixture of hydrocarbons.

$$\left.\begin{aligned} &nCO + (2n+1)H_2 \rightleftharpoons C_nH_{2n+2} + nH_2O \\ &nCO + 2nH_2 \rightleftharpoons C_nH_{2n} + nH_2O \end{aligned}\right\}\ \text{a mixture of paraffins and olefins}$$

   The conversion of water gas into methanol is also an important industrial process:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

   Either alkanes or alcohols result from different catalysts or conditions.

2. Acetylene is prepared, starting with coke, by way of calcium carbide:

$$CaO + 3C \underset{\text{furnace}}{\overset{\text{electric}}{\rightleftharpoons}} CaC_2 + CO \qquad \Delta H = +110\text{ kcal}$$

   Acetylene is produced by treating the calcium carbide with water:

$$CaC_2 + 2H_2O \rightleftharpoons C_2H_2 + Ca(OH)_2 \qquad \Delta H = -30\text{ kcal}$$

A great variety of valuable products is prepared from acetylene:

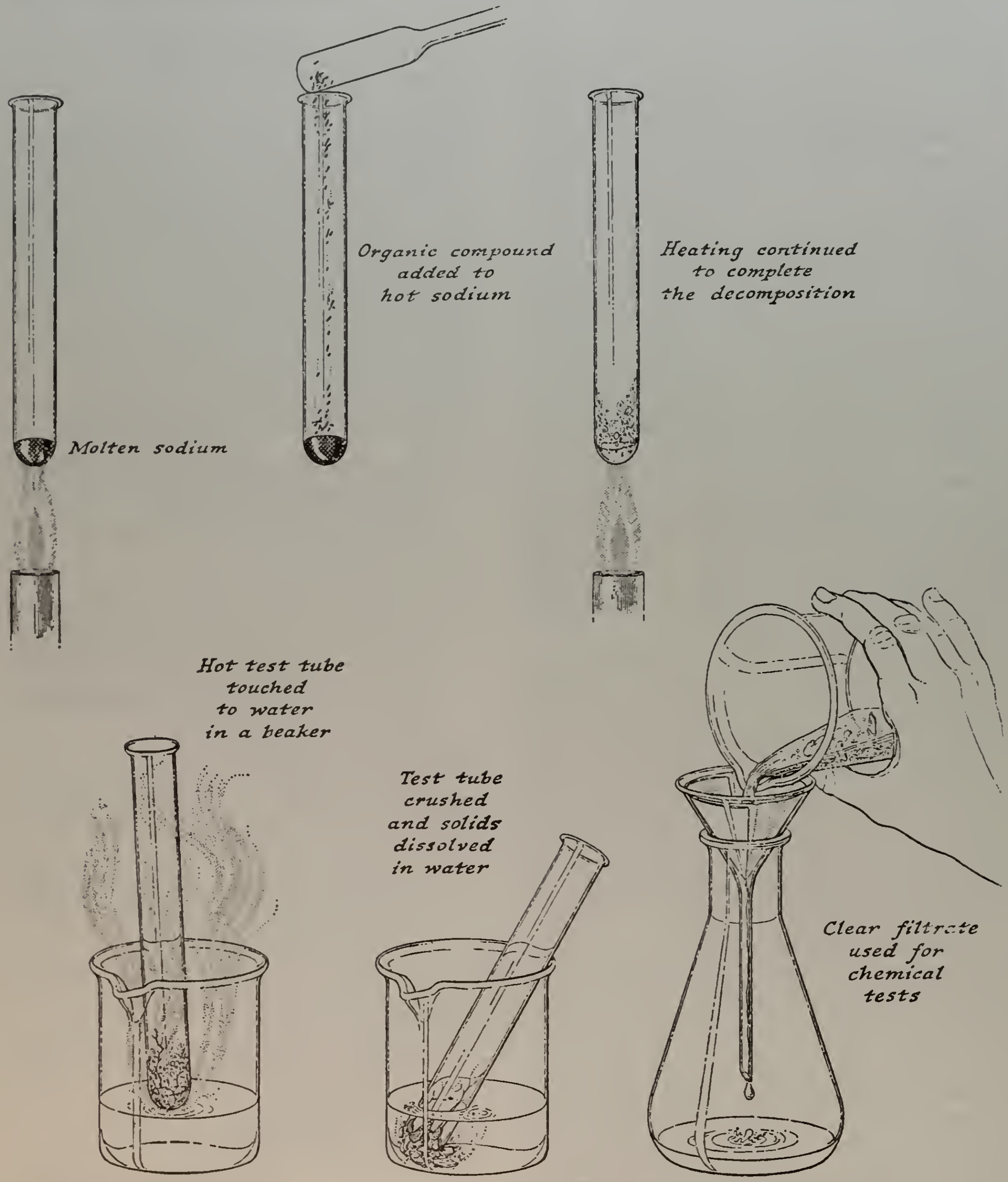
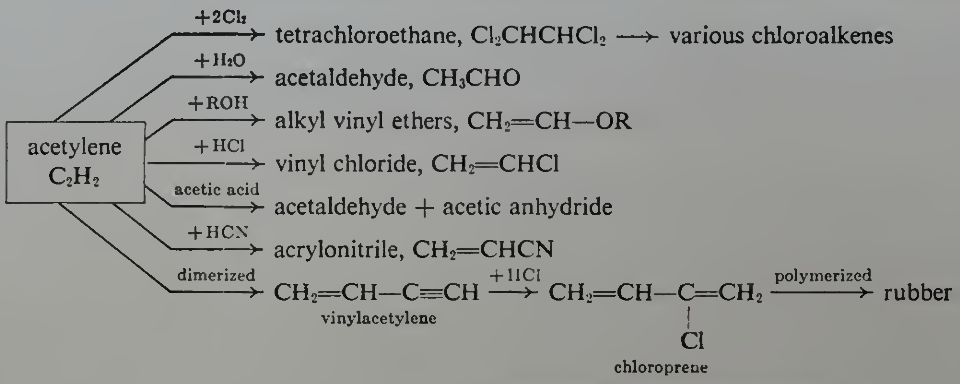


Fig. 18-3. **The sodium fusion test** *of an organic compound.*

Some suitable safety precautions if you demonstrate this are these: wear safety glasses; cut a slot halfway into wire gauze with asbestos center and place this over the beaker to prevent any expulsion of glass or liquid.



The vinyl compounds ($CH_2{=}CH{-}X$) are monomers used in synthetic plastic and fiber production.

From the foregoing examples it can be seen that a number of very important industrial organic chemicals can be produced by means of a few simple processes. These processes use raw materials (coal, coke, natural gas) that are cheap and very abundant. Thus acetylene, methanol, acetic acid, acetaldehyde, and vinyl compounds can be produced in vast quantities. The organic chemist can transform these into countless other compounds.

Petroleum-derived Chemicals

Petroleum is the remaining large source of carbon. Among the products of the petroleum industry are the simple olefins: ethylene, propylene, and the butenes. These are the raw materials for making alcohols, ketones, and esters.

It should be emphasized that economic considerations play an important part in shaping the direction of chemical development. A good deal of the effort of industrial chemists consists in finding ways to use the enormous amounts of the simple starting materials that are produced from the abundant sources of carbon.

Answers to Exercises and Problems

Ex. 18-1. Write the molecular formula for the carbon-hydrogen compound containing two carbon atoms and having empirical formula CH_2. What is its molecular weight?

Answer

$$2(CH_2) = C_2H_4$$
$$\text{mol wt} = 2(12) + 4(1) = 28$$

Ex. 18-2. Automobile antifreeze often contains a compound called ethylene glycol. Analysis of pure ethylene glycol shows that it contains only carbon, hydrogen, and oxygen. A sample of ethylene glycol weighing 15.5 mg is burned, and the weights of CO_2 and H_2O resulting are as follows.

weight of sample burned = 15.5 mg,
weight of CO_2 formed = 22.0 mg,
weight of H_2O formed = 13.5 mg.

What is the empirical formula of ethylene glycol?

Answer

(a) The number of moles of carbon atoms:

$$\text{wt } CO_2 = 22.0 \times 10^{-3}\text{ g}$$
$$\text{moles } CO_2 = \frac{22.0 \times 10^{-3}\text{ g}}{44.0\text{ g/mole}} = 0.500 \times 10^{-3}$$
$$\text{moles carbon atoms} = \text{moles } CO_2 = 0.500 \times 10^{-3}\text{ mole}$$

(b) The number of moles of hydrogen atoms:

$$\text{wt } H_2O = 13.5 \times 10^{-3}\text{ g}$$
$$\text{moles } H_2O = \frac{13.5 \times 10^{-3}\text{ g}}{18.0\text{ g/mole}} = 0.750 \times 10^{-3}$$
$$\text{moles H atoms} = 2 \times \text{moles } H_2O = 2(0.750 \times 10^{-3}) = 1.50 \times 10^{-3}\text{ mole}$$

(c) The rest of the sample is oxygen.

$$\begin{aligned}\text{wt sample} - \text{wt carbon} - \text{wt hydrogen}\\ &= \text{wt oxygen}\\ &= 15.5 \times 10^{-3}\\ &\quad - (0.500 \times 10^{-3}\text{ mole})(12.0\text{ g/mole})\\ &\quad - (1.50 \times 10^{-3}\text{ mole})(1.008\text{ g/mole})\\ &= 15.5 \times 10^{-3}\\ &\quad - 6.00 \times 10^{-3} - 1.50 \times 10^{-3}\\ &= 8.00 \times 10^{-3}\text{ g oxygen}\end{aligned}$$

$$\text{moles oxygen atoms} = \frac{8.00 \times 10^{-3}\text{ g oxygen}}{16.0\text{ g/mole}} = 0.500 \times 10^{-3}\text{ mole}$$

The mole ratio, then, can be represented by $C_{0.500}H_{1.50}O_{0.500}$, which gives the empirical formula CH_3O.

Ex. 18-3. Ethylene glycol, the example treated in Exercise 18-2, has an empirical formula of CH_3O. (Is this what you obtained?) A sample weighing 0.49 gram is vaporized completely at 200°C and at one atmosphere pressure. The volume measured under these conditions is 291 ml. This same volume, 291 ml, of oxygen gas at 200°C and one atmosphere weighs 0.240 gram. What is the molecular formula for ethylene glycol, CH_3O, $C_2H_6O_2$, $C_3H_9O_3$, $C_4H_{12}O_4$, or some higher multiple of CH_3O?

Answer

Using Avogadro's Hypothesis we can say we have the same number of molecules, and hence the same number of moles of ethylene glycol, as of oxygen in the identical volumes, 291 ml.

$$\text{moles } O_2 = \frac{0.240\text{ g}}{32.0\text{ g/mole}} = 0.00750\text{ mole } O_2$$

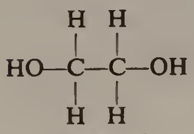
$$\text{moles ethylene glycol} = \text{moles } O_2 = 0.00750\text{ mole}$$

$$\text{molecular weight ethylene glycol} = \frac{0.49\text{ g}}{0.00750\text{ mole}} = 0.0654 \times 10^3 = 65\text{ g/mole}$$

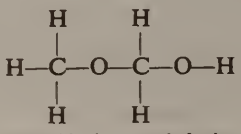
The molecular formula of ethylene glycol must be $C_2H_6O_2$, a mole of which weighs 62.1 grams. The other multiples of CH_3O give a molecular weight so far from 65 grams as to be ruled out.

Ex. 18-4. Ethylene glycol has empirical formula CH_3O and molecular formula $C_2H_6O_2$. Using the usual bonding rules (carbon is tetravalent; oxygen is divalent; hydrogen is monovalent), draw some of the structural formulas possible for this compound.

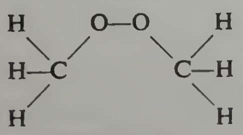
Answer



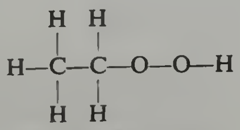
1,2-ethanediol



methyl hydroxymethyl ether

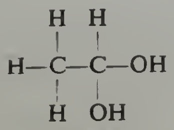


dimethyl peroxide



$$\begin{array}{ccccccccccc} & & H & & H & & & & & & \\ & & | & & | & & & & & & \\ H & - & C & - & C & - & O & - & O & - & H \\ & & | & & | & & & & & & \\ & & H & & H & & & & & & \end{array}$$

ethyl hydrogen peroxide



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & OH & & \end{array}$$

1,1-ethanediol

The names are given for your information. These compounds are known, but ethylene glycol consists only of the 1,2-diol.

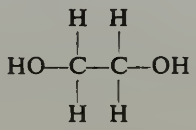
Ex. 18-5. Decide which of your structures in Exercise 18-4 best fits the following list of properties observed for pure ethylene glycol.

(a) It is a viscous (syrupy) liquid boiling at 197°C.
(b) It is miscible with water, that is, it dissolves, forming solutions, in all proportions.
(c) It is miscible with ethanol.
(d) It reacts with sodium metal, producing hydrogen gas.
(e) A 6.2 gram sample of ethylene glycol reacts with an excess of sodium metal to produce 2.4 liters of hydrogen gas at one atmosphere pressure and 25°C.

Answer

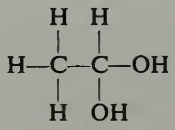
The purpose of the exercise is to show how proof of structure depends upon finding many self-consistent properties.

(a) These properties are consistent with the presence of hydrogen bonding. This would be exhibited most strongly by a structure that has two OH groups; less so by a structure that has one OH group, and not at all by the methyl peroxide.
(b) Again, this property is consistent with the presence of —OH and the consequent hydrogen bonding.
(c) The presence of —OH groups is consistent with this.
(d) The alcohol-like structure fits the evolution of H_2 when treated with Na.
(e) 6.2 grams of ethylene glycol is 0.1 mole. Since one mole of gas occupies 24.5 liters at 25°C and 1 atmosphere, one can assume the 2.4 liters at 25°C would be about 0.1 mole. Therefore one mole of ethylene glycol gives two moles of hydrogen atoms. This information, like that in (a), suggests the structure containing two OH groups, and not the structures containing a single OH (or OOH) group. All of the above observations are consistent with the structures



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ HO & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

and

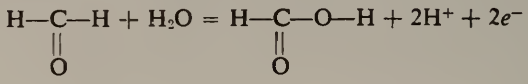


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & OH & & \end{array}$$

The 1,1-ethanediol is not stable; it decomposes to give acetaldehyde and water. The student will not know the reaction, but if you tell him that substances of this type are unstable he should reason that it cannot be the unknown test substance, which is stable enough to have a moderately high boiling point. The 1,2-diol structure can be deduced from the method of making ethylene glycol, and can be verified by other tests not mentioned (infrared, X-ray diffraction).

Ex. 18-6. Balance the half-reaction for the conversion of formaldehyde, HCHO, to formic acid, HCOOH.

Answer

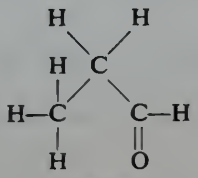


$$H-\underset{\underset{O}{\|}}{C}-H + H_2O = H-\underset{\underset{O}{\|}}{C}-O-H + 2H^+ + 2e^-$$

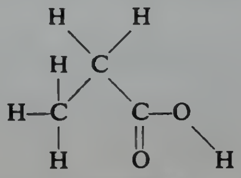
Ex. 18-7. There is a compound called propanol with structural formula $CH_3CH_2CH_2OH$. If it is oxidized carefully, an aldehyde called propionaldehyde is obtained. Vigorous oxidation gives an acid called propionic acid. Draw structural formulas like those shown in Figures 18-6 and 18-7 for propionaldehyde and propionic acid.

Answer

Although there is nothing in Figures 18-6 or 18-7 to suggest a zigzag chain, the single bonds formed by carbon are tetrahedral. Recall Chapter 16, where the bonding of carbon was discussed;



propionaldehyde



propionic acid

Ex. 18-8. Balance the half-reaction involved in the oxidation of ethanol to acetic acid. Compare the number of electrons released per mole of ethanol with the number per mole of methanol in the equivalent reaction (*13c*). How many electrons would be released per mole of propanol in the oxidation to propionic acid?

Answer

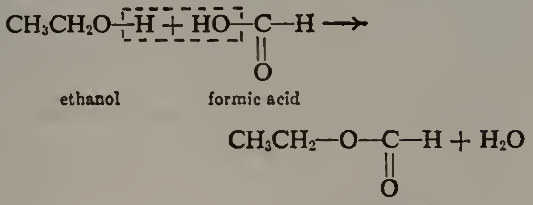
$$CH_3CH_2OH + H_2O = CH_3COOH + 4H^+ + 4e^-$$

In equation (*13c*), four electrons are released per mole of methanol. The same number of electrons would be released were propanol oxidized to propionic acid. Four electrons will be released when any alcohol is oxidized to the corresponding acid. The change in functional group is the same; the skeletal group makes no difference.

Ex. 18-9. Write equations for the reaction of (a) ethanol and formic acid; (b) propanol and propionic acid; (c) methanol and formic acid. Name the esters produced.

Answer

(a)

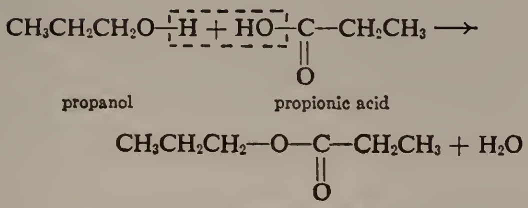


$$CH_3CH_2O{-}H + HO{-}\underset{\underset{O}{\|}}{C}{-}H \longrightarrow CH_3CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}H + H_2O$$

ethanol formic acid

ethyl formate

(b)

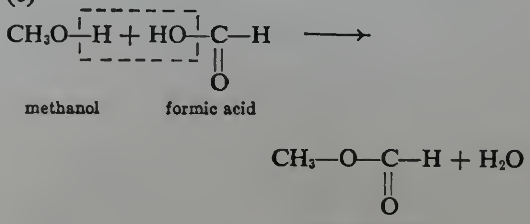


$$CH_3CH_2CH_2O{-}H + HO{-}\underset{\underset{O}{\|}}{C}{-}CH_2CH_3 \longrightarrow CH_3CH_2CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_2CH_3 + H_2O$$

propanol propionic acid

propyl propionate

(c)



$$CH_3O{-}H + HO{-}\underset{\underset{O}{\|}}{C}{-}H \longrightarrow CH_3{-}O{-}\underset{\underset{O}{\|}}{C}{-}H + H_2O$$

methanol formic acid

methyl formate

Ex. 18-10. Write the equilibrium expression relating the concentrations of reactants and products in reaction (*26*). Notice that the concentration of water must be included because it is not necessarily large enough to be considered constant.

Answer

$$K = \frac{[CH_3OH][CH_3COOH]}{[CH_3COOCH_3][H_2O]}$$

Ex. 18-11. A strong acid, such as hydrochloric acid or sulfuric acid, will catalyze reaction (*25*). Explain why this implies that these acids will catalyze reaction (*26*) as well. (Consult Section 8-2.3.)

Answer

Equation (*26*) is the reverse of equation (*25*). A catalyst increases the rate of both the forward and the reverse reactions.

Ex. 18-12. What are the empirical formulas of the three compounds shown in Figure 18-11? The molecular formulas? Which are structural isomers?

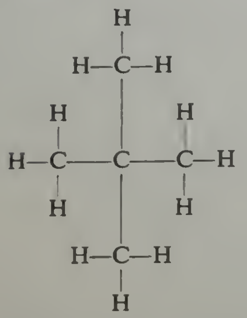
Answer

	Empirical Formula	Molecular Formula
n-Pentane	C_5H_{12}	C_5H_{12}
Isopentane	C_5H_{12}	C_5H_{12}
Cyclopentane	CH_2	C_5H_{10}

Only *n*-pentane and isopentane are structural isomers.

Ex. 18-13. There is one more alkane with molecular formula C_5H_{12}, called neopentane. Draw its structural formula.

Answer

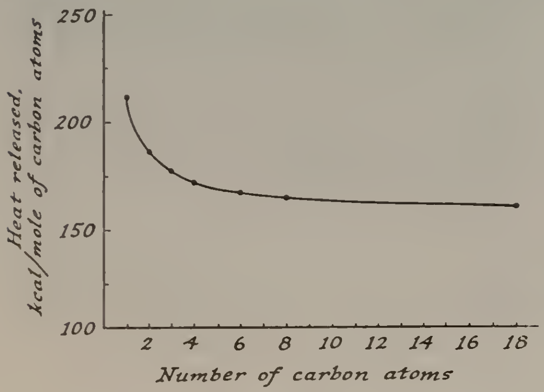


C_5H_{12}
neopentane or
2,2-dimethyl propane

A picture of neopentane is included in Textbook Figure 17-7.

Ex. 18-14. Using the data given in the last column of Table 18-III, plot the heat released per carbon atom against the number of carbon atoms for the normal alkanes. Consider the significance of this plot in terms of the molecular structures of these compounds.

Answer



The nearly flat portion of the curve suggests that a mole of CH_2 groups gives a certain amount of heat (~160 kcal) when burned. This is especially true if the number of carbons is greater than 5. The upswing at the left shows that the situation is different in short-chain compounds. One explanation is that a $—CH_3$ group has a different (higher) heat of combustion than a $>CH_2$ group. In the long-chain compounds the effect of the two terminal $—CH_3$ groups is "lost" by averaging over all the $>CH_2$ groups. In a smaller molecule there are not enough $>CH_2$ groups to allow such an averaging, and ΔH per atom rises toward the value for $—CH_3$.

Ex. 18-15. Take the letters *A*, *B*, *C*, and see how many different three-unit combinations you can make; for example, *ABC*, *BAC*, *AAC*, *CBC*, etc. This will convince you that a chain made of hundreds of groups with up to *thirty* different kinds of units in each group can have an almost unlimited number of combinations.

Answer

There are 27 combinations of the three letters.

AAA		*ABC*	*CBA*	*BBC*	*CBB*
AAB	*BAA*	*ACB*	*BCA*	*BCB*	
AAC	*CAA*	*ACC*	*CCA*	*BCC*	*CCB*
ABA		*BAB*		*CAC*	
ACA		*BAC*	*CAB*	*CBC*	
ABB	*BBA*	*BBB*		*CCC*	

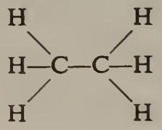
Some students are interested in how large the number of combinations will be as n (the number of different units) goes up. The formula is n^n, since there are n choices to be made and n ways each choice can be made. Those combinations written side-by-side differ only if there are additional units attached to them. There are 18 different three-unit combinations.

Pr. 1. What information is revealed by the empirical formula? The molecular formula? The structural formula? Demonstrate, using ethane, C_2H_6.

Answer

The empirical formula gives the *relative* number of atoms of each kind. The molecular formula gives the total number and kind of atoms in one molecule. The structural formula shows the total number of atoms, their kind, and their bond connections:

empirical CH_3
molecular C_2H_6
structural



Pr. 2. Write the balanced equation for the complete burning of methane.

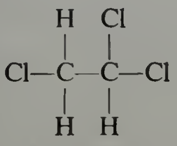
Answer

When organic compounds are burned in air, or oxygen, the carbon is converted to CO_2, the hydrogen to water. Methane will then react as follows:

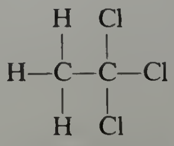
$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$

Pr. 3. Draw the structural formulas for all the $C_2H_3Cl_3$ compounds.

Answer

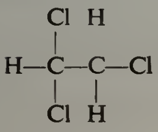
(1) 
$\mathrm{Cl-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-Cl}$

1,1,2-trichloroethane

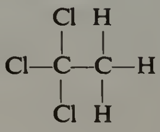
(2) 
$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-Cl}$

1,1,1-trichloroethane

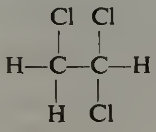
There are only two. The following structures, which may appear to be different, are simply different ways of writing the above two:


$\mathrm{H-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-Cl}$

(a)


$\mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-H}$

(b)


$\mathrm{H-\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-H}$

(c)

There are two ways to bring about an apparent change in the structure. One is to rotate the complete molecule; structures (b) and (2) are related in this fashion. The other way is to rotate part of the molecule (along a C—C bond usually) relative to the other part. Structures (a) and (c) are related to (1) by this operation. The structural formulas we draw are really projections of a three-dimensional molecule. Use ball and stick models to illustrate these rotations. Remind the student that kinetic motion will cause the molecules to tumble and spin so that different orientations of a molecule in space do not constitute different isomers. The molecule has the same properties no matter how it is turned.

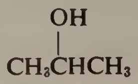
Pr. 4. Draw the structures of two isomeric compounds corresponding to the empirical formula C_3H_8O.

Answer

There are two propanols,

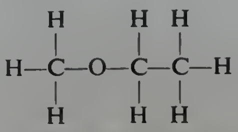
$CH_3CH_2CH_2OH$

1-propanol


$CH_3\overset{OH}{C}HCH_3$

2-propanol

and the arrangement

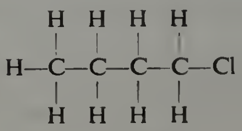

$\mathrm{H-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$

ethyl methyl ether

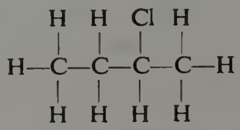
also represents a compound isomeric with these.

Pr. 5. Draw the structural formulas of the isomers of butyl chloride.

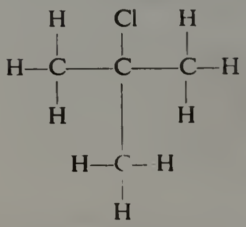
Answer


$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-Cl}$

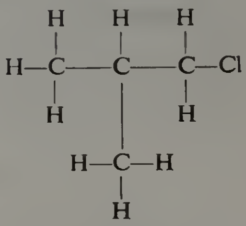
1-chlorobutane


$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$

2-chlorobutane


$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H-\underset{H}{C}-H}{C}}-\overset{H}{\underset{H}{C}}-H}$

2-chloro-2-methylpropane


$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H-\underset{H}{C}-H}{C}}-\overset{H}{\underset{H}{C}}-Cl}$

1-chloro-2-methylpropane

See the answer to Problem 18-3 for discussion of other formulas that only appear to be different.

Pr. 6. What angle would you expect to be formed by the C, O, H nuclei in an alcohol molecule? Explain.

Answer

The geometry of the *p* orbitals would suggest 90° (see Textbook p. 263). A bent molecule is expected. The observed angle is 109 ± 2°.

Pr. 7. When 0.601 gram of a sample having an empirical formula CH_2O was vaporized at 200°C, and one atmosphere pressure, the volume occupied was 388 ml. This same volume was occupied by 0.301 gram of ethane under the same conditions. What is the molecular formula of CH_2O?

One mole of the sample when reacted with zinc metal, liberated (rather slowly) $\frac{1}{2}$ mole of hydrogen gas. Write the structural formula.

Answer: The molecular formula is $C_2H_4O_2$.

Answer

Equal volumes at identical conditions contain the same number of moles. Thus,

$$0.301 \text{ g ethane} \times 30.1 \text{ g/mole} = 0.0100 \text{ mole ethane}$$

Thus 0.601 gram of unknown equals 0.0100 mole; therefore 60.1 grams are 1.00 mole. The formula must be some multiple of CH_2O. The corresponding weights of one mole are

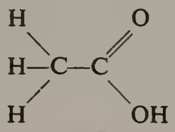
CH_2O	30 g
$C_2H_4O_2$	60 g
$C_3H_6O_3$	90 g

Thus the molecular formula is $C_2H_4O_2$.

The structural formula follows from these facts:

(1) The reaction with Zn to give hydrogen indicates an acid.

(2) One mole of unknown gives ½ mole of H_2, indicating that there is only one active hydrogen atom. The formula that best fits these data is



acetic acid

Pr. 8. A 100 mg sample of a compound containing only C, H, and O was found by analysis to give 149 mg CO_2 and 45.5 mg H_2O when burned completely. Calculate the empirical formula.

Answer

$$149 \text{ mg } CO_2 \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1}{44.0 \text{ g/mole}} = 3.40 \times 10^{-3} \text{ mole } CO_2$$

$$45.4 \text{ mg } H_2O \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1}{18.0 \text{ g/mole}} = 2.52 \times 10^{-3} \text{ mole } H_2O$$

Each mole of CO_2 contains one mole of C atoms, and each mole of H_2O contains two moles of H atoms.

$$3.40 \times 10^{-3} \text{ mole } CO_2 \times \frac{1 \text{ mole C}}{\text{mole } CO_2} \times \frac{12 \text{ g C}}{\text{mole C}} = 40.8 \times 10^{-3} \text{ g C}$$

$$2.52 \times 10^{-3} \text{ mole } H_2O \times \frac{2 \text{ mole H}}{\text{mole } H_2O} \times \frac{1 \text{ g H}}{\text{mole H}} = 5.04 \times 10^{-3} \text{ g H}$$

Oxygen must make up the rest of the 100 mg sample.

$$100 - 40.8 - 5.04 = 54.2 \text{ mg O}$$

$$54.2 \text{ mg O} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1}{16 \text{ g O/mole}} = 3.39 \times 10^{-3} \text{ mole O}$$

The moles of each kind of atom are:

	Actual	Relative	
C	3.40×10^{-3}	1 or	2
H	5.04×10^{-3}	1.48	3
O	3.39×10^{-3}	1	2

The empirical formula is $C_2H_3O_2$.

Pr. 9. How much ethanol can be made from 50 grams of ethyl bromide? What assumptions do you make in this calculation?

Answer

The maximum possible yield of ethanol that can be obtained is calculated on the assumption that the hydrolysis

$$CH_3CH_2Br + OH^- = CH_3CH_2OH + Br^-$$

can be carried to completion and that all of the ethyl group in the starting material is recovered in the ethanol. That is, *one mole* of ethyl bromide gives *one mole* of ethanol. In practice, some CH_3CH_2Br is always found to exist in the equilibrium mixture. The molecular weights are: ethyl bromide, 108.9; ethanol, 46.0.

$$50 \text{ g ethyl bromide} \times \frac{1}{108.9 \text{ g/mole}} = 0.46 \text{ mole}$$

$$0.46 \text{ mole ethyl bromide} \times \frac{1 \text{ mole ethanol}}{1 \text{ mole ethyl bromide}} = 0.46 \text{ mole ethanol}$$

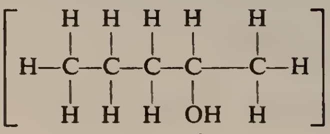
$$0.46 \text{ mole ethanol} \times \frac{46.0 \text{ g}}{\text{mole}} = 21 \text{ g ethanol}$$

or

20 g ethanol

Pr. 10. Write the balanced equation for the production of pentanone from pentanol, using dichromate ion as the oxidizing agent.

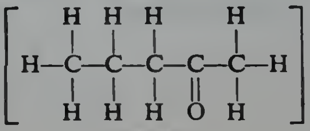
Answer



$$3\left[\begin{array}{cccccc} & H & H & H & H & H \\ & | & | & | & | & | \\ H- & C- & C- & C- & C- & C-H \\ & | & | & | & | & | \\ & H & H & H & OH & H \end{array}\right] + Cr_2O_7^{-2}(aq)$$

2-pentanol

$+ 8H^+(aq) \longrightarrow 3$

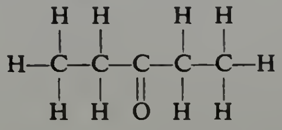


$$3\left[\begin{array}{c} \text{H}\;\;\text{H}\;\;\text{H}\;\;\;\;\;\text{H} \\ \text{H—C—C—C—C—C—H} \\ \text{H}\;\;\text{H}\;\;\text{H}\;\;\text{O}\;\;\text{H} \end{array}\right]$$

2-pentanone

$+ 2Cr^{+3}(aq) + 7H_2O$

The same equation applies if 3-pentanol is used, giving 3-pentanone,

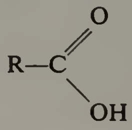


$$\begin{array}{c} \text{H}\;\;\text{H}\;\;\;\;\;\text{H}\;\;\text{H} \\ \text{H—C—C—C—C—C—H} \\ \text{H}\;\;\text{H}\;\;\text{O}\;\;\text{H}\;\;\text{H} \end{array}$$

Pr. 11. One mole of an organic compound is found to react with ½ mole of oxygen to produce an acid. To what class of compounds does this starting material belong?

Answer

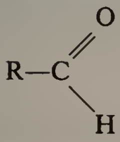
In terms of the general formula, the acid can be represented as



Since the reaction is stoichiometrically defined in the question as

$$\text{unknown} + \tfrac{1}{2}O_2 \longrightarrow RCOOH$$

the starting material must be the aldehyde,



Pr. 12. Using the information given in Table 7-II, determine the reaction heat per mole of $C_2H_6(g)$ for the complete combustion of ethane.

Answer

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) = 2CO_2(g) + 3H_2O(g)$$

		ΔH (kcal)
$C_2H_6(g)$	$= 2C(s) + 3H_2(g)$	20.2
$2C(s) + 2O_2(g)$	$= 2CO_2(g)$	2(−94.0)
$3H_2(g) + \frac{3}{2}O_2(g)$	$= 3H_2O(g)$	3(−57.8)
$C_2H_6(g) + 3\frac{1}{2}O_2(g)$	$= 2CO_2(g) + 3H_2O(g)$	$\Delta H = -341.2$ kcal/mole $C_2H_6(g)$

Pr. 13. An aqueous solution containing 0.10 mole/liter of chloroacetic acid, ClH_2CCOOH, is tested with indicators, and the concentration of $H^+(aq)$ is found to be 1.2×10^{-2} M. Calculate the value of K_A (if necessary, refer back to Section 11-3.2). Compare this value with K_A for acetic acid—the change is caused by the substitution of a halogen atom near a carboxylic acid group.

Answer

$$ClH_2CCOOH \rightleftharpoons ClH_2CCOO^- + H^+$$

$$K_A = \frac{[H^+][ClH_2CCOO^-]}{[ClH_2CCOOH]}$$

In an aqueous solution of pure acid, $[H^+] = [ClH_2CCOO^-] = 1.2 \times 10^{-2}$.

$$K_A = \frac{(1.2 \times 10^{-2})^2}{(0.10)} = 1.4 \times 10^{-3}$$

The acetic acid dissociation constant is $K = 1.8 \times 10^{-5}$. The increased acid strength of chloroacetic acid is considered to result from chlorine, with its high ionization energy, pulling electrons from the carboxyl group, weakening the O—H bond.

Pr. 14. Give simple structural formulas of

(a) an alcohol,
(b) an aldehyde, and
(c) an acid,
each derived from methane; from ethane; from butane; from octane.

Answer

Alcohol	Aldehyde	Acid
CH_3OH	$HCHO$	$HCOOH$
C_2H_5OH	CH_3CHO	CH_3COOH
C_4H_9OH	C_3H_7CHO	C_3H_7COOH
$C_8H_{17}OH$	$C_7H_{15}CHO$	$C_7H_{15}COOH$

Pr. 15. Write the equations for the preparation of methylamine from methyl iodide.

Answer

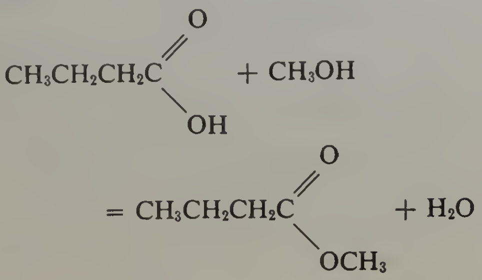
$NH_3(aq) + CH_3I = CH_3NH_3^+(aq) + I^-(aq)$
$NH_3(aq) + CH_3NH_3^+(aq)$
$= CH_3NH_2 + NH_4^+(aq)$

as given on Textbook p. 337, equations 22 and 23.

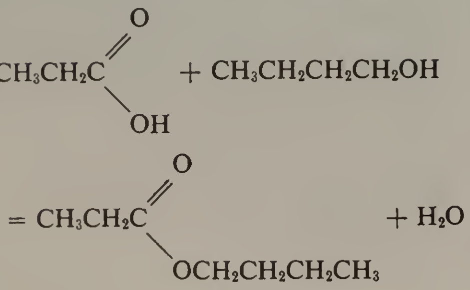
Pr. 16. Write equations to show the formation of the esters, methyl butyrate and butyl propionate.

Answer

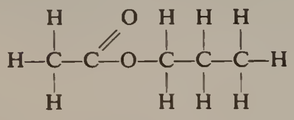
(a)



(b)



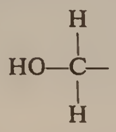
Pr. 17. Given the structural formula



for an ester, write the formula of the acid and the alcohol from which it might be made.

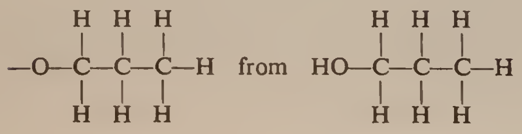
Answer

An alcohol has a group of the type



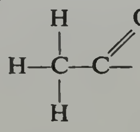
$$\mathrm{HO{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}}$$

hence that part of the ester derived from the alcohol is the propyl group,

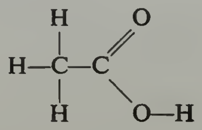


$$\mathrm{{-}O{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}H} \quad \text{from} \quad \mathrm{HO{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}H}$$

The remainder,



came from acetic acid,

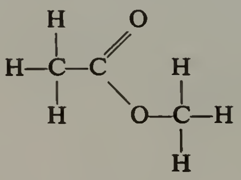


Pr. 18. How much acetamide can be made from 3.1 grams of methyl acetate? See equation (27), p. 338. Assume the ester is completely converted.

Answer: 2.5 grams acetamide.

Answer

The molecular weight of methyl acetate,



is $3(12) + 6(1) + 2(16) = 36 + 6 + 32 = 74$ g/mole.

$$3.1 \text{ g methyl acetate} \times \frac{1}{74 \text{ g/mole}} = 0.042 \text{ mole}$$

$$(0.042 \text{ mole methyl acetate})\left(\frac{1 \text{ mole amide}}{1 \text{ mole acetate}}\right)$$
$$= 0.042 \text{ mole acetamide}$$

$$0.042 \text{ mole amide} \times \frac{59 \text{ g}}{\text{mole}}$$
$$= 2.48$$

or 2.5 g acetamide

Pr. 19. An ester is formed by the reaction between an acid, RCOOH, and an alcohol, R′OH, to form an ester RCOOR′ and water. The reaction is carried out in an inert solvent.

(a) Write the equilibrium relation among the concentrations, including the concentration of the product water.

(b) Calculate the equilibrium concentration of the ester if $K = 10$ and the concentrations *at equilibrium* of the other constituents are:

$[RCOOH] = 0.1\ M;$
$[R'OH] = 0.1\ M;$
$[H_2O] = 1.0\ M.$

(c) Repeat the calculation of Part (b) if the equilibrium concentrations are:

$$[RCOOH] = 0.3\ M;$$
$$[R'OH] = 0.3\ M;$$
$$[H_2O] = 1.0\ M.$$

Answer

(a) $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$

$$K = \frac{[RCOOR'][H_2O]}{[RCOOH][R'OH]}$$

(b) $$10 = \frac{[RCOOR'](1.0)}{(0.1)(0.1)}$$

$$[RCOOR'] = \frac{10(0.1)(0.1)}{1.0} = 0.1\ M$$

(c) $$10 = \frac{[RCOOR'](1.0)}{(0.3)(0.3)}$$

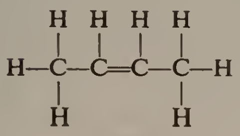
$$[RCOOR'] = \frac{10(0.3)(0.3)}{1.0} = 0.9\ M$$

Suppose we have a small amount of a valuable acid that we wish to convert into the methyl ester. If a very large excess of methanol is used, the conversion of the acid into the ester will be nearly complete. The disadvantage of using one reactant in large excess is that the percentage of *this* reactant that is converted to ester is small. But when the alcohol is, for example, the inexpensive and easily available methanol, this is not an important consideration and is far outweighed by the advantage of practically *complete* conversion of the other reagent (the acid) into ester.

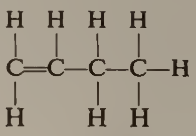
Pr. 20. Give the empirical formula, the molecular formula, and draw the structural formulas of the isomers of butene.

Answer

The empirical formula is CH_2; the molecular formula is C_4H_8.

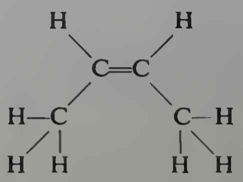


2-butene



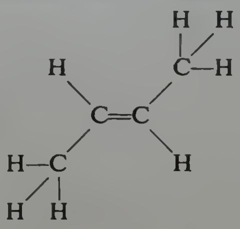
1-butene

The isomer 2-butene exists in two forms



cis-2-butene

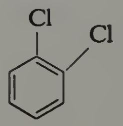
and



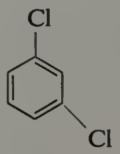
trans-2-butene

Pr. 21. There are three isomers of dichlorobenzene (empirical formula C_3H_2Cl). Draw the structural formulas of the isomers.

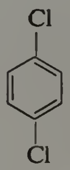
Answer



1,2-dichlorobenzene
or
*ortho*dichlorobenzene

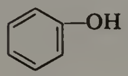


1,3-dichlorobenzene
or
*meta*dichlorobenzene



1,4-dichlorobenzene
or
*para*dichlorobenzene

Pr. 22. Consider the compound phenol.



(a) Predict the angle formed by the nuclei COH. Explain your choice in terms of the orbitals used by oxygen in its bonds.

(b) Predict qualitatively the boiling point of phenol. (The boiling point of benzene is 80°C.) Explain your answer.

(c) Write an equation for the reaction of phenol as a proton donor in water.

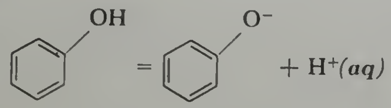
(d) In a 1.0 M aqueous solution of phenol, $[H^+] = 1.1 \times 10^{-5}$. Calculate K.

Answer

(a) Since the oxygen uses p orbitals in its bonding, the two bonds should form an angle near 90°. This angle should be about 105°, based on the value for water and alcohols. The functional group attached to —OH has little effect on the bond angle.

(b) The boiling point of phenol should be greater than that of benzene because it can form hydrogen bonds, whereas benzene cannot. The observed value is 182°C.

(c)



or

$C_6H_5OH(aq) = C_6H_5O^-(aq) + H^+(aq)$

(d)

$$K = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]}$$

$$[H^+] = [C_6H_5O^-] = 1.1 \times 10^{-5}\ M$$

$$[C_6H_5OH] = 1.0 - (1.1 \times 10^{-5}) \approx 1.0\ M$$

$$K = \frac{(1.1 \times 10^{-5})^2}{1.0} = 1.2 \times 10^{-10}$$

General Comments on Remaining Chapters

Beyond Chapter 18 the Textbook material and laboratory work have a new character. New principles are rarely encountered; instead the usefulness of those already studied is demonstrated in several new areas of chemistry. The Textbook and experiments are a deliberate review of basic concepts through use.

Because of the change described, there is less need to adhere to a particular order of Textbook and lab topics. You should pick them to suit your class and the time available, taking full advantage of the chance to review. Experiments 33–44 do not have the close connection to a given section of the Textbook that has characterized the first 32 experiments. The arrangement below shows some alternate possibilities.

Expt.	Placed With	Also Covers
30, 31	Halogens (Chapter 19)	oxidation-reduction (Chapter 12)
32	Elements of row three (Chapter 20)	acids and bases (Chapter 11)
33–36	Qualitative analysis	solubility (Chapter 10)
36	Qualitative analysis	acids and bases (Chapter 11)
37	Transition elements (Chapter 22)	equilibrium (Chapter 9)
38, 40, 41	Transition elements (Chapter 22)	oxidation-reduction (Chapter 12)

CHAPTER

19

THE HALOGENS

Intent and Approach

This chapter is the first of five dealing with special groups of elements within the periodic table. It focuses on the halogens, column VII, and conveys the similarities and systematic differences displayed by these elements. In directing the study of this chapter, encourage students to concentrate on these similarities and differences. Also encourage them to examine the chemical behavior of the group with these regularities and differences in mind.

Chapter 19 also represents a shift, which continues for the remainder of the course, from an emphasis on principles to an emphasis on the descriptive side of chemistry. Bring the principles in as much as possible, and relate them to the description of the halogens.

Outline

1. In the first main section of the chapter, we focus on the properties of the halogens, calling specific attention to their toxic character. Electron configuration (19-1.1), as well as covalent radii and ionic radii (19-1.2) are given detailed consideration.
2. Van der Waals forces are related to boiling points and melting points (19-1.2).
3. After some remarks on their preparation (19-2.1), the principal reaction exhibited by halogens—oxidation-reduction—is discussed (19-2.2).
4. The reduction of halogens is related to E° (19-2.2). One portion of this section (reduced type) is devoted to a comparison of the energy required for electron removal, dehydration, molecule formation and condensation of the four halogens.
5. Iodimetry—the use of the I^-–I_2 half-reaction for both oxidation and reduction—is discussed (19-2.3).
6. The positive oxidation states of the halogens, oxyacids, and oxyanions are briefly discussed (19-2.4).
7. Self-oxidation-reduction is discussed and illustrated via the formation of hypochlorite and chlorate ions (19-2.5).
8. The chapter concludes with a section on the exceptional qualities of fluorine (19-2.6).

New Concepts

This is a descriptive chapter whose primary intent is not to introduce new concepts, but to reinforce and apply some already studied. Some new concepts are introduced, however.

1. Self-oxidation-reduction.
2. The increase in acid strength with increase in oxidation number.
3. Oxidizing agents and reducing agents.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems* EASY	MEDIUM	HARD	*Topic*
Reviews 6-13/6-19							
S 19-1 (pp. 352–356)	1	Discussion	1, 2	2, 3	1, 4	5, 6	Electron configuration
Expt. 30	2	Expt. 30					Electrolysis of KI
S 19-2/19-2.3 (pp. 356–358)	3	Discussion Film: BROMINE —ELEMENT FROM THE SEA	3–5	**10***	7, 9, 11	8, **12**, 13	Reduction of Halogens
S 19-2.4/19-2.6 (pp. 358–362)	4	Discussion	6	14	15–17, 19, 20	**18**	Positive oxidation states, Fluorine
Expt. 31	5	Expt. 31					Chemistry of Iodine
	6	Review					

* Boldface indicates problems whose answers are given in the Textbook.

Familiar concepts which should be applied are:

1. Structure of matter (electron configuration and molecular shape).
2. Oxidation-reduction.
3. Net equations for reactions.
4. Equilibrium.
5. Energy in reactions.
6. Acids and bases.
7. Species in aqueous solutions.

Development

INTRODUCTION

Keep in mind that the halogens are not unknown to the student. A section of Chapter 6 (pp. 96–99, Textbook) is specifically devoted to them. Textbook Table 6-VI enumerates many of the empirical properties, and these are also discussed in the section. A review of that section along with the study of Sec. 19-1 (pp. 352–356, Textbook) is a good way to initiate this chapter.

PROPERTIES OF THE HALOGENS (19-1)

One striking thing about the halogens is that they are all colored. This is a good time to point out that most nonmetallic elements (again, the rare gases are exceptions) are colored. Note the following portion of the periodic table.

					He colorless
B black, brown	C black	N colorless	O (blue)*	F pale yellow-green	Ne colorless
	Si grey	P red, white, plus others	S yellow	Cl yellow-green	Ar colorless
			Se red, grey	Br red-brown	Kr colorless
				I violet	Xe colorless

* Ozone is deep-blue—almost black as a pure liquid.

The colors probably result from the covalent bonding present and the position of the electron energy levels. The *Background Discussion* contains more information.

Electron Configurations of the Halogens (19-1.1)

This section gives nothing beyond Chapter 15 but applies that material directly to halogens.

The Sizes of Halogen Atoms and Ions (19-1.2)

This section mentions how atomic and ionic radii are obtained; how these radii change in going down the column; and how they are related to melting point, boiling point, bond energy, and dissociation constants (Table 19-II in the Textbook). Use Problems 3, 4, and 5 to emphasize the regularity of increase in atomic and ionic size, and also the regularity of melting point and boiling point increases. Be sure to make the distinction that covalent radii show the size "within a molecule"—that is, for atoms bonded together. Van der Waals radii show the distance of approach "between molecules"—

that is, how close two nonbonded atoms can come.

Expt. 30, THE ELECTROLYSIS OF AQUEOUS POTASSIUM IODIDE,
fits here. See p. 641 for guide.

HALOGEN REACTIONS AND COMPOUNDS (19-2)

Preparation of the Halogens (19-2.1)

The object of this section is to show the use of chemical principles in the production of some elements. The exercise that comes in this section (Ex. 19-4) helps show how calculations are used in deciding whether a proposed method of preparation can work. The technological problems involved in making a process feasible may be considerable. Chemical engineers usually devote their efforts to this activity.

Reduction of the Halogens (19-2.2)
(reduced type, in part)

You can add some vitality to these sections by demonstrating the statements on Textbook p. 357. The best practice is to have the students work out the answers ahead of time, using $E°$ values. Problem 9 is specifically for such use. With this background, consult H. N. Alyea and F. B. Dutton, *Tested Demonstrations in Chemistry*, Div. Chem. Education, ACS, Easton, Pennsylvania (p. 44) for details. Make the demonstration a fast one, showing $Cl_2 + Br^-$ and $Br_2 + I^-$.

The series of steps postulated in equations (*8*) to (*11*) are an example of a Born-Haber cycle. Such cycles are useful for breaking a process into imagined component parts. It is also used to calculate the energy required in one particular step if that for all others is known. This is the usual way to get values for equation (*9*), because electron affinity measurements are difficult to make. The *trend* of values is probably the important aspect to look at. The exact values are not crucial.

Film, BROMINE—ELEMENT FROM THE SEA
fits here. See p. 649 for summary.

Iodimetry (19-2.3)

The versatility of iodimetry can be realized from the large number and variety of substances for which it is used. Some of these are simple ions (Fe^{+3}, Cu^{+2}, Ce^{+4}); others are more complex ($Cr_2O_7^{-2}$, MnO_4^-, BrO_3^-); and still others are molecules (Cl_2, O_3, H_2O_2).

You will observe that we have purposely not told the student about the thiosulfate part of iodimetry. It is used for practical reasons, but the resulting procedure is too complicated for this course. In theory the iodine couple with starch could be used as given in the Textbook.

Positive Oxidation States of the Halogens:
The Oxyacids (19-2.4)

This section offers a chance to employ the student's background on equilibrium, acidity, oxidation number, bonding, and structure. Show him how the things he studied as separate parts of chemistry come together when the chemistry of a group of elements is studied.

The equilibrium

$$Cl_2 + H_2O = HOCl + HCl$$

is common in swimming pools. The equilibrium constant is about 3×10^{-4}. The oxyacids have these values of K_A:

HOCl	3.6×10^{-8}
HOClO	—
$HOClO_2$	~3
$HOClO_3$	large

The more or less tetrahedral structure of the halogen oxyacids fits with the shape found for other sp^3 bonded compounds. The electrons needed to form the various bonds all find appropriate vacant orbitals.

You can make a point about oxidation numbers here. Although we attach little importance to the particular values chemists have chosen to use, the fact that an element *changes* oxidation number *is* important. It means there is a different arrangement of electrons around the atom and, thus, that different properties and behavior are to be expected. The Textbook equations (*15*)–(*17*) on p. 360 form the heart of Expt. 31, which is conveniently discussed here.

Self-oxidation-reduction: Disproportionation (19-2.5)

This short section illustrates a particular type of reaction. The halogens are not unique in displaying this type of reaction. Consider

$$2SnO = Sn + SnO_2$$
$$6B_2H_5Cl = 5B_2H_6 + 2BCl_3$$

Other examples could be cited, especially among the elements in the middle part of the periodic table.

Special Remarks on Fluorine (19-2.6)

This section is devoted to the uniqueness of fluorine. Hydrogen bonding has been encountered before, in relation to water and ethyl alcohol (see p. 329). Point out that F^- is a very strong base; its hydrogen bonding and polarity are associated properties. Use the fact that HF is mentioned as a polar solvent to remark that liquid ammonia and acetic acid are also polar solvents in which an acid–base system of proton donation and acceptance can exist. Relate this to any discussion you might have had on this point in the acid–base chapter (see p. 356 for background discussion).

Expt. 31, SOME CHEMISTRY OF IODINE, fits here. See p. 644 for guide.

EXPERIMENT 30 THE ELECTROLYSIS OF AQUEOUS POTASSIUM IODIDE

PURPOSE. To give the student first-hand experience with one of the halogens as illustrative of the group. To review oxidation-reduction reactions and solubility differences.

PRELAB DISCUSSION. Remind the student of his prior observation of electrolysis of water (Chapter 3) and of his experience in the electrolytic deposition of copper and silver (Expt. 25).

TIMING. Assign this experiment anytime during Chapter 19, but remember that the questions require knowledge from Sec. 19-2.4.

EQUIPMENT NEEDED (PER GROUP). The experiment should probably be performed by groups, preferably of not more than four, although you might give it as a demonstration.

U-tube (experiment suggests 150 mm, but any length is satisfactory; 80 mm works well)
D.C. source (12 volts) (see lab hint 1)
pair of carbon electrodes
pair of connecting wires with end clips
ring stand and clamp
pipet or medicine dropper
2–3 ml 0.1 *M* ferric chloride in dropper bottle ($2.7\ g\ FeCl_3 \cdot 6H_2O/100\ ml$)
indicator solution (few drops) or paper (see lab hint 2)
25–100 ml 0.5 *M* potassium iodide solution; choose amount to fill U-tube (83 g KI/liter)
1–2 ml carbon tetrachloride

TIME REQUIRED. The student will need one 45–50 minute laboratory period. Convenient stopping place: anywhere if apparatus may be left set up.

PRECAUTIONS. Take precautions appropriate to your D.C. source. Iodine may stain fingers, but may be removed if sodium thiosulfate is used promptly. Use a solution, or moisten a few crystals held in the palm of the hand, and rub the stained finger in this.

LABORATORY HINTS

1. Your physics department may be able to supply D.C. sources. Heathkit "battery eliminators" are fine. Selenium rectifiers are often available at educational surplus stores; a combination of a suitable rectifier and a variable resistor makes a good source.
2. Universal indicator solution may be made as follows: Prepare

   0.3 g Methyl Red/100 ml ethanol
   0.6 g Bromthymol Blue/100 ml ethanol

   For 200 ml of universal indicator, mix and shake well

   10 ml Methyl Orange solution (from Expt. 18) (0.1 g Methyl Orange/100 ml water)
   10 ml Methyl Red solution prepared above
   10 ml Bromthymol Blue solution prepared above
   7 ml phenolphthalein solution (from Expt. 23) (1.0 gram phenolphthalein/100 ml 50% ethanol)
   110 ml ethanol
   53 ml water

   Either an indicator paper such as Hydrion paper or the indicators recommended with Expt. 18 may be used. A color comparison set should be provided for whatever indicators are used. Alizarin Yellow R, with a *p*H range 10–12, and Indigo Carmine ($11\frac{1}{2}$–13) are appropriate here, but should not be specifically designated, since this would give away the anticipated result. See the answer to question 2.

RESULTS. The observations as such are very interesting, but the student will have difficulty interpreting what happens. He will observe the brown color streaming down from the anode and filling the base of the U-tube. For Part (c) he will surely write $2I^- = I_2 + 2e^-$ and, if encouraged to recall Expt. 20, Part II, he will realize that I_2 is not very soluble in water. In question 1 the student is told that $I_2 + I^- = I_3^-$.

After using the indicator and doing Part (g), he should have no difficulty identifying the reaction for Part (d) as $2H_2O + 2e^- = H_2 + 2OH^-$, and he will be able to decide this on the basis of $E°$ values.

For Part (g) the equation is

$$Fe^{+3} + 3OH^- = Fe(OH)_3 \qquad K_{sp} = 4 \times 10^{-38}$$

I_2 is also produced, and can be identified by the CCl_4 test.

For Part (h) he will observe the lavender, and finally deep purple, color of the iodine in carbon tetrachloride. Part II of Expt. 20 gives this "test."

A number of extensions of this experiment may be of interest if time permits. A one milliliter sample of solution at the cathode may be removed at ten-minute intervals and titrated (0.1 *M* HCl is suitable). The electrodes may be reversed, the tube may be clamped at different angles, the depth of the electrodes may be changed, the concentration of the KI solution may be varied, and the solution may be stirred. See the answer to question 3.

ANSWERS TO QUESTIONS

1. As iodine is produced at the anode, it forms the brown complex ion I_3^- with the iodide ion of the electrolyte solution.

   (a) Write the equation for the reaction using reversible arrows to show the equilibrium involved.

   (b) What effect did the addition of CCl_4 have upon the equilibrium? Use your observations on the color of the two layers to explain the effect.

   Answer: (a) $I_2 + I^- \rightleftharpoons I_3^-$.

   (b) Since I_2 is very soluble in CCl_4, the equilibrium is shifted to the left, and the deep purple color is obtained in the lower layer while the color in the aqueous layer fades, since the I^- left there is colorless.

2. (a) What is the approximate hydrogen ion concentration around the cathode? What is the hydroxide ion concentration? Does the equation you wrote for the cathode half-reaction account for this result?

   (b) Write the equation for the reaction of 0.1 *M* $FeCl_3$ with the sample of solution taken from the cathode side.

   Answer: (a) By using universal after 10–15 minutes, the student will probably report $[H^+] = 10^{-10}$, or $pH = 10$, since this indicator does not change beyond *p*H 10. If phenolphthalein or litmus have been used he will know only that the solution is alkaline. Use of the indicators from Expt. 18 will allow a report of *p*H 12 or 13. The equation for Part d in this experiment accounts for this. Titration after 15 minutes gave 0.1 *M* OH^-, and after 30 minutes, gave about 0.15 *M* OH^-, indicating a OH^- concentration of about 10^{-1}, or about *p*H 13.

   (b) $Fe^{+3}(aq) + 3OH^- = Fe(OH)_3(s)$

3. When iodine, I_2, reacts with a basic solution, it undergoes a self-oxidation-reduction reaction to form iodide ions, I^-, and iodate ions, IO_3^-, both of which are colorless. Give a plausible

explanation of the sharp color boundary noted near the bottom of the U-tube in terms of your knowledge of the products at each electrode. Write the equation for the reaction involved.

Answer: If the student has observed carefully, he will note that gravity strongly influences the accumulation of the I_2 and thereby the I_3^- in the bottom of the U-tube. Stirring is limited in this region. Further observation on this may be obtained by tipping the U-tube, and possibly by raising and lowering the electrodes, or by stirring the solution.

The boundary is kept "sharp" by a balance between the diffusion rates of OH^- (downward) and I_3^- (upward), plus the reactions

$$I_3^- = I_2 + I^-$$

and

$$3I_2 + 6OH^- = IO_3^- + 5I^- + 3H_2O$$

The last reaction is discussed in the Textbook, p. 360.

POSTLAB DISCUSSION. Use the reactions observed here to lead into Expt. 31.

EXPERIMENT 31 SOME CHEMISTRY OF IODINE

PURPOSE. To study a representative halogen with emphasis on its oxidation states.

PRELAB DISCUSSION. In Expt. 30 some of the reactions of iodine were observed. In this experiment the behavior of iodine will be studied as a representative of the halogen family. Most students will need help in working out many of the equations, but they should be encouraged to try them by themselves first. If the products are correctly identified, they should be able to balance the equations.

EQUIPMENT NEEDED (PER STUDENT OR GROUP)

burner, ring stand, and clamp
3 or more test tubes (13 × 100 mm)
1 hard glass test tube (18 × 150 mm) (see lab hint 2)
stirring rod
test tube holder
funnel and filter paper or centrifuge

Chemicals

small iodine crystals (about 1 g total)
0.5 g potassium iodate (KIO_3)
1.2 g sodium metabisulfite ($Na_2S_2O_5$)

The following should be supplied in dropper bottles (see lab hint 1):

3–4 ml 6 *M* KOH (33.6 g/100 ml)
1 ml 6 *M* HNO_3 (39.4 ml conc./100 ml)
3 ml 0.1 *M* $AgNO_3$ (1.7 g/100 ml)
10 ml saturated KIO_3 (about 10 g/100 ml)
2 ml 6 *M* H_2SO_4 (34 ml conc./100 ml)
12 ml 0.1 *M* KI (8.3 g/500 ml)
15 ml starch solution (2 g/500 ml) (make as in lab hint 1, p. 247, but omit H_2SO_4)
0.5 ml 5% NaOCl (commercial bleach)
0.5 ml 3% H_2O_2

TIME REQUIRED. One period of 45–50 minutes might be sufficient, but the entire experiment will probably take longer. Convenient stopping places: after nearly every step of the procedure, but especially after Part I (15 minutes) or I and II (30–40 minutes).

PRECAUTIONS. Solid and gaseous iodine will stain skin and clothing. These vapors irritate mucous membranes. Be sure to caution students to heat the tube in part II c very gently. Good ventilation must be provided. Use a hood if available. See *Precautions*, Expt. 30, for stain removal from hands.

LABORATORY HINTS

1. The solutions should be used in dropper bottles, but the KOH should not be stored in bottles with a ground glass joint, nor should the HNO_3 be stored for a long time with a rubber dropper.
2. Note that for Part II b, an 18 × 150 mm tube is called for so that there will be a greater cool, condensing surface for the iodine vapors and more reactant surface from which vapors may escape.

DISCUSSION OF OBSERVATIONS—PRELIMINARY TEST. This test will reveal the presence of 1×10^{-7} grams of iodine per milliliter. Additional discussion of the iodine-starch complex may be found on p. 322 of Steiner and Campbell, *General Chemistry*, Macmillan, New York.

When the water containing excess iodine crystals is warmed, students will observe some purple vapors rise above the water. Usually a faint color develops in the water, which may be due to the slight dissolution of I_2. It is more likely, however, that the chlorination of the water gives enough Cl^- to form a complex with the iodine and that this is responsible for the dissolution of I_2 and the resultant color. Tap water develops this color, but properly distilled water does not.

PART I

(a) A heavy cream-yellow precipitate forms.

$$Ag^+(aq) + I^-(aq) = AgI(s) \tag{1}$$

(b) When a drop or two of bleach is added, a blue color appears, showing that the bleach has oxidized the I^- to I_2.

$$2I^- + OCl^- + H_2O = I_2 + Cl^- + 2OH^- \tag{2}$$

When additional bleach is added, the color disappears, since the I_2 is further oxidized to IO_3^-.

$$2OH^- + I_2 + 5OCl^- = 2IO_3^- + 5Cl^- + H_2O \tag{3}$$

Or, in one step, the reaction is

$$I^- + 3OCl^- = IO_3^- + 3Cl^- \tag{4}$$

If desired, the student could test for the Cl^- by adding $AgNO_3$ to the bleach alone and to a comparable amount of the product of this reaction. Since the action of the NaOCl with water is such that OH^- is produced, one may also interpret the disappearance of the I_2 as being due to the OH^- (see discussion of Part III). If acid is added with the bleach, the color does not disappear.

(c) With H_2O_2, the I_2 forms as revealed by the starch indicator. The reaction is

$$2I^- + 2H^+ + H_2O_2 = I_2 + 2H_2O \tag{5}$$

The appearance of color is delayed and depends upon $[H^+]$. With base added, no evident reaction takes place, and with the addition of acid, it is much increased. It may be that, with base, IO_3^- is formed.

PART II

(a) A thick, dark-brown precipitate forms. After filtering or centrifuging this from the liquid, the solid will be identified as iodine. To test, add a little water and starch solution. Part II of Expt. 20 may be recalled and carbon tetrachloride used to give the characteristic violet solution.

$$5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O \tag{6}$$

Since basic solution (that is, OH^-) favors the formation of I^- and IO_3^- in reaction (*6*), there is no change here. The conclusion is that H^+ is necessary for I^- and IO_3^- to produce iodine.

(b) Note *Precautions* and lab hint 2. When solid KIO_3 is heated with $Na_2S_2O_5$, a brown color is observed, soon followed by fumes of gaseous I_2. This will condense to the characteristic, shiny, gray solid on the cooler portions of the test tube. The student cannot be expected to write the equation for this:

$$2KIO_3(s) + 5Na^+(aq) + 5HSO_3^-(aq) = I_2(s) + 3NaHSO_4(s) + 2NaKSO_4(s) + H_2O(g) \tag{7}$$

Although the student actually added $Na_2S_2O_5$, water reacts with this compound to produce $Na^+(aq) + HSO_3^-(aq)$. Another form of the equation is

$$4KIO_3(s) + 5Na_2S_2O_5(s) = 2I_2(s) + 5Na_2SO_4(s) + 2K_2SO_4(s) + 3SO_3(g) \tag{8}$$

There will almost certainly be some moisture in the air, with the result that H_2SO_4 rather than SO_3 will be the final product.

In Expt. 14, a reaction between IO_3^- and HSO_3^- was carried out in dilute solution. Since oxidation states had not been discussed at that time, a discussion of these reactions can be made here if you have some extra time. The net reaction is given by equation (*7*), or, in ionic form,

$$2IO_3^- + 5HSO_3^- = I_2 + 5SO_4^{-2} + 3H^+ + H_2O \tag{9}$$

This reaction takes place in stages: a slow reaction in which iodate is reduced to iodide,

$$IO_3^- + 3HSO_3^- = I^- + 3HSO_4^- \text{ (or } 3SO_4^{-2} + 3H^+\text{)} \qquad (10)$$

a fast reaction between iodate and iodide to form iodine,

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O \qquad (6)$$

and a very fast reaction in which I_2 is reduced to I^-,

$$I_2 + HSO_3^- + H_2O = 2I^- + SO_4^{-2} + 3H^+ \qquad (11)$$

Reaction (*10*) produces iodide, which by reaction (*6*) can form iodine. Reaction (*11*) prevents iodine formation until all the HSO_3^- is used. Then the excess IO_3^- does react with I^- to give I_2. In the reaction between the solids, (*7*) and (*8*), it is likely that SO_2 forms from decomposition of the $Na_2S_2O_5$ and that this reduces the IO_3^-. The I_2 is driven from the reaction site, hence it is not converted to I^- even though there is an excess of $Na_2S_2O_5$. These reactions illustrate several changes of oxidation state for iodine:

reaction (*6*)	-1 and $+5$ to 0
reaction (*7*), (*8*), and (*9*)	$+5$ to 0
reaction (*10*)	$+5$ to -1
reaction (*11*)	0 to -1

PART III

(a) The iodine dissolves, giving a colorless solution:

$$5(\tfrac{1}{2}I_2 + e^- = I^-)$$
$$\tfrac{1}{2}I_2 + 6OH^- = IO_3^- + 3H_2O + 5e^-$$

The net reaction is

$$3I_2 + 6OH^- = IO_3^- + 5I^- + 3H_2O \qquad (12)$$

(b) When acid is added, a deep brown-black solid results. This is $I_2(s)$.

$$IO_3^- + 5I^- + 6H^+ = 3I_2(s) + 3H_2O \qquad (13)$$

(c) The solid iodine redissolves in KOH (reaction *12*).

(d) When the solution containing I_2 in KOH is cooled, a small amount of white solid (KIO_3) is formed.

(1) When this is dried and heated with $Na_2S_2O_5$, the brown color characteristic of I_2 will be noted, and some I_2 vapor (lavender) will be produced (see Part II b).

(2) Yellow AgI forms as a cream-yellow precipitate when $AgNO_3$ is added to the decanted liquid. This will be enough like Part I a to be recognized, although the presence of OH^- will result in *some* brown $Ag_2O(s)$.

ANSWERS TO QUESTIONS

1. Write the equations for the reactions observed in Parts I a, I b, and I c.

   Answer: Included above—Equations (*1*), (*2*), and (*3*).

2. (a) How did the results in Part III d (1) compare with those obtained in Part II b?
   (b) How did the test with 0.1 *M* silver nitrate in Part III d (2) compare with the results of Part I a?
   (c) What do you conclude about the ionic species formed when I_2 reacts with 6 *M* KOH as in Part III a?

Answer: (a) They were very similar. Both had the brown color characteristic of $I_2(s)$ and the lavender vapor of $I_2(g)$.
(b) A cream-yellow precipitate formed [see discussion for Part III d (2)].
(c) Both I^- and IO_3^- are formed.

3. Write the equation for the self-oxidation-reduction reaction of iodine in a basic solution. Write the equation for the reverse of this reaction in an acid solution.

Answer: See equations (*12*) and (*13*) in Parts III a and III b.

4. In which oxidation state do the halogens most commonly occur in nature? Explain your answer in terms of the electronic structure of this species for chlorine.

Answer: The −1 oxidation state is most common, and this may be explained by noting the position of the halogens in the periodic table. Their electronic structure is such that the addition of 1 more electron results in an inert gas (stable) electron arrangement. For example, the electron arrangement of Cl^- is

$$2s^1 \quad 2s^2 2p^6 \quad 3s^2 3p^6$$

which is the same as that of Ar.

5. How would you prepare elemental fluorine, F_2? Consult the oxidation-reduction table in Appendix 8 to check the feasibility of your method.

Answer: The student will discover that, since $E°$ for the reaction $2F^- = 2e^- + F_2(g)$ is −2.87 volts, there is no oxidizing agent that he can select. He may suggest electrolysis, which is correct. For a more complete discussion, the more able student may look up the details in an encyclopedia or other reference.

6. Sodium iodate can be obtained from the plateaus of Chile. Suggest a commercial method for obtaining elemental iodine from this source.

Answer: The student will be led (by Part II b) to suggest heating it with $Na_2S_2O_5(s)$ or $HSO_4^-(aq)$. These reactions will work. In practice a more complex procedure is used. Bisulfite is used to produce I^-, which is precipitated as CuI. This compound is finally oxidized by Fe_2O_3. The equations are:

$$IO_3^-(aq) + 3HSO_3^-(aq) = 3HSO_4^-(aq) + I^-(aq)$$

$$2I^-(aq) + 2Cu^{+2}(aq) + HSO_3^-(aq) + H_2O = 2CuI(s) + HSO_4^-(aq) + 2H^+(aq)$$

$$2CuI + 6H_2SO_4 + 2Fe_2O_3 = 2CuSO_4 + H_2O + I_2$$

The $CuSO_4$ is reused to supply the $Cu^{+2}(aq)$ in the second step.

POSTLAB DISCUSSION. Point out that the other halogens display similar reactions. Show some of these—for example, the reactions of each halogen with Br^-, NaOCl, and H_2O_2, and reactions for the bromate and chlorate ions.

Supplementary Material

Articles

J. H. Simons, "Fluorocarbons," *Scientific American*, November 1949, pp. 44–47.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

BROMINE—ELEMENT FROM THE SEA

CHEM Study Films

Running Time: 22 minutes

This film, made in collaboration with Dr. L. J. Hollenberg, first demonstrates reactions of Br_2 with metals and nonmetals. Then a laboratory preparation of Br_2 is developed, showing the oxidation-reduction reactions. Finally, the same principles are shown in action in a commercial plant which extracts Br_2 from sea water.

Background Discussion

POSITIVE OXIDATION STATES

There is some evidence, especially for iodine, that in some compounds the halogens may actually have positive ionic charges. For instance, a solution of I_2 in benzophenone (and other organic solvents) conducts an electric current. This can be explained by some dissociation to ions:

$$I_2 = I^+ + I^-$$

In addition, iodine forms salt-like compounds such as ICN (iodine cyanide) and INCO (iodine cyanate) as well as I^{+3} compounds.

$I(C_2H_3O_2)_3$	iodine acetate
$I_2(SO_4)_3$	iodine sulfate
$I(IO_3)_3$	iodine iodate

In many compounds, however, the positive character of the halogens is largely a matter of the arbitrariness of oxidation number. The compounds are largely covalent in bonding. Examples are the oxyanions given in the Textbook (IO_3^-, ClO_4^-, etc.) and the compounds of the halogens with each other (including ICl, IF_5, ClF_3, and several others).

THE OXYGEN COMPOUNDS OF HALOGENS

The oxyacids discussed in the text are like the "common" acids in that they form salts and anhydrides. Some examples are:

Anhydride	Acid	Salt
SO_3	H_2SO_4	M_2SO_4
NO_2	HNO_3	MNO_3
Cl_2O	HClO	MClO
ClO_2	$HClO_2$	$MClO_2$
Cl_2O_6	$HClO_3$	$MClO_3$
Cl_2O_7	$HClO_4$	$MClO_4$

All these chlorine oxides are known (but are very unstable); the acids exist in solution, but only the perchlorate has been isolated. The salts have all been prepared as crystalline solids.

The oxides of the other halogens are not so numerous, at least in our present state of knowledge. This is partly a result of their instability, which means they are not well known. The regularity of the chlorine compounds and the relation between them and well known systems can be used to show the organization achieved by the periodic table.

THE COLOR OF INORGANIC COMPOUNDS

Most nonmetallic elements are colored (see p. 637). Such colors result from the absorption of part of the white light striking the substance. These bands (and similar, invisible ones in the ultraviolet region) occur when electrons absorb the correct size energy quantum to move to another level. The quantum is used to effect the movement; whatever color corresponds to that quantum size disappears. The substance will then have a complementary color.

There appears to be a connection between covalent bonding and color. Pauling (*The Nature of the Chemical Bond*, p. 105 ff.) gives a table relating covalent character and color for a number of sulfides and halides of eleven metals. In each case, where there is more than about 75% covalent character, the substances are colored. In fact, the color is deeper when there is a larger percent of covalent bonding.

Color also seems to be more common for ions or atoms that have high polarizability—that is, whose electron symmetry is easily deformed by the electric field of another atom or ion. Larger atoms, with their less strongly held outer electrons, tend to have high polarizability. These factors fit the elemental halogens quite well. They are covalently bonded, the larger atoms have deeper color, and their polarizability follows accordingly.

The blue color listed for oxygen is probably due to some other cause, although it, of course, appears blue because part of the light striking it is absorbed. An oxygen molecule does not have a simple, covalent double bond. Evidence, mainly its paramagnetic and spectroscopic behavior, suggests that there are two unpaired electrons in each O_2. The unusual electron structure probably contains appropriate levels, such that the red light is absorbed and the remaining light is blue. The color of metals depends on different, more complex electronic phenomena and is best omitted from discussion.

PREPARATION AND USES OF HALOGENS

The most general preparative method is electrolysis, although all but fluoride ions can also be chemically oxidized. Bromine and iodine are usually produced by chemical means.

The major uses of halogens can be summarized as follows.

Fluorine	CaF, NaF	soldering fluxes, insecticides,
	CCl_2F_2	Freon (refrigerant), insect repellant,
	HF	rocketry, petroleum refining
Chlorine	NaOCl $CaOCl_2$	bleaching fabric. wood, paper pulp
	Cl_2	water treatment, making Br_2
	$CHCl_3$, CCl_4	solvents
Bromine	$C_2H_4Br_2$	leaded gasoline
	AgBr	photography
Iodine	AgI	photography
	I_2 (+ KI)	antiseptic

Chlorine is most used (about 400,000 tons a year in the U.S.); bromine next most (about one-twentieth as much as chlorine); and fluorine and iodine still less.

Answers to Exercises and Problems

Ex. 19-1. Using the carbon atom covalent radius 0.77 A, and the covalent radii given in Figure 19-3, predict the C—X bond length in each of the following molecules: CF_4, CBr_4, CI_4. Compare your calculated bond lengths with the experimental values: C—F in CF_4 = 1.32 Å, C—Br in CBr_4 = 1.94 Å, C—I in CI_4 = 2.15 Å.

Answer

	Calculation	Observed
CF_4	0.77	
	0.72	
	1.49 Å	1.32 Å
CBr_4	0.77	
	1.14	
	1.91	1.94
CI_4	0.77	
	1.33	
	2.10	2.15

Ex. 19-2. On the basis of the trend in atomic size, what trend is expected in the ionization energy E_1 of the halogen atoms? Compare your prediction with the actual trend in E_1, given in Table 19-1.

Answer

As the atom gets larger, it should become easier to remove an electron, thus E_1 should decrease as we go down in the periodic table. This is in accord with the experimental trend.

Ex. 19-3. At the left electrode in Figure 19-5, the half-reaction occurring is $Cl^- \longrightarrow \frac{1}{2}Cl_2(g) + e^-$, and at the right electrode the half-reaction is $Na^+ + e^- \longrightarrow Na(l)$. Which electrode is the anode and which is the cathode? With these half-reactions, balance the net reaction occurring in the electrolysis cell.

Answer

Oxidation occurs at the anode. Therefore the left electrode is the anode at which Cl^- is oxidized to $Cl_2(g)$. Reduction occurs at the cathode. The right electrode is the cathode at which Na^+ is reduced to $Na(l)$.

Balanced net reaction:

$$Na^+ + Cl^- \longrightarrow Na(l) + \tfrac{1}{2}Cl_2(g)$$

Ex. 19-4. From the $E°$'s for the half-reactions of the type $2X^- = X_2 + 2e^-$, show that Cl_2 can be used to produce Br_2 from Br^- and I_2 from I^- but not to produce F_2 from F^-.

Answer

$$\begin{aligned} 2I^- &\longrightarrow I_2 + 2e^- & E° &= -0.53 \text{ volt} \\ 2Br^- &\longrightarrow Br_2 + 2e^- & E° &= -1.06 \text{ volts} \\ 2Cl^- &\longrightarrow Cl_2 + 2e^- & E° &= -1.36 \text{ volts} \\ 2F^- &\longrightarrow F_2 + 2e^- & E° &= -2.87 \text{ volts} \end{aligned}$$

Both I^- and Br^- lose electrons more readily than Cl^-, hence can gain electrons from Cl_2 (as shown by $E°$ values). But Cl^- releases electrons more readily than does F^-, hence F_2 will react with Cl^- to give Cl_2 and F^- (rather than the reverse).

Ex. 19-5. Balance the reaction that occurs when I^- is oxidized to I_2 by MnO_4^- in acid solution, producing Mn^{+2}.

Answer

$$MnO_4^- + I^- + H^+ \longrightarrow Mn^{+2} + I_2 + H_2O$$

By the oxidation number method,

Iodine $-1 \xrightarrow{+1} 0$

Manganese $+7 \xrightarrow{-5} +2$

Therefore five iodine atoms must react for each manganese:

$$MnO_4^- + 5I^- + H^+ \longrightarrow Mn^{+2} + \tfrac{5}{2}I_2 + H_2O$$

Balancing hydrogen and oxygen gives the equation

$$MnO_4^- + 5I^- + 8H^+ \longrightarrow Mn^{+2} + \tfrac{5}{2}I_2 + 4H_2O$$

Ex. 19-6. Show that when an aqueous solution of NaCl is being electrolyzed, vigorous stirring in the cell might permit reaction (*23*) to occur.

Answer

In an electrolytic cell containing an aqueous solution of NaCl, the anode reaction produces chlorine gas; the cathode reaction produces OH^- and H_2. The reactions are

$$2Cl^- = Cl_2 + 2e^- \qquad \text{(anode reaction)}$$
$$2e^- + 2H_2O = H_2(g) + 2OH^- \qquad \text{(cathode reaction)}$$

The vigorous stirring brings the Cl_2 and OH^- into contact, permitting this additional reaction to occur:

$$Cl_2 + 2OH^- = Cl^- + ClO^- + 2H_2O$$

Pr. 1. Give the electron configuration for each of the trio F^-, Ne, Na^+. How do the trios Cl^-, Ar, K^+, and Br^-, Kr, Rb^+ differ from the above?

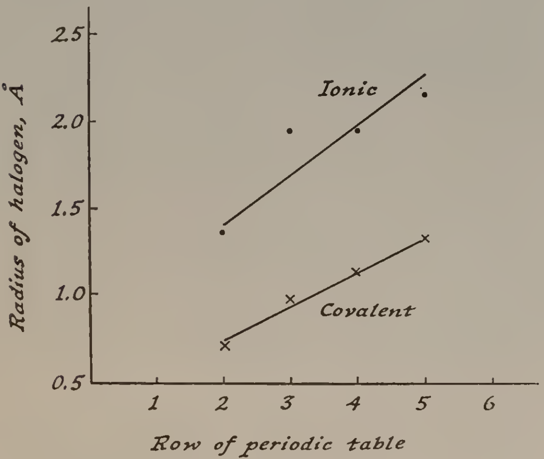
Answer

F^-	$1s^22s^22p^6$
Ne	$1s^22s^22p^6$
Na^+	$1s^22s^22p^6$

These species each have the *same* electron configuration. They are called isoelectronic. The species Cl^-, Ar, K^+ all have more electrons $1s^2$, $2s^22p^6$, $3s^23p^6$, and Br^-, Kr, Rb^+ have still more: $1s^2$, $2s^22p^6$, $3s^23p^6$, $3d^{10}4s^24p^6$. The second trio is larger than the first by the $3s^23p^6$ electrons; the third is larger than the second by the $3d^{10}4s^24p^6$ electrons. Note that, in each trio, the outermost groups are the same kind of electrons, p^6.

Pr. 2. Table 19-II contains values for the covalent radii and the ionic radii of the halogens. Plot both radii versus row number. What systematic changes are evident in the two curves?

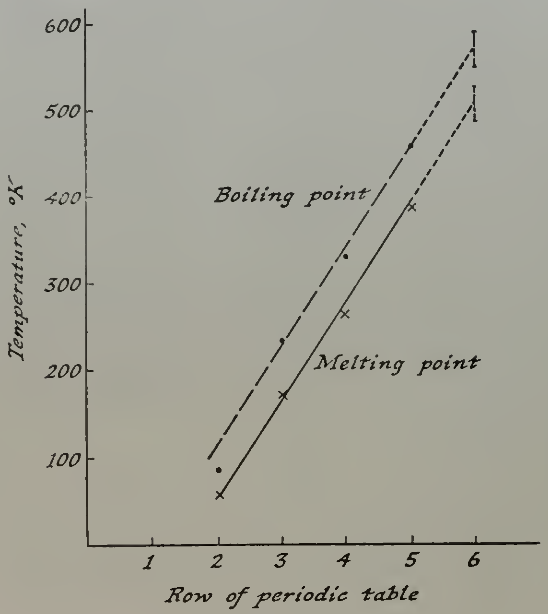
Answer



In both curves the increase in radius is almost linearly related to row number. In both cases the change from fluorine to chlorine is sharper than the subsequent changes from chlorine to bromine to iodine. Remember that fluorine and chlorine are not as widely separated in atomic number as are chlorine, bromine, and iodine. Successive electron levels do not add as much to radius, because the increased nuclear charge pulls the inner levels in.

Pr. 3. Using the data from Table 19-II, plot on one set of axes the melting and boiling points of the halogens versus row number.

Answer



The curves are nearly linear with row number. Recall that in Chapter 6 the student learned that the physical properties of all columns do not change in the same way (the alkali metals have the opposite trend in melting point). Avoid the incorrect idea that melting point always increases as atomic weight increases.

Pr. 4. For astatine, use your graphs from Problems 2 and 3 as a basis for a prediction of its covalent radius, ionic radius of the −1 ion, melting point, and boiling point.

Answer

If we use the graphs from Problems 2 and 3, we see that the covalent radius would probably be in the range 1.4–1.6 Å. The ionic radius would be expected to be 2.2–2.5 Å. The melting point would be expected to be 480–530°K (207–257°C). The boiling point would be expected to be 550–600°K (277–327°C).

For the radii, the span of atomic number from iodine to astatine is 32, as contrasted with 18 from bromine to iodine. This might explain why the astatine radii may be somewhat higher than a linear extrapolation would make it. Note that the part of the question on melting and boiling points was asked in Problem 21, Chapter 6.

Pr. 5. Predict the molecular structures and bond lengths for SiF_4, $SiCl_4$, $SiBr_4$, and SiI_4, assuming the covalent radius of silicon is 1.16 Å.

Answer

The bonding in silicon is that described as sp^3, and the bonds are tetrahedrally oriented, as in CH_4, shown in Textbook Figure 16-11. The predicted bond lengths are:

	SiF	SiCl	SiBr	SiI
Silicon radius	1.16 Å	1.16 Å	1.16 Å	1.16 Å
Halogen radius	+.72	+.99	+1.11	+1.33
Calculated bond length	1.88 Å	2.15 Å	2.27 Å	2.49 Å
Experimental bond length	(1.59 Å)	(2.01 Å)	(2.15 Å)	(2.43 Å)
Difference	0.29 Å	0.14 Å	0.12 Å	0.06 Å

Notice the trend in the difference between predicted and experimental values. This trend can be explained in terms of the *difference* in ionization energies. The very large difference between E_1 of silicon and E_1 of fluorine implies ionic character in the bond, which tends to strengthen and shorten the bond. This ionization energy difference decreases from 224 kcal, F—Si, to 53 kcal, I—Si.

Pr. 6. Explain in terms of nuclear charge why the K^+ ion is smaller than the Cl^- ion, though they are isoelectronic (they have the same number of electrons).

Answer

These two ions have the same number of electrons, in the same orbitals, but the greater nuclear charge in K^+ "pulls" the electrons closer to the nucleus, and it is smaller than that of Cl^-. The values of ionic radii are: K^+, 1.55 Å; Cl^-, 1.81 Å.

Pr. 7. Can aqueous bromine, Br_2, be used to oxidize ferrous ion, $Fe^{+2}(aq)$, to ferric ion, $Fe^{+3}(aq)$ (use Appendix 3)? Aqueous iodine, I_2?

Answer

$$\begin{array}{ll} 2I^- \longrightarrow I_2 + 2e^- & E^\circ = -0.53 \text{ volt} \\ Fe^{+2} \longrightarrow Fe^{+3} + e^- & E^\circ = -0.77 \text{ volt} \\ 2Br^- \longrightarrow Br_2 + 2e^- & E^\circ = -1.06 \text{ volts} \end{array}$$

Since Fe^{+2} is above Br_2 in the E° table, reaction can occur,

$$2Fe^{+2} + Br_2 \longrightarrow 2Fe^{+3} + 2Br^-$$

Since Fe^{+2} is below I_2 in the E° table, reaction cannot occur appreciably. (In fact, the reverse reaction furnishes a practical means of reducing Fe^{+3} to Fe^{+2}.)

Pr. 8. What will happen if F_2 is bubbled into 1 M NaBr solution? Justify your answer using E° values.

Answer

$$\begin{array}{ll} 2Br^- \longrightarrow Br_2 + 2e^- & E^\circ = -1.06 \text{ volts} \\ H_2O \longrightarrow \tfrac{1}{2}O_2(g) + 2H^+ + 2e^- & \\ & E^\circ = -1.23 \text{ volts} \\ 2F^- \longrightarrow F_2 + 2e^- & E^\circ = -2.87 \text{ volts} \end{array}$$

By the E° values, fluorine can oxidize either Br^- or H_2O, producing Br_2 and O_2. Both of these reactions would be expected to occur, but the relative amounts would depend upon the conditions.

Pr. 9. Using E° values, predict what will happen if, in turn, each halogen beginning at chlorine is added to a 1 M solution of ions of the next lower halogen: Cl_2 to Br^-, Br_2 to I^-. Which halogen is oxidized and which is reduced in each case?

Answer

$$\begin{array}{rl} F_2 + 2e^- = 2F^- & E^\circ = 2.87 \text{ volts} \\ 2Cl^- = Cl_2 + 2e^- & E^\circ = -1.36 \text{ volts} \\ \hline F_2 + 2Cl^- = 2F^- + Cl_2 & E^\circ = +1.51 \text{ volts} \end{array}$$

F_2 will be reduced to $2F^-$, thus oxidizing $2Cl^-$ to Cl_2. Chlorine will be formed. Similar equations will hold for each pair tested:

$$\begin{array}{ll} Cl_2 + 2Br^- = 2Cl^- + Br_2 & E^\circ = 0.30 \text{ volt} \\ Br_2 + 2I^- = 2Br^- + I_2 & E^\circ = 0.53 \text{ volt} \end{array}$$

Pr. 10. Write a balanced equation for the reaction of dichromate and iodide ions in acid solution. Determine E° for the reaction

$Cr_2O_7^{-2}(aq) + I^-(aq) + H^+(aq)$ gives

$Cr^{+3}(aq) + I_2 + H_2O$

Answer: $E^\circ = +0.80$.

Answer: Using the $E°$ table of half-reactions, we find

$$\begin{array}{rl}
14H^+ + Cr_2O_7^{-2} + 6e^- = 7H_2O + 2Cr^{+3} & E° = +1.33 \text{ volts} \\
3(2I^- = I_2 + 2e^-) & E° = -0.53 \text{ volt} \\
\hline
Cr_2O_7^{-2} + 6I^- + 14H^+ = 2Cr^{+3} + 3I_2 + 7H_2O & E° = +0.80 \text{ volt}
\end{array}$$

Pr. 11. Balance the equation for the reaction of iodine with thiosulfate ion:

$$I_2 + \underset{\text{thiosulfate ion}}{S_2O_3^{-2}(aq)} \text{ gives } \underset{\text{tetrathionate ion}}{S_4O_6^{-2}(aq)} + I^-(aq)$$

What is the oxidation number of sulfur in the tetrathionate ion?

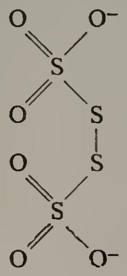
Answer: Using oxidation numbers, we obtain

$$\text{I (oxid. no.} = 0) \xrightarrow{-1} \text{I (oxid. no.} = -1) \qquad \text{S (oxid. no.} = +2) \xrightarrow{+\frac{1}{2}} \text{S (oxid. no.} = +2.5)$$

thus we need two sulfur atoms for each I atom:

$$I_2 + 2S_2O_3^{-2} = S_4O_6^{-2} + 2I^-$$

The fractional oxidation number can be taken as a clue that not all the sulfur atoms in dithionate are identical. The ion is thought to have the structure



which does have two kinds of sulfur atoms.

Pr. 12. How many grams of iodine can be formed from 20.0 grams of KI by oxidizing it with ferric chloride ($FeCl_3$)? Determine $E°$.

Answer: 15.3 grams of I_2.

Answer

$$\begin{array}{rl}
2I^- = I_2 + 2e^- & E° = -0.53 \text{ volt} \\
2Fe^{+3} + 2e^- = 2Fe^{+2} & E° = +0.77 \text{ volt} \\
\hline
2I^- + 2Fe^{+3} = I_2 + 2Fe^{+2} & E° = +0.24 \text{ volt}
\end{array}$$

STEP I $\quad \text{moles} = \dfrac{\text{grams}}{\text{grams/mole}} \qquad 20.0 \times \frac{1}{166} = 0.120 \text{ mole KI}$

STEP II $\quad (\text{moles KI})\left(\dfrac{\text{moles } I_2}{\text{mole KI}}\right) \qquad 0.120 \times \frac{1}{2} = 0.0600 \text{ mole } I_2$

STEP III $\quad (\text{moles } I_2)\left(\dfrac{\text{g}}{\text{mole}}\right) \qquad 0.0600 \times 254 = 15.3 \text{ g } I_2$

Pr. 13. Balance the equation for the reaction between SO_2 and I_2 to produce SO_4^{-2} and I^- in acid solution. Calculate $E°$. From Le Chatelier's Principle, predict the effect on the $E°$ in this reaction if $H^+ = 10^{-7}$ *M* is used instead of $H^+ = 1$ *M*.

Answer

$$\begin{array}{rlrl}
SO_2(g) + 2H_2O & \longrightarrow 2e^- + SO_4^{-2} + 4H^+ & E^\circ = & -0.17 \text{ volt} \\
-(2I^- & \longrightarrow 2e^- + I_2) & E^\circ = & -0.53 \text{ volt} \\
\hline
SO_2(g) + 2H_2O + I_2 & \longrightarrow SO_4^{-2} + 4H^+ + 2I^- & E^\circ = & (-0.17) - (-0.53) \text{ volt} \\
 & & E^\circ = & +0.36 \text{ volt}
\end{array}$$

By Le Chatelier's Principle, reducing the concentration of a product increases the tendency to form products. Hence E° will be still more positive in dilute H^+.

Pr. 14. What is the oxidation number of the halogen in each of the following: HF, $HBrO_2$, HIO_3, ClO_3^-, F_2, ClO_4^-?

Answer

HF, oxid. no. = −1

$HBrO_2$, oxid. no. = +3

HIO_3, oxid. no. = +5

ClO_3^-, oxid. no. = +5

ClO^-, oxid. no. = +1

F_2, oxid. no. = 0

ClO_4^-, oxid. no. = +7

Pr. 15. Comparable half-reactions for iodine and chlorine are shown below.

$$\begin{array}{ll}
\tfrac{1}{2}I_2 + 3H_2O \longrightarrow IO_3^- + 6H^+ + 5e^- & E^\circ = -1.195 \text{ volts} \\
\tfrac{1}{2}Cl_2 + 3H_2O \longrightarrow ClO_3^- + 6H^+ + 5e^- & E^\circ = -1.47 \text{ volts}
\end{array}$$

(a) Which is the stronger oxidizing agent, iodate, IO_3^-, or chlorate, ClO_3^-?

(b) Balance the equation for the reaction between chlorate ion and I^- to produce I_2 and Cl_2.

Answer: (a) Chlorate ion is a stronger oxidizing agent than iodate ion because the E° for Cl_2–ClO_3^- is more negative than that for I_2–IO_3^-.

(b)

$$\begin{array}{c}
5(2I^- \longrightarrow I_2 + 2e^-) \\
-2(\tfrac{1}{2}Cl_2 + 3H_2O \longrightarrow ClO_3^- + 6H^+ + 5e^-) \\
\hline
10I^- + 2ClO_3^- + 12H^+ \longrightarrow 5I_2 + Cl_2 + 6H_2O
\end{array}$$

Pr. 16. Two half-reactions involving chlorine are

$$\begin{array}{rl}
2Cl^- \longrightarrow Cl_2 + 2e^- & E^\circ = -1.36 \text{ volts} \\
Cl_2 + 2H_2O \longrightarrow 2HOCl + 2H^+ + 2e^- & E^\circ = -1.63 \text{ volts}
\end{array}$$

(a) Balance the reaction in which self-oxidation-reduction of Cl_2 occurs to produce chloride ion and hypochlorous acid, HOCl.

(b) What is the oxidation number of chlorine in each species containing chlorine?

(c) What is E° for the reaction?

(d) Explain, using Le Chatelier's Principle, why the self-oxidation-reduction reaction occurs in 1 M OH^- solution instead of 1 M H^+.

Answer: (a) Reversing the first reaction, we have

$$\begin{array}{ll}
Cl_2 + 2e^- \longrightarrow 2Cl^- & E^\circ = +1.36 \text{ volts} \\
Cl_2 + 2H_2O \longrightarrow 2HOCl + 2H^+ + 2e^- & E^\circ = -1.63 \text{ volts} \\
\hline
2Cl_2 + 2H_2O \longrightarrow 2Cl^- + 2HOCl + 2H^+ &
\end{array}$$

or

$$Cl_2 + H_2O \longrightarrow Cl^- + HOCl + H^+ \qquad E^\circ = -0.27 \text{ volt}$$

(b) Cl_2 (oxid. no. = 0); Cl^- (oxid. no. = −1); HOCl (oxid. no. = +1).

(c) $E^\circ = -0.27$ volt.

(d) Changing the concentration of H^+ from 1 M to 10^{-14} M (as it is in 1 M OH^-) increases the tendency to form products so as to partially compensate for the removal of H^+. Equilibrium is shifted toward products, as discussed in Sec. 19-2.5.

Pr. 17. How many grams of SiO_2 would react with 5.00×10^2 ml of 1.00 *M* HF to produce SiF_4?

Answer:

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

STEP I

$$\left(\frac{\text{ml}}{\text{ml/liter}}\right)\left(\frac{\text{moles}}{\text{liter}}\right)$$

$$\left(\frac{5.00 \times 10^2}{1000/1}\right)(1.00) = 0.500 \text{ mole HF}$$

STEP II

$$(\text{moles HF})\left(\frac{\text{moles } SiO_2}{\text{mole HF}}\right)$$

$$0.500 \times \tfrac{1}{4} = 0.125 \text{ mole } SiO_2$$

STEP III

$$(\text{moles } SiO_2)\left(\frac{\text{g}}{\text{moles}}\right)$$

$$0.125 \times 60.1 = 7.51 \text{ g } SiO_2$$

Pr. 18. A water solution that contains 0.10 *M* HF is 8% dissociated. What is the value of its K_A?

Answer: 6.9×10^{-4}.

Answer

$$\begin{array}{lcccc} & HF(aq) = & H^+(aq) + & F^-(aq) & \\ \text{Initial conc.} & 0.10 & 0 & 0 & M \\ \text{Equil. conc.} & 0.092 & 0.008 & 0.008 & M \end{array}$$

$$K_A = \frac{[H^+][F^-]}{[HF]} = \frac{(0.008)^2}{(0.092)}$$

$$= \frac{64 \times 10^{-6}}{9.2 \times 10^{-2}} = 6.9 \times 10^{-4}$$

Pr. 19. From each of the following sets, select the substance which best fits the requirement specified.

(a) Strongest acid	HOCl, HOClO, $HOClO_2$
(b) Biggest atom	F, Cl, Br, I
(c) Smallest ionization energy	F, Cl, Br, I
(d) Best reducing agent	F^-, Cl^-, Br^-, I^-
(e) Weakest acid	HF, HCl, HBr, HI
(f) Best hydrogen bonding	HF, HCl, HBr, HI

Answer

(a) $HClO_3$ ($HOClO_2$); explained on p. 358 of Textbook.

(b) I; explained on p. 354 of Textbook.

(c) I; explained on p. 353 of Textbook.

(d) I^-; explained on p. 357 of Textbook.

(e) HF; explained in Appendix 2 of Textbook.

(f) HF; explained in Chapter 17 of Textbook.

Part (f) may be hard for the student. The better students may get the correct answer by comparing Textbook Figures 17-6 and 17-14.

Pr. 20. Describe two properties that the halogens have in common, and give an explanation of why they have these properties in common.

Answer

(a) They exist as diatomic molecules in the gas phase. This is explained by noting that each atom has one unshared electron. Two atoms can share these unpaired electrons, thereby forming a covalent bond. This sharing fills all the valence orbitals without using a higher energy level, hence the molecules are diatomic, not triatomic, etc.

(b) All halogens form compounds of the form M_1X_1, where *M* is an alkali metal and *X* is a halogen. The reason for this is that each alkali atom can donate one electron (leaving an inert gas electron configuration), whereas each halogen can accept an electron, thereby also gaining the electron configuration of an inert gas. Hence one atom of an alkali satisfies one atom of a halogen.

(c) All halogens form covalent bonds with hydrogen and with carbon. The reason for this is, again, the possibility of sharing electrons without using orbitals of greater energy than are used by the electrons of the atom.

(d) All halogens form compounds with the alkali metals (and others), which form ionic solids. The reason is that given in (b); in addition, the electron configuration of the inert gas has spherical symmetry. This allows the formation of undirected (i.e., ionic) bonds.

(e) All the halogens have some oxidizing ability. This is a result of their affinity for electrons.

(f) All the halogens can be made gaseous at fairly low temperatures. This is a result of their molecular (rather than ionic or network) structures. Their limited capacity to form bonds leads to their simple structure.

CHAPTER

20

THE THIRD ROW OF THE PERIODIC TABLE

Up to the present, we have been carefully constructing a set of concepts which can aid in organizing many of the facts of chemistry. We are now ready to apply these concepts to the third row of the table.

Intent and Approach

In this chapter we continue to avoid an encyclopedic recitation of facts; such an approach is deadly. Instead we "wonder why" properties of the elements are as they are; usually an "explanation" or correlation can be given by reference to earlier ideas such as the three states of matter, electronic structure, oxidation-reduction, acid–base theory, or other concepts.

Keep applying and stressing our earlier concepts! At worst, the "explanations" which we give serve as convenient mnemonic devices; at best, they represent partial answers to the important question of *why.*

Our explanations are always overly simplified expressions of rather complex processes. The thermochemical cycle for $E°$, given in the *Background Discussion* (p. 671), will illustrate the complexity of a typical problem. Note that we have selected only a few of the variables in our Textbook discussion, but we can make a fairly good case in support of the idea that these are the important, or key, variables. It is not necessary to develop the whole quantitative cycle for the students, but you should be familiar with the whole development in case questions arise.

Challenge the student; can he see how predictions can be made? Whether his predictions are right or wrong is less important than that he develop an ability to think through a problem, sort out the variables, and arrive at a logical answer. If his answer is wrong, it is instructive for him to see where the model he used broke down. This is the route of science. He can learn a lot from his mistakes. Making predictions and testing them are what make science more intriguing than any man-made puzzle.

Outline

1. The physical properties of the third-row elements range from those typical of metals on the left to those typical of nonmetals on the right. These physical properties can be correlated by applying the concepts of bonding (20-1.1 to 20-1.3).
2. The gradual decrease in the ability of an element to serve as a reducing agent and the gradual increase in its ability to act as an oxidizing agent as we go from left to right in the third row is interpreted in terms of a thermochemical cycle. Elements to the right tend to exist in several oxidation states (20-2.1 to 20-2.3).
3. The gradual change from basic hydroxide through amphoteric hydroxide to acidic hy-

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
Reread pp. 101–103 S 20-1 (pp. 364–366)	1	Expt. 32, Demo.* Discussion	1, 2	1, 2	3, 4		Physical Properties
S 20-2 (pp. 367–369)	2	Discussion	3, 4	9	5, 10–12	**6**†–8	Oxidation-reduction
Expt. 32	3	Expt. 32					
S 20-3 (pp. 370–372)	4	Discussion		14	15	**13**, 16	Acidic and Basic Properties of Hydroxides
S 20-4 (pp. 373–374)	5	Discussion Review				17	Occurrence and Preparation

Note: Expt. 33 fits between Chapters 20 and 21. Expt. 34 (Chapter 21) requires extensive preparation.

* Demonstration portion only.

† Boldface indicates problems whose answers are given in the Textbook.

droxide can be described in terms of the extent to which the metal-oxygen or the oxygen-hydrogen bond is weakened by suitable electron shifts. The lower acids of phosphorus represent exceptions to the trends cited (20-3.1 to 20-3.3).

4. Descriptive information on occurrence and preparation is tabulated (20.4).

New Concepts

This chapter is designed to utilize previously developed concepts rather than to develop new ones. One new idea is introduced, however—some substances can act as *either* an acid or a base; they are *amphoteric.*

Development

Remember, the theme is: let us apply our basic concepts to some specific elements of the table. We should be able to *predict* behavior in many instances. The third-row elements are not completely new to the student. Chapter 6 devotes several pages (101–103) to them.

Throughout this chapter one of your underlying themes should be that a large change in properties is evident as one considers the elements *across* a row. These tend to be changes of *kind*, as opposed to the changes of magnitude observed within a column. Thus the bonding in a row changes from metallic to covalent; ionization energy from low to high; melting and boiling points from medium to high to low. As an example of the variation of properties within a column, the previous chapter showed that the halogens are all covalently bonded; that ionization energy is high for each; and that phase changes occur in each at moderately low temperatures.

Another theme to stress is that the change observed in a given property is usually the result of changes in several factors. Although each factor may change quite a bit, we observe only the summation of these changes. We have illustrated such combinations of effects several times and will continue to do so.

Finally, remember that in our treatment of energy relations we consider only ΔH; although the randomness factor is mentioned, we do not use it here. The *Background Discussion* gives some reasons why this approximation is acceptable if not exact. But keep in mind that the completely correct way to think of energy changes is to consider them as changes in free energy—a composite of heat and entropy terms,

$$\Delta F = \Delta H - T\Delta S$$

Expt. 32, SOME CHEMISTRY OF THE THIRD-ROW ELEMENTS (Demonstration portion), fits here. See p. 665 for guide.

PHYSICAL PROPERTIES OF THE ELEMENTS (20-1)

Sodium, Magnesium, and Aluminum: Metallic Solids (20-1.1)

Silicon: A Network Solid (20-1.2)

Phosphorus, Sulfur, and Chlorine: Molecular Solids (20-1.3)

Make a real effort to obtain samples of most of the elements of the third row. Have the students examine them carefully to *see* the trends in properties. Be careful in explaining physical properties that you don't fall into the old error of identifying low-melting materials as covalent, high-melting materials as ionic, etc. *Melting point is properly described in terms of the geometry of the bonds,* not in terms of bond types between atoms. Remember that red and white phosphorus both contain covalent bonds. Differences in their properties are not due to bond type but to bond geometry.

When we consider the elements in a row of the periodic table, from alkali metals to column 4, we note a decrease in their tendency to form metallic bonds and an increase in their tendency to form covalent linkages between atoms. We note also that, in columns 3, 4, and 5 of the table, the elements at the bottom exhibit a greater tendency to form metallic bonds than do those at the top. Make a point of this. With this observation in mind, it is not surprising to find that silicon is similar to diamond in many ways, though it is below carbon in the table and shows some trend toward metallic character. It is actually intermediate in properties; it is a semiconductor.

The remarks in the Textbook (p. 365) about silicon may bring up questions about transistors and other devices of modern solid state physics. These are best turned aside as too complex. You might point out that the periodic table summarizes the compositions used. Most transistors (and other solid state devices) are made of highly purified Si or Ge, to which is added a small amount (literally a few parts per million) of elements from an adjacent column. The process is called "doping." If column 3 (the boron column) elements are used, a deficiency of electrons results and gives the positive, or *p*-type, device. Column 5 elements give an excess of electrons and lead to the negative, or *n*-type device. These added atoms can also cause defects, or distortions of the crystal lattice. These defects often contribute to the properties. This whole subject is being intently studied by physicists and chemists.

The structure of the various phosphorus modifications is not always clear-cut. A *very brief* summary of them is given below.

Modification	Density	Structure	Remarks
White	1.82	P_4, tetrahedral	In gas or solution: structure of solid is not known. Above 800°C, some P_2 is formed by dissociation.
Red	~2.2	Unknown	Polymer, mixture of several allotropes.
Violet	2.35	Monoclinic	Polymer.
Black (iron-gray with metallic luster)	2.70	Layers of infinite zig-zag chains.	Polymer, produced only at 200°C and 12,000 atm.

All the colored forms transform to the white allotrope on heating. The polymeric structure makes them all relatively nonvolatile.

THE ELEMENTS AS OXIDIZING AND REDUCING AGENTS (20-2)

Sodium, Magnesium, and Aluminum: Strong Reducing Agents (20-2.1)

Silicon, Phosphorus, and Sulfur: Oxidizing and Reducing Agents of Intermediate Strengths (20-2.2)

Chlorine: A Strong Oxidizing Agent (20-2.3)

From left to right the elements in the table become weaker as reducing agents and stronger as oxidizing agents. Sodium is a strong *reducing* agent; Mg not so strong; Al weaker; Si weaker still; P very weak. Sulfur has reducing tendencies apparent only in special cases; chlorine is predominantly an oxidizing agent; and Ar is inert.

More quantitative data illustrating this point, and data showing the proper quantitative interpretation of thermochemical cycles, are discussed on p. 671. Don't get into difficulty here by confusing reactivity of a metal (i.e., high or low activation energy) with strength as a reducing agent (i.e., $E°$ value or $\Delta F°$ for reduction process). Nor should you confuse rate of reaction with whether a reaction can occur. Silicon is a better reducing agent than phosphorus, but it is difficult to initiate reactions involving Si. Phosphorus, in contrast, reacts readily.

Expt. 32, COMPARISON OF THE RELATIVE ACID-BASE STRENGTH OF THE HYDROXIDES OF ROW 3 (Student portion), fits here. See p. 666 for guide.

THE ACIDIC AND BASIC PROPERTIES OF THE HYDROXIDES (20-3)

Sodium and Magnesium Hydroxides: Strong Bases (20-3.1)

Aluminum Hydroxide: Both an Acid and a Base (20-3.2)

Silicon, Phosphorus, Sulfur, and Chlorine Oxyacids (20-3.3)

The basic behavior of hydroxides may be treated in terms of the breaking of an M—O bond or in terms of the addition of an H^+ to an —OH group still attached to the metal. For example we might write

$$AlOH^{+2}(aq) + H^+(aq) \longrightarrow Al^{+3}(aq) + OH^-(aq) + H^+(aq) \longrightarrow Al^{+3}(aq) + H_2O$$

or

$$AlOH^{+2}(aq) + H^+(aq) \longrightarrow AlOH_2^{+3}(aq) \longrightarrow Al^{+3}(aq) + H_2O$$

The two equations suggest a difference in the actual mechanism by which the process occurs. At the present our experimental methods will not differentiate the two mechanisms, thus there is no need to make a big point of how the aquated ion is formed.

Although we can't legitimately identify differences between $Al^{+3}(aq)$ ions made by different mechanisms, we can note that *a water molecule bound to an ion such as Al^{+3} is polarized, or has a different electron configuration, and hence a different bond energy than a water molecule in the solvent.* A high positive field on the metal cation pulls electrons away from the O—H bond, promoting acid behavior. On the other hand, a weak field resulting from low charge and large size of the cation makes for a weak metal-oxygen bond, making either the loss of an OH^- or the addition of an H^+ to an attached OH^- easier. These are the extremes developed in the Textbook. Amphoteric substances are midway between the extremes and can serve as either acid or base.

The brief discussion on the acids of phosphorus notes that all are true acids of approximately equal strength. No effort is made to justify this point. Indeed, the observant student will note that acids of phosphorus appear to be an exception to the rules developed in the previous paragraphs. A more detailed examination of this point is given in the *Background Discussion* and can be presented to interested students at your discretion. But an immediate and general answer is that, because hydrogens are attached directly to phosphorus in hypophosphorus and phosphorus acids, the formal rules applied to the oxyacids of sulfur and chlorine do not apply to these phosphorus compounds.

OCCURRENCE AND PREPARATION OF THE THIRD-ROW ELEMENTS (20-4)

Occurrence in Nature (20-4.1)

Mode of Preparation of the Element (20-4.2)

Some Properties of the Second- and Third-row Elements (20-4.3)

Sodium

$2NaCl(molten) = 2Na + Cl_2$ electrolysis

or

$2NaOH = 2Na + H_2 + O_2$

Magnesium

$Mg^{+2}(aq) + Ca(OH)_2 = Mg(OH)_2 + Ca^{+2}(aq)$

$Mg(OH)_2 + 2HCl(aq) = MgCl_2 + 2H_2O$

$MgCl_2(molten) = Mg + Cl_2(g)$ electrolysis

Aluminum

$4Al^{+3} + 6O^{-2} = 4Al + 3O_2(g)$ solvent is molten Na_3AlF_6; electrolysis

Silicon

$SiO_2 + 2C = 2CO(g) + Si$ high-temperature electric furnace, Fe added

The product becomes badly contaminated with SiC unless iron is added. In the presence of iron, carbide formation is suppressed, but iron is an impurity. For alloying steel (a major use). the iron is not harmful.

$SiCl_4 + Mg = 2MgCl_2 + Si$

Other reducing metals may be used.

Phosphorus

$2Ca_3(PO_4)_2 + 10C + 6SiO_2 = 6CaSiO_3 + P_4 + 10CO(g)$ high temperature used

$2P_2O_5 + 10C = P_4 + 10CO(g)$

Sulfur

Occurs as an element. This is not too strange, since its reactivity as a reducing agent or as an oxidizing agent is only mild.

Chlorine

See Sodium.

Argon

Obtained by first liquefying, then distilling, air.

EXPERIMENT 32 SOME CHEMISTRY OF THE THIRD-ROW ELEMENTS

PURPOSE. To investigate chemical trends in the third row of the periodic table.

PRELAB DISCUSSION. The teacher's demonstration serves as a prelab discussion for this experiment. Remind students of their previous work using indicators to find the concentration of H^+ in aqueous solutions (Chapter 11 and Expt. 18), and demonstrate the indicators that you plan to have them use in this experiment.

DEMONSTRATION PORTION

EQUIPMENT NEEDED (SEE ALSO STUDENT PORTION BELOW)

samples (1–2 g) of Na, Mg, Al, Si, P_4 (both red and white if desired), S, Cl_2 (about 500 ml), and Ar (100 ml)
12 test tubes (18 × 150 mm)
indicator solution or Hydrion paper
3 *M* HCl (25 ml conc. HCl/100 ml H_2O)
conductivity apparatus (p. 157)
burner

TIMING. Give this demonstration early in Chapter 20. You may do it all in one day or over several days. The demonstration should be complete before the questions at the end of the experiment are assigned.

TIME REQUIRED. Allow one period for the demonstration portion.

PROCEDURE	DISCUSSION
1. *Show each element in its uncombined form.* Page 130 contains directions for making a sodium sample of good visibility. Cl_2 may be freshly generated or obtained from a cylinder.	Show general appearance and discuss reactions with air.
2. Add a small amount of each element to water (save solutions). The activity of Mg with steam may be shown by passing steam over hot Mg turnings in a large pyrex test tube. Once the Mg is warmed the burner should be turned off for safety. The Cl_2 is merely bubbled through water.	Discuss nature of reactions (rates, products, equations).
3. Test the solutions produced in (2) with indicator solution or Hydrion paper.	Call attention to the changing character, from basic to acidic.
4. Add a small amount of each element that has not reacted with water to a little dilute acid (2 or 3 *M* HCl). More concentrated acid may be used if no reaction occurs.	Point out the influence of the protective oxide coating on aluminum. Discuss the products, and write equations.
5. Test the electrical conductivity of the solids by touching the electrodes of the conductivity apparatus to the ends of a short piece of each solid. Na in a glass tube works well for this if the electrodes can be touched to either end. Use only a small piece of phosphorus.	Ask for probable results if we were to try this with solid Cl_2 and Ar. The molecular crystals would not conduct.

STUDENT PORTION

Equipment Needed (per individual or pair)

11 or more test tubes (7 should be 18 × 150 mm; the others may be 13 × 100 mm)

10 ml or 25 ml graduate

Solids (see lab hint 1)

0.2 g Na_2O_2
0.07 g P_4O_{10}
0.2 g MgO
0.3 g hydrous silicon dioxide ($SiO_2 \cdot nH_2O$)

Solutions (see lab hint 2)

3 ml universal indicator (lab hint 2, Expt. 30) or Hydrion paper may be used (see lab hint 4)
3 ml 6 *M* $NH_3(aq)$ (400 ml conc. $NH_3(aq)$/1000 ml)
7 ml 1 *M* $Al(NO_3)_3$ (375 g $Al(NO_3)_3 \cdot 9H_2O$/1000 ml) (see lab hint 3)
10 ml 6 *M* HCl (513 ml conc. HCl/1000 ml)
10 ml 0.5 *M* H_2SO_4 (28 ml conc. H_2SO_4/1000 ml)
10 ml 0.5 *M* $HClO_4$ (55 ml 60% reagent $HClO_4$/1000 ml)
10 ml 6 *M* NaOH (240 g NaOH/1000 ml)

TIME REQUIRED. If reagents are conveniently placed for each student (one supply bottle for each 2 or 3), a 30–40 minute period is enough.

PRECAUTIONS. Remind students that solids are to be added gradually to water. This is important for P_4O_{10}, which reacts violently.

LABORATORY HINTS

1. To save time have on display by each solid reagent a sample of the proper amount in a test tube so that the students may estimate rather than weigh these.
2. Place solutions in dropper bottles (or in squeeze bottles). Be sure not to store 6 *M* NaOH in a bottle with a ground glass joint.
3. Prepare the $Al(OH)_3$ according to the directions given in the Laboratory Manual. If no precipitate forms, add more base. The material must be freshly prepared, because in the procedure given commercial alumina will not dissolve in the acid.
4. If universal indicator is used, a color comparison standard should be provided. The indicators for Expt. 18 are not satisfactory here because their *p*H ranges lie too close to the extremes (*p*H 1–4.5 and *p*H 10–13).

ANSWERS TO QUESTIONS

1. Write an equation for each reaction between a third-row element and water as observed in the class experiment.

   Answer

$$\begin{aligned} Na(s) + H_2O(l) &= Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g) \\ Mg(s) + H_2O(g) &= MgO(s) + H_2(g) \\ Cl_2(g) + H_2O(l) &= 2H^+(aq) + Cl^-(aq) + ClO^-(aq) \end{aligned}$$

2. Write an equation for each reaction observed between each of the oxides Na_2O, MgO, P_4O_{10}, and water.

   Answer

$$2Na_2O(s) + 2H_2O(l) = 4Na^+(aq) + 4OH^-(aq)$$

or

$$Na_2O_2(s) + 2H_2O(l) = 2Na^+(aq) + 4OH^-(aq)$$

Note: The strong NaOH destroys the indicators, so dilute before testing.

$$MgO(s) + H_2O(l) = Mg^{+2}(aq) + 2OH^-(aq) \qquad \text{(very slight solubility)}$$
$$P_4O_{10}(s) + 6H_2O(l) = 9H^+(aq) + HPO_4^{-2}(aq) + H_2PO_4^-(aq) + 2PO_4^{-3}(aq)$$

Most students will write $H^+(aq)$ and $PO_4^{-3}(aq)$, hence this will give an opportunity to discuss equilibria considerations and the stepwise ionization of such polybasic acids as H_3PO_4.

There is no reaction evident between $Al(OH)_3$ and water or $SiO_2 \cdot nH_2O$ and water. The student did not see the oxides of sulfur and chlorine reacting with water, since he was supplied with the acids.

3. Write an equation for each reaction observed between a slightly soluble hydroxide of a third-row element and the following: (a) 6 M HCl; (b) 6 M NaOH.

Answer: (a) $Mg(OH)_2 + 2H^+(aq) = Mg^{+2}(aq) + 2H_2O$
$Al(OH)_3(s) + 3H^+(aq) = Al^{+3}(aq) + 6H_2O$
or
$Al(OH_2)_6{}^{+3}(aq)$
(b) $Al(OH)_3(s) + OH^-(aq) = Al(OH)_4{}^-(aq)$
$SiO_2 \cdot nH_2O + 2OH^-(aq) = SiO_3{}^{-2}(aq) + H_2O$

4. (a) Which of the seven hydroxide solutions were acidic? Which of the seven hydroxide solutions were basic?
(b) How does their basicity and acidity correlate with their position in the third row?

Answer: (a) The hydroxides $ClO_3(OH)$, $SO_2(OH)_2$, $PO(OH)_3$, $SiO_2 \cdot nH_2O$ were acidic, since these tested so with an indicator or when dissolved in a base. The hydroxides NaOH and $Mg(OH)_2$ were basic.
(b) Hydroxides of elements at the left end of the third row are basic; hydroxides of those at the right are acidic.

5. Which of the slightly soluble hydroxides is amphoteric—that is, which dissolved in both 6 M HCl and 6 M NaOH and thus showed both basic and acidic properties?

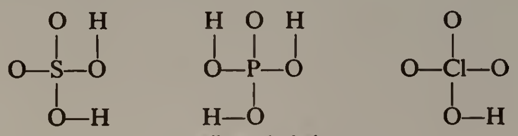
Answer: $Al(OH)_3$, since this dissolved in both an acid and a base.

6. What can be deduced concerning the strength of the H—O bonds in the hydroxides that have acidic properties compared with those that have basic properties?

Answer: The H—O bond is less strong in hydroxides that have acidic properties.

7. Draw diagrams to show the spatial arrangement of the atoms in the hydroxides of sulfur, phosphorus, and chlorine (H_2SO_4, H_3PO_4, $HClO_4$).

Answer



all tetrahedral

This question is intended to emphasize the atomic geometry in these acids. It is best not to bring up the double bonds to oxygen in order to avoid having to discuss the situation in which more than eight valence electrons surround the central atom.

Supplementary Material

None.

Background Discussion

In this chapter we have examined the physical properties of the third-row elements, their oxidizing and reducing properties, and the acid–base characteristics of their hydroxides. We have approached these properties in terms of simple models and ideas developed earlier in the book. It would be comforting, indeed, if we could tell you now that your students, armed with our simple array of concepts, could correctly predict all of the facts of inorganic and organic chemistry. *Unfortunately this is not so.* Even the most experienced chemists are used to finding that their predictions are not confirmed by the facts, but this does not make them less willing to predict. "Wondering why" a prediction failed is a favorite sport—one that frequently results in basic contributions to chemistry. We are going to examine in more detail the predictions made in Chapter 20 and explore more carefully the basis for those predictions. Frequently, the process is much more complex than our initial version.

PHYSICAL PROPERTIES OF THE ELEMENTS

In our discussion of the physical properties of the elements, network solids with strong bonds are recognized as nonvolatile substances; larger molecules with many atoms are recognized as being less volatile than molecules composed of smaller groups of atoms; and the light, monatomic elements are recognized as being the most volatile of all. We emphasize that the difference in volatility between a many-atom molecule and a diatomic molecule *is not due to differences in weight* (that is, to forces of gravity) as might at first seem reasonable, *but to differences in van der Waals forces which are partly related to the size of the molecule.*

A simple calculation of the energy required to lift a mole of molecules will show how small this value is. Suppose we must lift S_8 molecules 2 meters; then the work is

$$\left(8 \times 32 \frac{\text{g}}{\text{mole}}\right)(200\ \text{cm})\left(980 \frac{\text{cm}}{\text{sec}^2}\right)$$

This is 5.0×10^7 ergs/mole or 1.2 calories—quite small compared to 20,160 calories for the total energy of vaporization.

We noted in the *Development* section that the comparison of sulfur and phosphorus was really more complex than our simple treatment implied. This is due in large measure to the complexities of liquid sulfur. After the initial melting process, liquid sulfur goes through many changes before it finally vaporizes. The monoclinic and rhombic forms of solid sulfur are made up of S_8 rings. At the melting point (119° for monoclinic sulfur) the orderly arrangement of these rings in a crystal lattice is destroyed, and we obtain a light-yellow, free-flowing liquid, composed largely of S_8 units. This is the lambda form of liquid sulfur. As this form is heated it becomes more and more viscous and deepens in color. At 200° it is dark brown and viscous. Above 250°C the viscosity diminishes, and at 400° it is again quite mobile.

The viscosity (and other) changes of sulfur during heating can be explained in this way:

melting	S_8 rings freed to move
viscous region (~170–225°C)	S_8 rings open and polymerize
mobile region (250°C)	polymer chain broken to shorter units; some rings reform
vaporization	quite short chains or rings (at 450°C and 500 mm the vapor is 54% S_8, 37% S_6, 5% S_4, and 4% S_2)

A change in molecular arrangement in the liquid can bring about a drastic change in volatility. We are not really surprised that a system composed of polymeric sulfur chains shows a very low vapor pressure. Molecules leave the liquid only as the chains are broken up into shorter units. Phosphorus does not show this odd behavior in the liquid state, but it does have numerous allotropic forms, several of them polymeric.

You may notice that our description of metals has been terse and that we have made no effort to relate many of the obvious properties of metals to their electronic structure. For example, we haven't considered why metals have a luster or why gold and copper have distinctive colors. Attempts to explain these very obvious and simple properties lead us to theoretical complications well beyond our purpose here. A simple treatment of the details of the structure and properties of metals is many years away; this is one of the challenges of tomorrow's chemistry.

THE ELEMENTS AS OXIDIZING AND REDUCING AGENTS

The Textbook discussion summarizes evidence of several kinds which shows that the elements become weaker reducing agents and better oxidizing agents from left to right along a row of the table. A more standardized and quantitative comparison of the reducing properties of the elements can be obtained by comparing *E*° values for the elements as reducing agents in acidic solution.

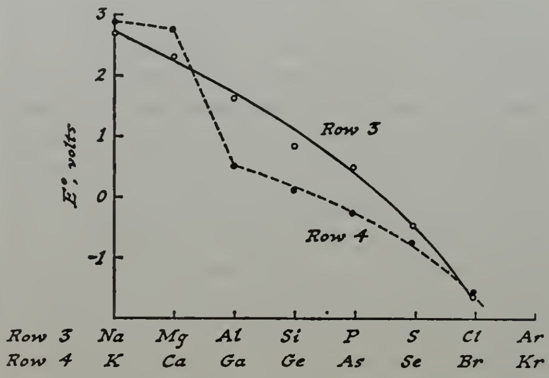
E° values for the third row are given in Table 20-I and are plotted in Figure 20-1. A rapid decrease in strength of the element as a reducing agent is clearly apparent. Note that Si is somewhat out of line; this fact may well be associated with the unusual stability of the solid silicon structure which we noticed earlier. A similar trend is noted in basic solution; see Figure 20-2.

Table 20-I

E° Values for Third-row Elements in Acidic Solution

Reaction	*E*°
$Na = Na^+ + e^-$	2.71
$Mg = Mg^{+2} + 2e^-$	2.37
$Al = Al^{+3} + 3e^-$	1.66
$Si + H_2O = SiO_2 + 4H^+ + 4e^-$	0.86
$P + 2H_2O = H_3PO_2 + H^+ + e^-$	0.51
$P + 3H_2O = H_3PO_3 + 3H^+ + 3e^-$	0.50
$S + 3H_2O = H_2SO_3 + 4H^+ + 4e^-$	−0.45
$\frac{1}{2}Cl_2 + H_2O = HClO + H^+ + e^-$	−1.63
Ar = no reaction	

Fig. 20-1. **E°** *for oxidation of third- and fourth-row* **elements** *in acidic solution.*



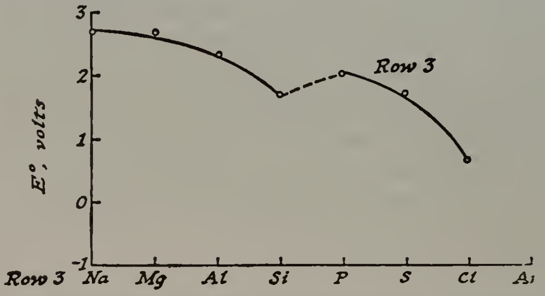


Fig. 20-2. **E° for oxidation of third-row elements** *in basic solution.*

The elements of the fourth row show something of the same trends found in the elements

Table 20-II

E° Values for Selected Fourth-row Elements in Acidic Solution

Reaction	*E*°
$K = K^+ + e^-$	2.92
$Ca = Ca^{+2} + 2e^-$	2.87
$Ga = Ga^{+3} + 3e^-$	0.53
$Ge + 2H_2O = GeO_2 + 4H^+ + 4e^-$	0.15
$As + 3H_2O = H_3AsO_3 + 3H^+ + 3e^-$	−0.25
$Se + 3H_2O = H_2SeO_3 + 4H^+ + 4e^-$	−0.74
$Br_2 + H_2O = HBrO + H^+ + e^-$	−1.59
Kr = no reaction	

of the third row. Oxidation potentials for the nontransition elements of the fourth row are given in Table 20-II for comparison with the data for the third row.

Notice that potassium and calcium are stronger reducing agents than sodium and magnesium but that at gallium the curve drops well below the point for aluminum (see Figure 20-1). This effect is related to the fact that the Ga^{+3} ion has eighteen outer electrons as compared to eight for the Al^{+3} ion. The effects of the completed 3*d* orbitals then follow consistently from Ga to Se, for which the oxidation potentials are significantly lower than those of the third-row elements.

One other caution relative to the interpretation of the above data in terms of descriptive chemistry must be inserted. The foregoing $E°$ values for the third-row elements lead us unambiguously into certain conclusions which appear to be in conflict with known descriptive chemistry. For example, the potential values suggest that silicon is a *more reactive* element than white phosphorus, yet anyone who has handled both white phosphorus and silicon knows that white phosphorus is stored under water to prevent it from catching on fire when in contact with air, whereas silicon is a surprisingly unreactive elementary substance. The anomaly is easily explained; silicon, because it has an unusually stable elemental structure, has a very high activation energy, thus reactions involving silicon are hard to start. Once a reaction is started, however, silicon is a powerful reducing agent. Phosphorus, on the other hand, has a low activation energy and appears to be quite reactive. Other examples are numerous. Aluminum is sometimes considered to be a noncorrodable, unreactive metal, yet the electrode potential suggests that it is a very strong reducing agent. The two facts are harmonized by recognition of the fact that exposed aluminum is covered with a closely adhering coat of Al_2O_3 which must be broken before aluminum can react. The oxide Al_2O_3 is quite unreactive, but once reaction of aluminum is initiated, it becomes a very powerful reducing agent. It can be used to produce elemental iron and silicon from their oxides in vigorous, almost violent, reactions.

THERMOCHEMICAL CYCLES IN CELL OPERATION

In several earlier situations we have found it instructive to use a thermochemical cycle to analyze factors involved in a chemical process. A brief form of such an analysis is applied to the $E°$ values for sodium in the Textbook, but you may benefit from a more quantitative explanation. Let us consider the oxidation of a hypothetical metal, *M*:

$$M(s) = M^+(aq) + e^-$$

Although our thermochemical cycle uses only ΔH, and not ΔF, the analysis of a cycle provides interesting bits of information.

Consider the following steps:

1. Solid metal is vaporized; an endothermic process:

   $$M(s) + \text{heat} = M(g) \qquad \Delta H_1 \text{ is positive}$$

2. The gaseous metal is ionized; an endothermic process:

   $$M(g) + \text{heat} = M^+(g) + e^- \qquad \Delta H_2 \text{ is positive}$$

3. The gaseous metal ion is dissolved in water; an exothermic process:

   $$M^+(g) + nH_2O = M^+(aq) + \text{heat} \qquad \Delta H_3 \text{ is positive}$$

The total process is then:

$$M(s) + nH_2O \longrightarrow M^+(aq) + e^- \qquad \Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Our analysis indicates that ΔH_{total} will be more negative and that the process will have a greater tendency to occur spontaneously if ΔH_1 and ΔH_2, the positive quantities, are small. These conditions are met if a metal is easily vaporized or easily ionized. By the same token, a large negative value for the heat of hydration of the gaseous ion, ΔH_3, makes ΔH_{total} more negative.

What values do the quantities ΔH_1, ΔH_2, ΔH_3, and ΔH_{total} have, and what is their relation to $E°$? Let us consider Na and H_2 as examples.

	Sodium	kcal
1.	$Na(s) + 23\ kcal = Na(g)$	$\Delta H_1 = 23$
2.	$Na(g) + 118\ kcal = Na^+(g) + e^-$	$\Delta H_2 = 118$
3.	$Na^+(g) + H_2O(excess) = Na^+(aq) + 97\ kcal$	$\Delta H_3 = -97$
Total:	$Na(s) + H_2O(excess) = Na^+(aq) + e^-$	$\Delta H_{total} = 23 + 118 - 97 = +44\ kcal$

	Hydrogen	kcal
1.	$\frac{1}{2}H_2(g) + 52\ kcal = H(g)$	$\Delta H_1 = 52$
2.	$H(g) + 313\ kcal = H^+(g) + e^-$	$\Delta H_2 = 313$
3.	$H^+(g) + H_2O = H^+(aq) + 256\ kcal$	$\Delta H_3 = -256$
Total:	$\frac{1}{2}H_2(g) + H_2O = H^+(aq) + e^-$	$\Delta H_{total} = 52 + 313 - 256 = +109\ kcal$

At first glance it may be surprising to find that ΔH_{total} for converting sodium to aquated Na^+ is positive (*endothermic* process), particularly when we remember that Na reacts exothermically when placed in water, forming $Na^+(aq)$. Remember, however, that the equation

$$Na(s) = Na^+(aq) + e^-$$

is *not* an adequate description of the reaction of sodium and water. It gives no account of the hydrogen which is formed. The half-cell equations for *sodium* and *hydrogen* must be *combined* to describe the reaction of sodium in water:

$$\begin{array}{ll} Na(s) + H_2O = Na^+(aq) + e^- & \Delta H = +44\ kcal \\ e^- + H^+(aq) = \frac{1}{2}H_2(g) + H_2O & \Delta H = -109 \\ \hline Na(s) + H^+(aq) = Na^+(aq) + \frac{1}{2}H_2(g) & \Delta H = -65 \end{array}$$

When we consider the whole process as in the last equation, ΔH_{total} is negative, as our past experience indicates. We certainly have no past experimental experience to indicate that ΔH_{total} for the equation $Na(s) = Na^+(aq) + e^-$ should be negative. In fact, there is no experiment which reveals ΔH for this process.

What is the relationship between the above values of ΔH and the value of E° for Na? Our earlier equations for E° gave the relationship

$$\Delta F = -nFE^\circ$$

and we know that

$$\Delta F = \Delta H - T\Delta S$$

In short, we may write

$$-nFE^\circ = \Delta H - T\Delta S$$

or

$$E^\circ = \frac{-\Delta H}{nF} + \frac{T\Delta S}{nF}$$

If we substitute the ΔH value (−65 kcal/mole) above, we find that it alone accounts for almost all the voltage of the Na-$Na^+(aq)$ half-cell. There are two points to note:

(1) Our arbitrary choice of zero potential for the H^+-$H_2(g)$ half-cell means all the other E° values include the ΔH of this reaction.

(2) The predominance of the ΔH term (over ΔS) happens often enough that we can use ΔH alone *as a first approximation* for analyzing E° values.

A number of qualitative relationships arising from this approximation are well known to you. A high value of E° should be expected if $\Delta H_{sublimation}$ and $\Delta H_{ionization}$ for the metal are low. You have frequently told students that Na will lose electrons easily, hence its E° value is high. As the above discussion shows, the fact that Na loses electrons readily is not the whole story, but it is certainly one of the more important parts of the more complete analysis.

THERMOCHEMICAL CYCLES IN REACTIONS NOT INVOLVING A SOLVENT

Finally, it is fruitful to note that the preceding discussion is appropriate only for considering ions in aqueous solution. A reaction carried out in the absence of water involves a new cycle, in which the lattice energy of the solid formed is an important term. A cycle suitable for considering the reaction

$$2Al(s) + Fe_2O_3(s) = 2Fe(s) + Al_2O_3(s)$$

is described below.

1. Metallic aluminum is vaporized:

$$2Al(s) + 150\text{ kcal} = 2Al(g) \qquad \Delta H_1 = +150\text{ kcal}$$

Heat is absorbed.

2. Aluminum vapor is ionized:

$$2Al(g) + 2464\text{ kcal} = 2Al^{+3}(g) + 6e^- \qquad \Delta H_2 = +2464\text{ kcal}$$

Heat is absorbed.

3. Solid iron oxide is broken into its component ions when the *lattice energy* of Fe_2O_3 is supplied:

$$Fe_2O_3(s) + 3192\text{ kcal} = 2Fe^{+3}(g) + 3O^{-2}(g) \qquad \Delta H_3 = +3192\text{ kcal}$$

Heat is absorbed.

4. The $Fe^{+3}(g)$ ion picks up electrons to give metallic iron in the vapor phase:

$$2Fe^{+3}(g) + 6e^- = 2Fe(g) + 2514\text{ kcal} \qquad \Delta H_4 = -2514\text{ kcal}$$

Heat is liberated.

5. The iron vapor condenses to give iron metal:

$$2Fe(g) = 2Fe(s) + 194\text{ kcal} \qquad \Delta H_5 = -194\text{ kcal}$$

Heat is liberated.

6. The $Al^{+3}(g)$ ions and the remaining $O^{-2}(g)$ ions combine to give Al_2O_3 and give up the lattice energy of alumina:

$$2Al^{+3}(g) + 3O^{-2}(g) = Al_2O_3(s) + 3301\text{ kcal} \qquad \Delta H_6 = -3301\text{ kcal}$$

Heat is liberated.

The sum of all equations gives

$$2Al(s) + Fe_2O_3(s) = 2Fe(s) + Al_2O_3(s) + \text{heat}$$

$$\Delta H_{\text{total}} = \Delta H_t = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

$$\Delta H_t = 150 + 2464 + 3192 - 2514 - 194 - 3301$$

$$\Delta H_t = -203\text{ kcal}$$

As written above, ΔH_1, ΔH_2, and ΔH_3 are positive values. A large negative value for ΔH_t will be favored when ΔH_1, ΔH_2, and ΔH_3 have small positive values. On the other hand, ΔH_4, ΔH_5, and ΔH_6 have a negative sign, and a large *negative* value of ΔH_t (process favorable) can be attained by large negative values for ΔH_4, ΔH_5, and ΔH_6. The existence of a large negative value for ΔH_6 is specifically indicated in the Textbook discussion of the high lattice energy for Al_2O_3. This favors the process, since it implies a large negative value for ΔH_6. The overall process involves, however, sums of *very* large numbers, and a very small relative difference is of chemical significance. Since we have no way to measure the terms such as lattice energy directly, the foregoing data tend only to "explain," not predict, results.

THE ACIDS OF PHOSPHORUS

Arguments given in the Textbook for the strength of acids and bases lead to the conclusion that acids formed by elements in a higher oxidation state (i.e., higher oxidation number) should be stronger than those formed by elements in a lower oxidation state (i.e., lower oxidation number). This we find in agreement with such a generalization that says H_2SO_4 (S oxidation number = 6) is stronger than H_2SO_3 (S oxidation number = 4); $HClO_4$ (Cl oxidation number = 7) is stronger than $HClO_3$ (Cl oxidation number = 5). The acids of phosphorus present an exception to this generalization in that H_3PO_2, H_3PO_3, and H_3PO_4 are all of almost equal strength. This observation can be rationalized (if not predicted) on the basis of the known structures if we assume that hydrogen, attached directly to phosphorus in H_3PO_2 and H_3PO_3, is as effective in removing negative charge from the phosphorus as was the oxygen which the hydrogen replaced.

Answers to Exercises and Problems

Ex. 20-1. Write out the electron configuration of sodium, magnesium, and aluminum and find the ionization energies for all their valence electrons (Table 20-IV, p. 374). Account for the trend in the heats of vaporization and boiling points (Table 20-1) of these elements. Compare your discussion with that given in Section 17-1.3.

Table 20-1 (from Textbook)

Heats of Vaporization and Boiling Points of Metals

	Na	Mg	Al
ΔH_{vap}, kcal/mole	23.1	31.5	67.9
b.p. (°C)	889	1120	2327

Answer

		Ionization Energies of Successive Electrons in kcal/mole of electrons		
Na	$1s^2\ 2s^22p^6\ 3s^1$	118		
Mg	$1s^2\ 2s^22p^6\ 3s^2$	176	195	
Al	$1s^2\ 2s^22p^6\ 3s^23p^1$	138	244	656

These metals have successively more valence electrons per atom and are thus held together more tightly. This, combined with the increase in nuclear charge, explains the increase in energy needed to vaporize them and the temperature at which they boil.

Ex. 20-2. Using the principles discussed in Chapter 17, attempt to arrange the third-row elements from silicon through argon in order of increasing boiling point, starting with the element you think has the lowest boiling point. Be prepared to defend in a class discussion your choice of the position you assign each element in this sequence.

Answer

The order of increasing boiling points is: Ar, Cl, P, S, Si.

Argon b.p. = −185.7°C. The atoms have no orbitals available for bonding, hence only weak van der Waals forces operate between atoms.

Chlorine b.p. = −34.1°C. The element has discrete diatomic molecules, which exhibit more van der Waals interaction than do the smaller monatomic molecules of argon.

Phosphorus b.p. = 280°C. White phosphorus has discrete P_4 molecules in the vapor, in the solid, and probably in the liquid. See the following paragraph.

Sulfur b.p. = 445°C. See the following paragraph.

The boiling points of sulfur and phosphorus represent a reversal in order, based upon their arrangement in the periodic table. Sulfur is less volatile than phosphorus, yet smooth periodic relationships would suggest that sulfur should be more volatile. The only obvious correlation available to the student that would enable him to explain this anomaly is the observation that the unit of phosphorus is P_4, whereas that of sulfur is S_3. If we then invoke our "rule of thumb," which states that the strength of the van der Waals forces between molecules increases as molecular complexity increases, then we would expect stronger forces between S_8 units than between P_4 units, and sulfur should have the higher boiling point.

The above paragraph probably takes the student far enough with regard to the intent of the original question, but in reality the situation is, of course, far more complex, owing to the changes which occur in liquid sulfur. These are described in more detail in the *Background Discussion*. The more involved explanation leads to the same conclusion as does our simple one.

Be careful here to avoid offering the explanation that S_8 molecules are less volatile than the lighter P_4 molecules because S_8 is *heavier* than P_4. Gravitational forces are *trivial* in the process of vaporization. Higher interaction forces between molecules, not the greater weight of S_8 molecules, account for the lower volatility of sulfur.

Silicon m.p. = 1413°C; b.p. = 2355°C. The solid is a three-dimensional network, held together by chemical bonds between the atoms, not by van der Waals forces. In the liquid, the potential for forming covalent bonds still exists, and indeed many covalent bonds still do exist. The liquid is thought to consist of irregular chunks of silicon atoms bound together much as they were in the solid. To vaporize the liquid involves breaking still more covalent bonds and requires a higher temperature.

Ex. 20-3. Water saturated with SO_2 gas is a relatively mild but quite useful reducing agent. Which of the following aqueous ions might be reduced by it?

(a) Fe^{+3} to Fe^{+2}.
(b) Cu^{+2} to Cu^{+}.
(c) Sn^{+4} to Sn^{+2}.
(d) Hg^{+2} to $Hg(l)$.

Answer

(a) and (d), not (b) and (c). See $E°$ values.

$Sn^{+2} \longrightarrow 2e^- + Sn^{+4}$ $E° = -0.15$ volt
$Cu^{+} \longrightarrow e^- + Cu^{+2}$ $E° = -0.15$ volt
$SO_2(g) + 2H_2O \longrightarrow 2e^- + SO_4^{-2} + 4H^+$ $E° = -0.17$ volt
$Fe^{+2} \longrightarrow e^- + Fe^{+3}$ $E° = -0.77$ volt
$Hg(l) \longrightarrow 2e^- + Hg^{+2}$ $E° = -0.78$ volt

Ex. 20-4. Water containing dissolved Cl_2 is a useful oxidizing agent. Which of the following aqueous ions might be oxidized by it?

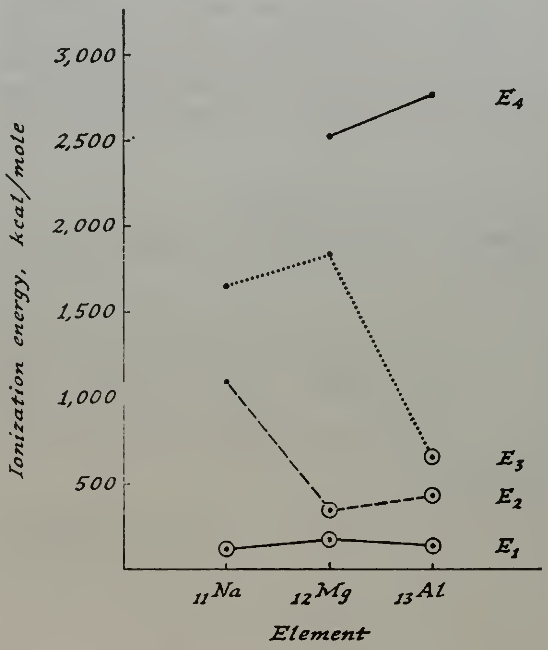
(a) Fe^{+2} to Fe^{+3}.
(b) Cu^{+} to Cu^{+2}.
(c) Sn^{+2} to Sn^{+4}.
(d) Mn^{+2} to $MnO_2(s)$.
(e) Mn^{+2} to MnO_4^-.

Answer

If the solution has Cl^- equal to 1 M, the concentration for which values in Appendix 8 apply, then $E°$ is $+1.36$ volts for reduction of $Cl_2(g)$ to $Cl^-(aq)$. This is a greater positive $E°$ than that of any half-reaction listed except (e). Mn^{+2} would not be oxidized to MnO_4^-.

Pr. 1. Make a graph with an energy scale extending on the ordinate from zero to 3000 kcal/mole and with the abscissa marked at equal intervals with the labels Na, Mg, and Al. Now plot and connect with a solid line the first ionization energies, E_1, of these three elements (see Table 20-IV). Plot E_2, and connect with a dashed line, E_3 with a dotted line, and E_4 with a solid line. Draw a circle around each ionization energy that identifies a valence electron.

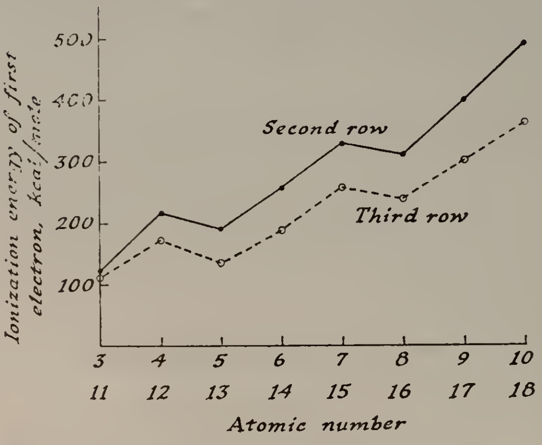
Answer



Pr. 2. Plot the ionization energy of the first electron removed from the atoms of both the second- and third-row elements against their atomic number (abscissa). What regularity do you observe?

Answer

Ionization energy increases as the row is traversed.



Pr. 3. Silicon melts at 1410°C and phosphorus (white) at 44°C. Explain this very great difference in terms of the structures of the solids.

Answer

Silicon, with its tetrahedral bonding, forms a network solid with covalent bonds. To melt silicon, covalent bonds must be broken, hence a very high temperature is needed. The P_4 molecule consumes the bonding capability of each phosphorus atom. These molecules are bonded together only by weak van der Waals interactions, therefore the melting point is low.

Pr. 4. Recalling the chemistry of nitrogen, write formulas for phosphorus compounds corresponding to

(a) ammonia,
(b) hydrazine,
(c) ammonium iodide.

Answer

(a) PH_3, phosphine.
(b) P_2H_4, "diphosphine."
(c) PH_4I, phosphonium iodide. This compound exists, but is much less stable than NH_4I.

Pr. 5. Write the formula for the fluoride you expect to be most stable for each of the third-row elements.

Answer

NaF, MgF_2, AlF_3, SiF_4, PF_5 or PF_3, SF_6 or SF_2, ClF, none with Ar. See p. 191 for remarks about XeF_4. Such compounds have not been reported for argon (as of the beginning of 1963).

Pr. 6. The heat of reaction for the formation of $MgO(s)$ from the elements is -144 kcal/mole of $MgO(s)$. How much heat is liberated when magnesium reduces the carbon in CO_2 to free carbon? See Table 7-II.

Answer: $\Delta H = -97$ kcal/mole MgO.

Answer

The overall reaction is:

$$2Mg(s) + CO_2(g) = 2MgO(s) + C(s)$$

This can be obtained as a result of the following reactions:

$$\begin{array}{rl} 2Mg(s) + O_2(g) = 2MgO(s) & \Delta H = -2(144)\text{ kcal} \\ CO_2(g) = C(s) + O_2(g) & \Delta H = +94\text{ kcal} \\ \hline 2Mg(s) + CO_2(g) = 2MgO(s) + C(s) & \Delta H = 194\text{ kcal} \end{array}$$

or

$$\Delta H = -97\text{ kcal/mole } MgO(s)$$

Pr. 7. Magnesium oxide is an ionic solid that crystallizes in the sodium chloride type lattice.

(a) Explain why MgO is an ionic substance.
(b) How many calories would be required to decompose 8.06 grams of MgO? (Use the data in problem 6.)
(c) Draw a diagram of a crystal of MgO.

Answer

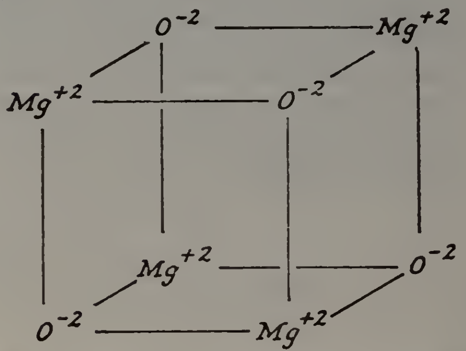
(a) Magnesium has low ionization energy, and oxygen has high ionization energy. These are conditions under which ionic bonding is expected.

(b)

$$8.06\text{ g MgO} = (8.06\text{ g})\left(\frac{1}{40.3\text{ g/mole}}\right)$$
$$= 0.200\text{ mole}$$
$$\text{heat absorbed} = (0.200\text{ mole})\left(+144\,\frac{\text{kcal}}{\text{mole}}\right)$$
$$= 28.8\text{ kcal}$$

Notice that the *formation* of MgO is exothermic ($\Delta H = -144$ kcal/mole), hence the *decomposition* is endothermic ($\Delta H = +144$ kcal/mole).

(c)



Pr. 8. Aluminum oxide (Al_2O_3) is thought to dissociate at high temperature (1950°C) according to the equation: $2Al_2O_3(s) = 4AlO(g) + O_2(g)$. The total vapor pressure at 1950°C is about 1×10^{-6} atm.

(a) Which element is oxidized and which is reduced in this reaction?
(b) Write the equation for the equilibrium constant.

(c) Calculate its value using partial pressure as the unit of "concentration" for the gases.

Answer

(a) Aluminum is reduced from oxidation number of +3 to +2. Oxygen is oxidized from −2 to zero.

(b) $K = [O_2][AlO]^4$.

(c) The gas partial pressures are:

for O_2: $\frac{1}{5}(1 \times 10^{-6}) = 0.2 \times 10^{-6}$ atm

for AlO: $\frac{4}{5}(1 \times 10^{-6}) = 0.8 \times 10^{-6}$ atm

$$K = (0.2 \times 10^{-6})(0.8 \times 10^{-6})^4 = 0.82 \times 10^{-31}$$

or

$$1 \times 10^{-31}$$

After this answer is obtained, some good questions to use in testing comprehension of the significance of the size of K are:

(1) Does a large fraction of $Al_2O_3(s)$ dissociate at 1950°C? (No.)

(2) Had K been very large, would $Al_2O_3(s)$ be useless as a refractory? (Yes, if thermodynamics were the only consideration. The rate might be so slow as to make its use practical. Our houses are generally made of materials that are not thermodynamically stable relative to combination with oxygen, but the rate of reaction is so low that nothing happens until the temperature is raised too high.)

Pr. 9. Explain the observation that phosphorus acts both as a weak reducing agent and as a weak oxidizing agent.

Answer

The valence electrons of phosphorus are held more strongly than are those of sodium, but less strongly than are those of chlorine. The ionization energy of P lies between that of Na and Cl. This can be interpreted as meaning that Cl has a greater, and Na a lesser, tendency to gain electrons than has P. When P combines with Cl, the bond-forming electrons will be nearer the Cl than the P. The P has "lost electrons"; it has acted as a reducing agent. When P combines with Na, the Na "loses" electrons; the P acts as an oxidizing agent. The small difference between the ionization energy of P and the ionization energies of other elements suggests why P is found to act as a weak reducing agent or a weak oxidizing agent.

Pr. 10. (a) What are the oxidation numbers of phosphorus in the two compounds phosphorous acid, H_3PO_3, and phosphoric acid, H_3PO_4?

(b) From the $E°$ values in Appendix 3, decide which of the following substances might be reduced by phosphorous acid: Fe^{+2}; Sn^{+4}; I_2; Cr^{+3}.

$$H_2O + H_3PO_3 \longrightarrow H_3PO_4 + 2H^+ + 2e^- \qquad E° = 0.276 \text{ volt}$$

(c) Balance the equation for the reaction between phosphorous acid and Fe^{+3} and calculate $E°$ for the reaction.

Answer

(a) H_3PO_3: oxid. no. of phosphorus = +3
H_3PO_4: oxid. no. of phosphorus = +5

(b) According to the $E°$ values, Sn^{+4} and I_2 might be reduced (the $E°$ values are, respectively, −0.15 volt and −0.53 volt), but Fe^{+2} and Cr^{+3} will not be appreciably reduced.

(c) Since $E°$ is +1.05 volts, the reaction has a high tendency to proceed as written below.

$$\begin{array}{rcl} H_2O + H_3PO_3 \longrightarrow H_3PO_4 + 2H^+ + 2e^- & & E° = +0.276 \text{ volt} \\ -2(Fe^{+2} \longrightarrow Fe^{+3} + e^-) & & E° = -0.77 \text{ volt} \\ \hline H_2O + H_3PO_3 + 2Fe^{+3} \longrightarrow 2Fe^{+2} + H_3PO_4 + 2H^+ & & E° = +0.276 - (-0.77) \\ & & \quad = 1.046 \text{ volts} \end{array}$$

Pr. 11. Answer the following in terms of electron configuration and ionization energy:

(a) Which elements in the second and third rows are strong
 (i) oxidizing agents?
 (ii) reducing agents?

(b) What properties do strong oxidizing agents have?

(c) What properties do strong reducing agents have?

Answer

(a) The elements on the right are good oxidizing agents.

Second row: oxygen and fluorine.
Third row: chlorine.

The elements on the left are good reducing agents.

Second row: lithium.
Third row: sodium and magnesium.

(b) Good oxidizing agents have:
  (i) almost-filled valence orbitals;
  (ii) high ionization energies.
(c) Good reducing agents have:
  (i) a few electrons more than an inert-gas electron configuration;
  (ii) low ionization energy.

Pr. 12. Of the elements Na, Mg, Al, which one would you expect to be most likely to

(a) form a molecular solid with chlorine?
(b) form an ionic solid with chlorine?

Answer

(a) It has been found that the less the difference in ionization energies between two bonded atoms, the greater the covalent character of the bond. On this basis, aluminum would most likely form a molecular solid with chlorine. The dimer Al_2Cl_6 is known to exist as a molecular liquid. This substance undergoes some strange changes as it is warmed. The solid is apparently ionic (it conducts electricity). Upon melting, there is a large (almost two-fold) increase in volume, and the conductivity vanishes. Apparently, discrete molecules are formed, which cannot pack as closely as the ions, nor conduct current.

(b) By the converse of the above argument, sodium is most likely to form an ionic solid with chlorine.

Pr. 13. One kilogram of sea water contains 0.052 mole of magnesium ion. What is the minimum number of kilograms of sea water that would have to be processed in order to obtain one kg of $Mg(OH)_2$?

Answer: 3.3×10^2 kg of sea water.

Answer

One mole of $Mg(OH)_2$ requires one mole of Mg^{+2}. Thus one kg of sea water will provide 0.052 mole of $Mg(OH)_2$.

$$\left[\frac{\text{moles } Mg(OH)_2}{\text{kg sea water}}\right]\left[\frac{1}{\text{moles } Mg(OH)_2/\text{kg}}\right]$$

$$= (0.052)\left(\frac{58 \times 10^{-3}}{1}\right) = 3.0 \times 10^{-3}\,\frac{\text{kg } Mg(OH)_2}{\text{kg sea water}}$$

What we want is the reciprocal of this,

$$\frac{1}{\text{kg } Mg(OH)_2/\text{kg sea water}}$$

$$= \frac{1}{3.0 \times 10^{-3}} = 3.3 \times 10^2\,\frac{\text{kg sea water}}{\text{kg } Mg(OH)_2}$$

Pr. 14. Why is aluminum hydroxide classed as an amphoteric compound?

Answer

Amphoteric substances can act as an acid and also as a base. This property is displayed by $Al(OH)_3$, since it dissolves readily *either* in strong acid or in strong base, though it has low solubility in a neutral solution.

$$Al(OH)_3(s) + 3H^+(aq) \longrightarrow Al^{+3}(aq) + 3H_2O$$
$$Al(OH)_3(s) + OH^-(aq) \longrightarrow Al(OH)_4^-(aq)$$

Pr. 15. Some of the following common compounds of the third-row elements are named as hydroxides and some as acids.

$NaOH$	sodium hydroxide
$Mg(OH)_2$	magnesium hydroxide
$Al(OH)_3$	aluminum hydroxide
$Si(OH)_4$	silicic acid (usually written H_4SiO_4)
$P(OH)_3$	phosphorous acid (usually written H_3PO_3)
$S(OH)_2$	not known
$Cl(OH)$	hypochlorous acid (usually written HOCl)

(a) Explain why these compounds vary systematically in their acid–base behavior.
(b) Write equations that show the reactions of each of these substances either as acids, as bases, or both.

Answer

(a) As the ionization energy of the atom M in the compound $M(OH)_n$ increases, electrons are drawn away from the oxygen atom, with the result that the oxygen atom binds its proton more weakly. Hence the acid strength tends to increase and base strength to decrease from left to right in the periodic table.

(b)

$$NaOH(s) + H^+(aq) \longrightarrow Na^+(aq) + H_2O$$
$$Mg(OH)_2(s) + 2H^+(aq) \longrightarrow Mg^{+2}(aq) + 2H_2O$$

$$\left.\begin{array}{l} Al(OH)_3(s) + 3H^+(aq) \longrightarrow \\ \qquad Al^{+3}(aq) + 3H_2O \\ Al(OH)_3(s) + OH^-(aq) \longrightarrow \\ \qquad Al(OH)_4^-(aq) \end{array}\right\} \text{Al(OH)}_3 \text{ is amphoteric}$$

$$Si(OH)_4(s) + OH^-(aq) \longrightarrow SiO(OH)_3^-(aq) + H_2O$$

$$P(OH)_3(s) + OH^-(aq) \longrightarrow PO(OH)_2^-(aq) + H_2O$$

$$ClOH(aq) + OH^-(aq) \longrightarrow Cl^-(aq) + H_2O$$

Pr. 16. A solution containing 0.20 M H_3PO_3, phosphorous acid, is tested with indicators, and the $H^+(aq)$ concentration is found to be 5.0×10^{-2} M. Calculate the dissociation constant of H_3PO_3, assuming that a second proton cannot be removed.

Answer

$$H_3PO_3 \rightleftharpoons H^+(aq) + H_2PO_3^-(aq)$$

$$K_A = \frac{[H^+][H_2PO_3^-]}{[H_3PO_3]}$$

$$[H^+] = [H_2PO_3^-] = 5.0 \times 10^{-2}\ M$$

$$[H_3PO_4] = 0.20 - 0.050 = 0.15\ M$$

$$K_A = \frac{(5.0 \times 10^{-2})(5.0 \times 10^{-2})}{(0.15)} = 1.7 \times 10^{-2}$$

Note: The second dissociation constant is 7×10^{-7}, hence this reaction forms only a negligible amount of H^+ and HPO_4^{-2}. Note also that the dissociation of H_3PO_3 cannot be neglected in estimating its concentration.

Pr. 17. Elemental phosphorus is prepared by the reduction of calcium phosphate, $Ca_3(PO_4)_2$, with coke in the presence of sand, SiO_2. The products are phosphorus, calcium silicate ($CaSiO_3$), and carbon monoxide.

(a) Write the equation for the reaction.

(b) Using 75.0 kg of the ore, calcium phosphate, calculate how many grams of P_4 can be obtained and how many grams of coke (assumed to be pure carbon) will be used.

Answer

(a) $$2Ca_3(PO_4)_2(s) + 10C(s) + 6SiO_2(s) = 6CaSiO_3(s) + 10CO(g) + P_4(g)$$

(b) Phosphorus

STEP I

$$[\text{g } Ca_3(PO_4)_2]\left[\frac{\text{moles}}{\text{g}}\right] = \text{moles } Ca_3(PO_4)_2$$

$$(75.0 \times 10^3)(\tfrac{1}{310}) = 2.42 \times 10^2 \text{ moles } Ca_3(PO_4)_2$$

STEP II

$$[\text{moles } Ca_3(PO_4)_2]\left[\frac{\text{moles } P_4}{\text{mole } Ca_3(PO_4)_2}\right] = \text{moles } P_4$$

$$(2.42 \times 10^2)(\tfrac{1}{2}) = 1.21 \times 10^2 \text{ moles } P_4$$

STEP III

$$(\text{moles } P_4)\left(\frac{\text{g}}{\text{mole}}\right) = \text{g } P_4$$

$$(1.21 \times 10^2)(\tfrac{124}{1}) = 1.50 \times 10^4 \text{ g } P_4$$

(b) Carbon

STEP I (from above)

STEP II

$$[\text{moles } Ca_3(PO_4)_2]\left[\frac{\text{moles C}}{\text{mole } Ca_3(PO_4)_2}\right] = \text{moles C}$$

$$(2.42 \times 10^2)(\tfrac{10}{2}) = 1.21 \times 10^3 \text{ moles C}$$

STEP III

$$(\text{moles C})\left(\frac{\text{g}}{\text{mole}}\right) = \text{g C}$$

$$(1.21 \times 10^3)(\tfrac{12}{1}) = 1.45 \times 10^4 \text{ g C}$$

CHAPTER

21

THE SECOND COLUMN OF THE PERIODIC TABLE: THE ALKALINE EARTHS

Intent and Approach

One purpose of this chapter is to confront the student forcefully with the idea that he is not studying "answers" but principles which he can apply to many particular cases. At this stage he has covered essentially all the basic ideas he will receive in this course. He is now given another chance to integrate them for still a different group of elements from those studied in Chapters 19 and 20.

Expt. 33, DEVELOPMENT OF A SCHEME OF QUALITATIVE ANALYSIS, USING REAGENTS LABELED A, B, C,
fits here. See p. 683 for guide.

Outline

1. Electron configuration (21-1), atomic size, and ionization energy (21-2) are taken up first. Chemical behavior is studied in terms of oxidation-reduction (21-3.1).
2. Acid–base properties of the oxides (21-3.2) and solubility (21-3.3) are discussed.
3. Occurrence and preparation of the elements are touched upon lightly (21-4).

New Concepts

None.

Development

This chapter brings up no new principles and follows the general path illustrated in Chapters 19 and 20. One general point that can be brought out during study of this chapter is the rough correspondence that exists between properties upon moving down a column and upon moving to the left in a row of the periodic table. This is another way of saying that the lower left corner of the table is occupied by the most metallic element and the upper right corner by the most nonmetallic (inert gases being excluded for these comparisons).

Another point to remember is that you should avoid emphasizing the differences between alkaline earth elements so much that their many similarities are obscured.

Expt. 34, THE RELATIVE SOLUBILITIES OF SOME COMPOUNDS OF SOME METALS OF THE SECOND COLUMN—QUALITATIVE ANALYSIS,
fits here. See p. 685 for guide.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*	*Topic*
Expt. 33	1	Expt. 33			
S 21-1/21-2.2 (pp. 377–379)	2, 3	Discussion	1–5	None	Electron Configuration, Atomic Size, Ionization Energy
S 21-2.3/21-3.2 (pp. 379–382)	4	Discussion	6–8		Chemical Properties
Expt. 34	5	Expt. 34			Solubility
S 21-3.3 (pp. 382–384)	6	Discussion	9, 10		Solubility
S 21-4 (pp. 384–385)	7	Discussion and review	11, 12		Occurrence and Preparation
Expt. 35 Expt. 36 These are optional experiments which give additional practice in testing the presence of ions. See pp. 688 and 690 for guides.					

Note: Experiment 37 (Chapter 22) requires ion-exchange columns which must be prepared in advance. Experiment 38 (Chapter 22) requires preparation of 12 solutions.

EXPERIMENT 33 DEVELOPMENT OF A SCHEME OF QUALITATIVE ANALYSIS USING REAGENTS LABELED *A, B, C*

PURPOSE. This experiment is an introduction to qualitative analysis and especially to Expts. 34, 35, and 36. It is intended that the student consider the chemicals only as solutions to be tested (I, II, III, and IV) and as reagents to use for identification (*A*, *B*, and *C*).

PRELAB DISCUSSION. This experiment is a test of organizing a mass of observed data into usable regularities. The procedure that students will develop is characteristic of many systems of qualitative analysis.

TIMING. Have the students do this experiment just before they read Chapter 21.

EQUIPMENT NEEDED (PER STUDENT)

A minimum of 4 small test tubes (13 × 100 mm)

The following reagents should be provided in dropper bottles—labeled only with letters and Roman numerals (no names or formulas). Each solution is 0.1 *M*, and 15 ml is sufficient for each student.

A	$AgNO_3$ (1.7 g/100 ml)
B	$Ba(NO_3)_2$ (2.6 g/100 ml)
C	$Zn(NO_3)_2$ [3.0 g $Zn(NO_3)_2 \cdot 6H_2O$/100 ml]
I	NaCl (0.6 g/100 ml)
II	Na_2SO_4 (1.4 g/100 ml or 3.2 g $Na_2SO_4 \cdot 10H_2O$/100 ml)
III	K_2CrO_4 (1.9 g/100 ml)
IV	$K_4Fe(CN)_6$ [4.2 g $K_4Fe(CN)_6 \cdot 3H_2O$/100 ml]

TIME REQUIRED. If one set of reagents is provided for each pair of students, ½ period is sufficient. There seems little need of a stopping place, but after (c) is convenient.

LABORATORY HINT. The use of test tubes is good practice for the following experiments, but the combinations may be tried out as spot tests, since only the occurrence of a reaction is being observed. For the same reason the student should be instructed to estimate one-milliliter quantities, and not to measure exactly.

RESULTS. Part (c), reagents and solutions:

	Reagents		
Solutions	*A* (Ag^+)	*B* (Ba^{+2})	*C* (Zn^{+2})
I (Cl^-)	white ppt	no reaction	no reaction
II (SO_4^{-2})	possible white ppt	white ppt	no reaction
III (CrO_4^{-2})	brick-red ppt	yellow ppt	no reaction
IV [$Fe(CN)_6^{-4}$]	white ppt	no reaction	white ppt (gelatinous)

Part (e), reagents and mixed solutions:

Mixed Solutions	Reagents *A*	*B*	*C*
I, II	white ppt	white ppt	no reaction
I, III	red ppt at first, changing to white*	yellow ppt	no reaction
I, IV	white ppt	no reaction	white ppt (gelatinous)
II, III	brick-red ppt	creamy-yellow ppt	no reaction
II, IV	white ppt	white ppt	white ppt (gelatinous)
III, IV	brick-red, changing partly to yellow or white	yellow ppt	white ppt (gelatinous)

* Students might report these as yellow rather than white, because of the CrO_4^{-2} color.

For the mixed unknowns, difficulty may be found with mixtures of I and IV, and II and III. If the student knows that the solution contains two unknowns, he can deduce that unknown I could be present with IV and that II could be present with III.

POSTLAB DISCUSSION. Be sure each student sees the use of the reactions as a "scheme" of analysis, and not as a hit-or-miss mixing. The order is not important; different students are expected to use different procedures, but each should have decided on an organized scheme and should succeed in identifying an unknown.

EXPERIMENT 34 THE RELATIVE SOLUBILITIES OF SOME COMPOUNDS OF SOME METALS OF THE SECOND COLUMN—QUALITATIVE ANALYSIS

PURPOSE. To study the slight differences in solubility of some second-column metallic compounds and to use these differences to devise a qualitative analysis scheme to establish the presence of these cations.

PRELAB DISCUSSION. None is needed, since this follows Expt. 33. Discuss the use of wire and flame tests if these are to be used (see lab hint 2).

TIMING. Assign the experiment early in Chapter 21, but after Expt. 33.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

a minimum of 5 small test tubes (13 × 100 mm)

10–15 ml of each reagent and of each test solution

Reagents (in dropper bottles):

2 *M* $(NH_4)_2CO_3$ with $NH_3(aq)$ [192 g $(NH_4)_2CO_3$ dissolved in water and 80 ml reagent (15 *M*) $NH_3(aq)$/liter]

0.5 *M* K_2CrO_4 (97 g/liter)

0.2 *M* $(NH_4)_2C_2O_4$ [28.4 g $(NH_4)_2C_2O_4 \cdot H_2O$/liter]

1 *M* $(NH_4)_2SO_4$ (132 g/liter)

6 *M* $NH_3(aq)$ [400 ml conc. $NH_3(aq)$/liter]

6 *M* HCl (515 ml conc. HCl/liter)

Test Solutions (in dropper bottles):

0.1 *M* $Ba(NO_3)_2$ (26 g/liter)

0.1 *M* $Sr(NO_3)_2$ (21 g/liter)

0.1 *M* $Ca(NO_3)_2$ [24 g $Ca(NO_3)_2 \cdot 4H_2O$/liter]

0.1 *M* $Mg(NO_3)_2$ [26 g $Mg(NO_3)_2 \cdot 6H_2O$/liter]

For confirmatory tests:

platinum or nichrome flame-testing wire (lab hint 2)

burner

5 ml 12 *M* HCl

TIME REQUIRED. Allow two periods

LABORATORY HINTS

1. Tell the students to estimate one-milliliter volumes rather than to use a graduate.
2. A small loop at the end of the wire is often used but is not essential. If you prefer that there be a loop in the test wire, you should make it before giving the wire to a student. The student should be asked not to unbend it. If the wire is imbedded in glass, the student must be cautioned not to touch the hot glass to the HCl or test solutions.

   It is very difficult to get rid of the short burst of yellow produced by sodium contamination. This is mentioned in the Laboratory Manual, but more discussion may be needed.

   The emission of specific wave lengths of energy by atoms should be discussed and the relationship of flame tests to more complete spectroscopic examination pointed out. Remind the student of the discussion in Chapter 15.

RESULTS

	CO_3^{-2}	CrO_4^{-2}	SO_4^{-2}	$C_2O_4^{-2}$	$NH_3(aq)$	Flame Test
Mg^{+2}	−	−	−	−	+(sl)	no color
Ca^{+2}	+	−	−	+	−	orange-red
Sr^{+2}	+	−	+	+	−	scarlet or crimson
Ba^{+2}	+	+	+	+	−	pale green

For a mixture of cations, the flame test will first reveal the red-orange from Ca^{+2}, then a flash of green from Ba^{+2}, and finally the crimson from Sr^{+2}. Be sure the concentrations for unknown solutions are the same as those for the test solutions.

The student should have no difficulty identifying an unknown containing one of these cations. Those doing the optional unknown will need help in developing a scheme of analysis. One scheme that the student might work out follows:

To 5 ml unknown:

Add 1 ml CrO_4^{-2} solution; filter or
centrifuge to remove Ba^{+2} if ppt forms. If no ppt,
add 1 ml SO_4^{-2} solution; filter or
centrifuge to remove Sr^{+2} if ppt forms. If no ppt,
add 1 ml $C_2O_4^{-2}$ solution; filter or
centrifuge to remove Ca^{+2} if ppt forms. If no ppt,
add 1 ml $NH_3(aq)$ to check
for Mg^{+2}. Confirm by flame tests.

QUESTIONS

1. (a) Which carbonate of the second-column metals has the greatest solubility? Which ones have a similar solubility?
   (b) Describe a possible separation of the cations based upon the above differences.

   Answer: (a) $MgCO_3$ has the greatest solubility; the others have similar solubilities, but lower than that for magnesium.
   (b) The Mg^{+2} ion could be separated from the other second-column cations by precipitating their carbonates and filtering.

2. (a) Which chromate of these metals is the least soluble?
   (b) How can this difference in solubility be used in an analytical separation of a solution containing 0.1 *M* solutions of Sr^{+2} and Ba^{+2}?

   Answer: (a) The least soluble chromate is $BaCrO_4$.
   (b) The Ba^{+2} could be precipitated from a 0.1 *M* solution and be separated from Sr^{+2} by filtration.

3. With which of the anions does the Mg^{+2} ion have the lowest solubility of all the cations?

   Answer: Mg^{+2} has the lowest solubility as $Mg(OH)_2$. In all other cases the Mg^{+2} compound is more soluble than that of the other alkaline earths.

4. Which oxalate of these metals is the most soluble?

   Answer: The most soluble oxalate is magnesium oxalate.

5. The solubility product constants, K_{sp}, for the sulfates of the cations of the second column are

		K_{sp}
($MgSO_4$ is very soluble)	$CaSO_4$	2.4×10^{-5}
	$SrSO_4$	7.6×10^{-7}
	$BaSO_4$	1.5×10^{-9}

If a 0.002 M solution of $(NH_4)_2SO_4$ were added to an equal volume of 0.002 M solutions of each of the cations of the second column, in which case would a precipitate form?

Answer

$$[SO_4^{-2}] = 1 \times 10^{-3}$$
$$[\text{cation}] = 1 \times 10^{-3}$$
$$\text{trial ion product} = (1 \times 10^{-3})(1 \times 10^{-3}) = 1 \times 10^{-6}$$

This ion product is greater than K_{sp} for $SrSO_4$ or $BaSO_4$. These two sulfates would precipitate.

POSTLAB DISCUSSION. Discuss both the regularities and the irregularities in trends of solubilities for these elements. Remind the students of Chapter 10 and your remarks there (see p. 311).

EXPERIMENT 35 QUALITATIVE ANALYSIS OF Ag^+, Hg_2^{+2}, AND Pb^{+2}

PURPOSE. To have the student develop a scheme of analysis using solubility information and the experience he had in performing Expts. 33 and 34.

PRELAB DISCUSSION. None is needed other than to mention that this experiment follows the same pattern as 33 and 34.

TIMING. This experiment can be done any time after Expts. 33 and 34.

EQUIPMENT NEEDED (PER INDIVIDUAL OR PAIR)

100 ml beaker
6 or more 13 × 100 mm test tubes
burner or hot plate, ring, gauze, ring stand
centrifuge desirable

Solutions (*in dropper bottles*):

1 ml 0.1 *M* $AgNO_3$ (1.7 g/100 ml)
1 ml 0.1 *M* $Hg_2(NO_3)_2$
[5.6 g $Hg_2(NO_3)_2 \cdot 2H_2O$/100 ml]
1 ml 0.1 *M* $Pb(NO_3)_2$ (3.3 g/100 ml)
2 ml 6 *M* HCl (51.3 ml conc./100 ml)
1 ml 0.1 *M* K_2CrO_4 (1.9 g/100 ml)
6 ml 6 *M* $NH_3(aq)$ (40 ml conc./100 ml)
3 ml 6 *M* HNO_3 (38.4 ml conc./100 ml)

TIME REQUIRED. With a set of reagents for each pair of students, one period should allow time for the determination of one unknown.

RESULTS. Chloride precipitates: $Hg_2Cl_2(s)$ is very bulky;
$PbCl_2(s)$ is fine and settles quickly;
$AgCl(s)$ is bulky, settles slowly unless centrifuged.

Solubilities for these are as follows (grams per 100 ml water):

Hg_2Cl_2;	0.00021 (18°C)	0.001 (43°C)
$PbCl_2$;	0.99 (20°C)	3.34 (100°C)
AgCl;	0.000089 (10°C)	0.0021 (100°C)

K_{sp} at 25°C:

AgCl;	1.7×10^{-10}
Hg_2Cl_2;	2×10^{-18}
$PbCl_2$;	1×10^{-4}
$PbCrO_4$;	2×10^{-16}

TABLE OF RESULTS

	Chloride Precipitate of		
Treatment	Ag^+	Hg_2^{+2}	Pb^{+2}
Placed in boiling water	remains	remains	dissolves
CrO_4^- added to hot solution	no change	turns black*	yellow ppt
6 *M* $NH_3(aq)$ added	dissolves	no change	remains
6 *M* HNO_3 added	reprecipitates	no change	remains

* The black color is produced by a reaction which forms Hg (black) and $HgNH_2Cl$ (white).

QUESTIONS AND EXERCISES

1. Write equations for all reactions occurring in this experiment.

Answer: The student will have no trouble with the reactions except for the silver ammonia complex.

Reactions in procedure (a), (b), and (c):

$$Pb^{+2}(aq) + 2Cl^-(aq) = PbCl_2(s)$$

When warmed $PbCl_2(s)$ dissolves to give $Pb^{+2}(aq)$.

$$\begin{aligned} Pb^{+2}(aq) + CrO_4^{-2}(aq) &= PbCrO_4(s) \\ Hg_2^{+2}(aq) + 2Cl^-(aq) &= Hg_2Cl_2(s) \end{aligned}$$

Reactions in procedure (e):

$$\begin{aligned} Ag^+(aq) + Cl^-(aq) &= AgCl(s) \\ Ag^+(aq) + NH_3(aq) &= Ag(NH_3)_2^+(aq) \\ NH_3 + H_2O &= NH_4^+(aq) + OH^-(aq) \\ H^+(aq) + OH^-(aq) &= H_2O \end{aligned}$$

2. Construct an outline (flow diagram) which summarizes the steps you would use to analyze an unknown containing all three cations, Ag^+, Hg_2^{+2}, and Pb^{+2}.

Answer: The following is an example of such an outline.

To 5 ml of sample add 2.5 ml 6 *M* HCl. Warm and decant.

To solid:	*To solution:*
Add $NH_3(aq)$; remaining ppt is Hg_2^{+2}. Decant and add HNO_3 to solution; ppt indicates Ag^+.	Add CrO_4^{-2}; ppt indicates Pb^{+2}.

POSTLAB DISCUSSION. None needed.

EXPERIMENT 36 DEVELOPMENT OF A SCHEME FOR THE ANALYSIS OF AN UNKNOWN CONTAINING VARIOUS ANIONS

PURPOSE. To have the student develop a scheme of analysis using solubility information and the experience he had in performing Expts. 33, 34, and 35.

PRELAB DISCUSSION. None is needed.

TIMING. Assign the experiment any time after Expts. 33, 34, and 35.

EQUIPMENT NEEDED (PER INDIVIDUAL OR PAIR)

a minimum of 4 small test tubes (13 × 100 mm)

solutions of ions for unknowns and reagents (in dropper bottles)

Approximately 5 ml of each except 10 ml of HNO_3:

0.1 M Na_2SO_4 (1.4 g anhydrous Na_2SO_4/100 ml)
0.5 M Na_2CO_3 (6.2 g $Na_2CO_3 \cdot H_2O$/100 ml)
0.1 M NaCl (0.6 g/100 ml)
0.1 M NaI (1.5 g/100 ml)
1.0 M HNO_3 (6.4 ml conc. reagent/100 ml)
0.1 M $Ba(NO_3)_2$ (2.6 g/100 ml)
0.1 M $AgNO_3$ (1.7 g/100 ml)
6 M $NH_3(aq)$ (40 ml conc. reagent/100 ml)

TIME REQUIRED. Allow one period.

RESULTS

Reagent Added	Ion in Solution Tested			
	$SO_4^{-2}(aq)$	$CO_3^{-2}(aq)$	$Cl^-(aq)$	$I^-(aq)$
$Ba^{+2}(aq)$	ppt (white)	ppt (white)	—	—
$H^+(aq)$ causes barium ppt to	remain	dissolve		
$Ag^+(aq)$	—	ppt (white)	ppt (white)	ppt (yellow)
$H^+(aq)$ causes silver ppt to	—	dissolve	remain	remain
$NH_3(aq)$ causes silver ppt to	—	dissolve	dissolve	remain

Many possible schemes of analysis can be devised using these reagents. It is important to encourage a logical development and originality in approach.

EXAMPLES

1. Precipitate formation with Ba^{+2} shows either SO_4^{-2} or CO_3^{-2}:

   A precipitate that dissolves with H^+ indicates CO_3^{-2}.
   A precipitate that does not dissolve with H^+ indicates SO_4^{-2} (or a mixture with an anion that forms a precipitate with Ba^{+2}).

2. Formation of a single precipitate with Ag^+ indicates CO_3^{-2}, Cl^-, or I^-:

   A precipitate that does not dissolve in $H^+(aq)$ or $NH_3(aq)$ indicates I^- (or a mixture).
   Precipitate formation with both Ag^+ and Ba^{+2} indicates CO_3^{-2} (or a mixture).
   A precipitate that forms with Ag^+ and dissolves in $NH_3(aq)$ indicates Cl^-.

3. A precipitate containing Ag_2CO_3, AgCl, and AgI must be separated:

   Filter and test the filtrate with Ba^{+2} to identify SO_4^{-2}.
   Add $NH_3(aq)$ to ppt, and filter; remaining ppt indicates I^-.
   Add acid to filtrate; ppt indicates Cl^-; bubbling indicates CO_3^{-2}.

   K_{sp} values:

$BaCO_3$;	8.1×10^{-9}	Ag_2CO_3;	6×10^{-12}
$BaSO_4$;	1.5×10^{-9}	AgCl;	1.7×10^{-10}
		AgI;	8.5×10^{-17}

EXERCISES

1. Write net ionic equations for the precipitation reactions which occurred when solutions of the anions were mixed with the solution containing Ba^{+2} ions.

   Answer: $Ba^{+2}(aq) + SO_4^{-2}(aq) = BaSO_4(s)$
   $Ba^{+2}(aq) + CO_3^{-2}(aq) = BaCO_3(s)$

2. Do the same for precipitation reactions which occurred in Part c with the Ag^+ ions.

   Answer: $Ag^+(aq) + CO_3^{-2}(aq) = Ag_2CO_3(s)$
   $Ag^+(aq) + Cl^-(aq) = AgCl(s)$
   $Ag^+(aq) + I^-(aq) = AgI(s)$

3. Write equations for the reactions which occurred when the precipitates were acidified with 1.0 *M* HNO_3.

   Answer: $BaCO_3(s) + 2H^+(aq) = Ba^{+2}(aq) + H_2O + CO_2(g)$
   $Ag_2CO_3(s) + 2H^+(aq) = 2Ag^+(aq) + H_2O + CO_2(g)$

4. Write equations for the reactions which occurred when the silver precipitates reacted with aqueous ammonia to form the complex ion, $Ag(NH_3)_2^+$.

   Answer: $AgCl(s) = Ag^+(aq) + Cl^-(aq)$
   $2NH_3(aq) + Ag^+(aq) = Ag(NH_3)_2^+(aq)$

POSTLAB DISCUSSION. This is a good time to discuss complex ions such as $Ag(NH_3)_2^+$ and their importance in qualitative analysis. It is also important to discuss the limitations of analytical schemes. This experiment works well when only these four anions are present without complications from other ions. The concentrations are also predetermined.

Supplementary Material

None.

Background Discussion

None.

Answers to Exercises

Ex. 21-1. On the basis of the electron configurations and positions in the periodic table, answer the following questions.

(a) Is calcium likely to be a metal or nonmetal?
(b) Is calcium likely to resemble magnesium or potassium in its chemistry?
(c) Is calcium likely to have a higher or a lower boiling point than potassium? Than scandium?

Answer

(a) Calcium is likely to be a metal. It has only two valence electrons, low ionization energies, and empty valence orbitals. It is in the left-hand portion of the periodic table, where metallic elements are found.
(b) Calcium is probably more like Mg than K. It has the same number of valence electrons as Mg, hence should form the same type of compounds and react in the same way. Similarities within a column are usually greater than those found within rows.
(c) The boiling point of Ca is likely to be between that of K and that of Sc. In general, the more valence electrons per atom in metallic solids, the higher the boiling point—providing usable orbitals are available for bonding. The measured values are 757°C for K, 3900°C for Sc; the value for Ca is given in some references as 1492°C. Call attention also to the heats of vaporization given in Textbook Table 17-I.

Notice that this trend is not necessarily observed among the melting points, in part because different crystal structures are being compared and in part because both liquid and solid involve about the same strength of metallic bonding; hence the contrast between the alkali, alkaline earth, and third-column elements is not pronounced.

Ex. 21-2. Predict the chemical formula and physical state at room temperature of the most stable compound formed by each alkaline earth element with

(a) chlorine;
(b) oxygen;
(c) sulfur.

Answer

The bonds are expected to be ionic—the combined elements are from opposite sides of the periodic table. All compounds will be solids.

(a) with chlorine	(b) with oxygen	(c) with sulfur
$BeCl_2$	BeO	BeS
$MgCl_2$	MgO	MgS
$CaCl_2$	CaO	CaS
$SrCl_2$	SrO	SrS
$BaCl_2$	BaO	BaS

Ex. 21-3. For each of the alkaline earths, calculate the ratio E_2/E_1. Account for the results in terms of the charges on the ions formed in the two ionization steps.

Answer

	Be	Mg	Ca	Sr	Ba
E_2/E_1	1.96	1.97	1.96	1.94	1.92

The ratio is almost constant and is very close to 2. The ratio can be accounted for by assuming that the first electron is pulled away from a +1 ion, and the second electron is pulled away from a +2 ion. Hence the work that must be done is about doubled. This conclusion is based upon the assumption that the first and second electrons are removed from approximately the same average radius.

Ex. 21-4. If the ionization energy E_1 is regarded as a measure of the distance between the electron and the nuclear charge, what do the ionization energies of Be and Ba indicate about the relative sizes of the two atoms?

Answer

Since it takes more energy to remove an electron from Be than from Ba, the electron must be much closer to the nucleus in Be than in Ba. *It is implied that the barium atom is much larger than the Be atom.*

Ex. 21-5. From the ionization energies, predict which solid substance involves bonds having the most ionic character: $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$. Which substance is expected to have most covalent character in its bonds?

Answer

The student should examine ionization energy differences in framing his answer.

Element (M)	$E_1(M)$ (kcal/mole)	$E_1(\mathrm{Cl})$ (kcal/mole)	$E_1(\mathrm{Cl}) - E_1(M)$ (kcal/mole)	
Be	214	300	86	most covalent character
Mg	175	300	125	
Ca	140	300	160	
Sr	132	300	168	
Ba	130	300	180	most ionic character

Ex. 21-6. From the density of each element, calculate the volume occupied by one mole of its atoms in the metallic state. Compare the trend in these molar volumes with the trend in the metallic radii shown in Table 21-II.

Answer

A sample calculation of the molar volume is shown for Be, and the results are given for the others:

Density of Be = 1.85 g/ml. One mole (9.01 g) will then occupy

$$\frac{9.01\ \mathrm{g}}{1.85\ \mathrm{g/ml}} = 4.87\ \mathrm{ml}$$

Element	Molar volume (ml)	Ionic radius (Å)
Be	4.87	0.32
Mg	13.9	0.78
Ca	25.9	1.08
Sr	33.7	1.25
Ba	39.2	1.44

The trends are parallel. Both molar volume and metallic radius increase from top to bottom in the periodic table. Call attention to the fact that densities expressed in g/ml cannot be readily interpreted, but when expressed in molar volumes, they can.

Ex. 21-7. The ease of removal of an electron from a gaseous atom, the ionization energy, is one of the factors that is important in fixing $E°$. Refer back to Table 21-III, and predict the trend in $E°$ that this factor would tend to cause.

Answer

As we proceed from Be to Ba, the ionization energy decreases steadily, meaning a decreasing amount of energy is needed to remove electrons. This would tend to cause $E°$ to become more positive, since a positive $E°$ implies an increased tendency to release electrons. This is the observed trend in $E°$. Notice that hydration effects, energy, and randomness, are important also.

Ex. 21-8. How much heat is evolved if one pound (454 grams) of lime is slaked according to reaction (*10*)? How many grams of water can be evaporated with this heat? (The heat of vaporization of water is about 10 kcal/mole.)

Answer

Slaking one pound of lime will evolve

$$\left(\frac{15.6\ \mathrm{kcal}}{\mathrm{mole\ CaO}}\right)\left(\frac{1}{56.1\ \mathrm{g/mole\ CaO}}\right)\left(\frac{454\ \mathrm{g}}{1\ \mathrm{lb}}\right) = 126\ \frac{\mathrm{kcal}}{\mathrm{lb}}$$

Since the heat of vaporization of water is 10 kcal/mole, 126 kcal will vaporize 12.6 moles, or (12.6 moles)(18.0 g/mole) = 227 g of water.

Ex. 21-9. In your notebook indicate one of the four answers

(i) none of the alkaline earth ions;
(ii) all alkaline earth ions;
(iii) Be^{+2}, Mg^{+2}, and Ca^{+2} but not Sr^{+2}, Ba^{+2}, or Ra^{+2};
(iv) Sr^{+2}, Ba^{+2}, and Ra^{+2} but not Be^{+2}, Mg^{+2}, or Ca^{+2}

for each of the following:

(a) ______ form compounds of low solubilities with Cl^-, Br^-, and I^-.

(b) ______ form compounds of low solubilities with sulfate, SO_4^{-2}.

(c) ______ form compounds of low solubilities with sulfide, S^{-2}.

(d) ______ form compounds of low solubilities with hydroxide, OH^-.

(e) ______ form compounds of low solubilities with carbonate, CO_3^{-2}.

Now compare your answer with Figures 10-5 and 10-6.

Answer

(a) i; (b) iv; (c) i; (d) iii; (e) ii.

Ex. 21-10. Suppose you have a solution in which the concentration of hydroxide ion is 1 *M*. How many moles per liter of the different alkaline earth ions listed in Table 21-VI could you have (at equilibrium) in this solution? If the concentration of hydroxide ions were 0.5 *M*, how would your answers change?

Answer

For each compound the answer will have the form

$$[M^{+2}][OH^-]^2 = K_{sp}$$

For $[OH^-] = 1\ M$ this becomes

$$[M^{+2}] = K_{sp}$$

If the concentration of OH^- is 0.5 *M*, then

$$[M^{+2}] = \frac{K_{sp}}{[OH^-]^2} = \frac{K_{sp}}{(0.50)^2} = \frac{K_{sp}}{0.25} = 4K_{sp}$$

There will be four times as much alkaline earth ion in the 0.5 *M* hydroxide solution.

Ex. 21-11. What property held in common by the following compounds accounts for their presence in natural mineral deposits: $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaSO_4$, and (in bones) $Ca_3(PO_4)_2$?

Answer

Each compound has low solubility in water.

Ex. 21-12. What property held in common by the alkaline earth elements accounts for the fact that the free elements are not found in nature?

Answer

Each element is easily oxidized, as shown by the E° values in Table 21-V.

CHAPTER

22

THE FOURTH-ROW TRANSITION ELEMENTS

Intent and Approach

Approach this chapter as new material with respect to description and as old material with respect to chemical principles. Although the elements studied are new, the chapter can be a valuable review of chemical principles. Emphasize the principles as much as possible; avoid letting the descriptive material hide them.

The first portion of this chapter (pp. 387–392) applies previously learned principles of electron configuration to *d* orbitals. Complex ions are treated much more extensively than before (pp. 392–398), building on previously developed concepts of molecular shape and its relations to electron configuration. The rest of the chapter, dealing with specific properties of the transition elements, offers an opportunity to stress regularities.

The chapter is intended to show the student:

(1) the regularities shown by elements with *d*-orbital valence electrons;

(2) the nature of complex ions and complex compounds;

(3) the relation between certain specific properties of transition elements and some of the chemical theories he has already learned.

Outline

1. The transition elements are defined (22-1) and their electron configurations examined (22-1.1). Multiple oxidation numbers and other common properties are discussed (22-1.2).
2. The types of complex ions and complex compounds are discussed in terms of geometry (22-2.1), bonding (22-2.2), and reactions.
3. Some special aspects of complex ions are considered: significance (22-2.3), amphoteric behavior (22-2.4), and natural occurrence (22-2.5).
4. Ten empirical properties of these transition elements are given in Textbook Table 22-III (p. 400). Seven of these properties are discussed in detail.
5. These ten transition elements are treated individually in Secs. 22-3.1 to 22-3.10. Iron is discussed most extensively; its occurrence, extraction, and tendency toward natural oxidation are presented in detail.

New Concepts

This chapter is not designed to introduce new concepts, but the following, already familiar concepts should be consciously reviewed as the chapter is studied.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*			*Topic*
				EASY	MEDIUM	HARD	
S 22-1 (pp. 387–392)	1	1–10	1–5	1	2, 3		Introduction, Definition, Properties
Expt. 39	2	Expt. 39					Complex salts
S 22-2/22-2.3 (pp. 392–396)	3	Expt. 39, Discussion		4	5–7		Complex ions
S 22-2.4/22-2.5 (pp. 396–398)	4	Discussion	6, 7				Naturally occurring complexes
S 22-3/22-3.4 (pp. 398–403)	5, 6	Discussion	8, 9		8–10	11	Sc–Cr
S 22-3.5/22-3.6 (pp. 403–406)	7	Discussion		12	13, 14		Mn–Co
S 22-3.7/22-3.10 (pp. 406–409)	8	Discussion	10	17	15, 16, 18–20		Ni–Zn
Expt. 37	9, 10	Expt. 37					Ion exchange
	11	Review					

Notes: Experiments 38, 40, and 41 are optional for this chapter. See pp. 709, 716, and 720 for guides.
Either of the films VANADIUM, A TRANSITION ELEMENT or HIGH TEMPERATURE RESEARCH can be shown any time after day 5.

More important (to this chapter) are:
- Electron configuration
- Ionization energy
- Geometry of molecules
- Isomerism
- Equilibrium
- Acid–base theory

Less important (to this chapter) are:
- Oxidation-reduction
- Reaction rates
- Energy in reactions

Development

Present this chapter first as an extension of previous knowledge and second as descriptive chemistry.

DEFINITION OF TRANSITION ELEMENTS (22-1)

Electron Configuration (22-1.1)

The orbital board and Textbook Figure 22-1 will help make the use of 3*d* orbitals reasonable. Exercises 22-1, 22-2, and 22-3 will help review the electronic structure. The *d* orbitals are somewhat buried, with the result that electrons in them are not readily accessible. This means they do not occupy "new" space at the outer part of the atom. This helps account for the near constancy of the atomic radius. The number of valence electrons is fixed by the energy needed to remove electrons, and the buried *d* electrons have little effect on this.

General Properties (22-1.2)

This section opens with some general remarks about properties. You will notice that some elements (Ag, Au, Hg, Pt, La, Ce) in addition to the fourth-row transition elements are included for comparison. This is a hint at the similarities among transition elements, which will be developed later, especially in Problem 8. A few uses are given, but you should not attempt to exhaust the subject. Save such material for Secs. 22-3.1 to 22-3.10. Finally, the wide variation of oxidation number is shown by an imaginary tour of the stock room. You can show many of these compounds as you make this point.

You will note that on Textbook p. 391, and later in the chapter, some compounds are given without names. This omission is deliberate, and is to avoid opening the door to a long discussion of inorganic nomenclature. Names for the compounds are:

$[Cr(NH_3)_6]Cl_3$;
  hexaamminechromium(III) trichloride
$[Cr(NH_3)_5Cl]Cl_2$;
  chloropentaamminechromium(III) dichloride
$[Cr(NH_3)_4Cl_2]Cl$;
  dichlorotetraamminechromium(III) chloride
$[Cr(NH_3)_3Cl_3]$;
  trichlorotriamminechromium(III)
K_3CrF_6;
  potassium hexafluorochromate(III)
$Na_3Cr(CN)_6$;
  sodium hexacyanochromate(III)
$KCr(SO_4)_2 \cdot 12H_2O$;
  potassium chromium sulfate, "chrome alum"

Naming such compounds will probably be interesting to only a few students, hence it is preferable that the class, as a whole, concentrate on the other aspects of complex ions.

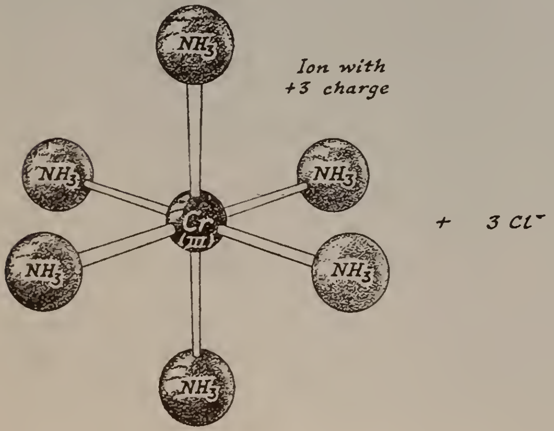
COMPLEX IONS (22-2)

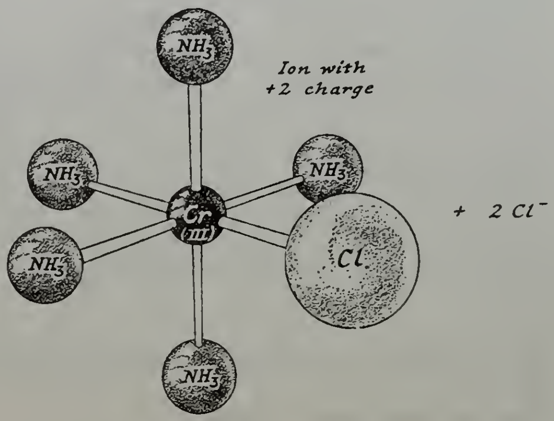
Experiment 39 introduces the section. Very little discussion should precede it. In this way it becomes a point of common experience for you and the students, and you can refer to this as the discussion develops.

Expt. 39, PREPARATION OF A COMPLEX SALT AND A DOUBLE SALT,
fits here. See p. 713 for guide.

Geometry of Complex Ions (22-2.1)

In approaching this section a brief review of solid geometrical figures may be useful. In particular the octahedron and tetrahedron should be demonstrated: the octahedron has eight triangular faces; the tetrahedron has four triangular faces. Note, however, that there are six (*not* eight) corners on the octahedron, and four on the tetrahedron. Link these shapes to coordination numbers (recall Expt. 27) and to the shapes of d^2sp^3 and sp^3 orbital representations (see the *Background Discussion* for the shape of *d* orbitals). See p. 723 for directions for making a tetrahedron and an octahedron. The $CrCl_3^-$ ammonia complexes on Textbook p. 395 can best be illustrated with models and by referring to Figure 22-4 in the Textbook. The compound $Cr(NH_3)_6Cl_3$ has the structure in which the three Cl^- ions are rather loosely attached. Here we have a complex cation. As fewer NH_3 molecules are involved, chloride ions join the complex structure and are more firmly held:



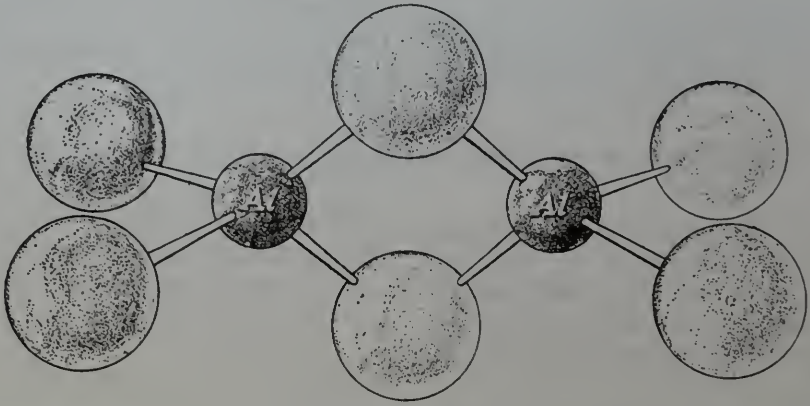


These firmly held chloride ions do not precipitate with Ag^+.

The discussion of ion geometry begins with coordination number—the number of *near* neighbors. The groups bound to a central atom do not necessarily lie at the same distance from it. This effect is observed for so simple a molecule as Al_2Cl_6 and is explained as resulting from different electronic environment—hence different bonding distances. In Al_2Cl_6 each Al is surrounded by four near chlorine atoms in a tetrahedral arrangement. The outer four chlorine atoms are 2.06 Å from the Al; the center two are 2.21 Å from the Al. The coordination number of Al is 4. As another example, dichromate ion can be considered as two tetrahedra joined at one corner (see Textbook Figure 22-9, p. 402). The outer O–Cr distance is 1.63 Å, the O–Cr distance in the Cr—O—Cr bonds is 1.91 Å.

A portion of the background material discusses models of some simple complexes. The bond distances are given with angles, as needed. The arrangements will be most clear if a ball-and-stick model is made so that the central ion can be seen. If this is done be sure to stress that the sticks do not represent bonds.

The principal shapes of complexes are linear (*sp* bonding), square planar (dsp^2), tetrahedral (sp^3), and octahedral (d^2sp^3). Only the second and last are new. Illustrate these shapes with the models described in the *Background Discussion*.



Bonding in Complex Ions (22-2.2)

Bonding here is not different from the kind that the student has already studied. Stable arrangements exist because electrons find energetically favorable positions between two nuclei. As in simpler molecules and ions, the extremes in type are called ionic and covalent bonds. In actual complex ions we find not only these types but intermediate ones of partial ionic character. The entire situation is no different from that described in Chapter 16. The presence of *d* orbitals gives no new bonding types, only some new shapes, as described above.

Significance of Complex Ions (22-2.3)

Beyond what is given in the Textbook, we feel that complex ions have significance because their study constitutes one of the areas of inorganic chemistry that is presently very active. They also represent an in-between area of chemistry, since many complexes have some organic portions.

Amphoteric Complexes (22-2.4)

Amphoteric (from the Greek word for "both") means that a compound can function as an acid or a base. It is most commonly applied to hydroxides, and indicates that they react to give a new species in either acidic or basic solutions. The behavior is not unique with complex ions *or* with transition elements. Note the equilibria

$$Al(OH)_3(H_2O)_3 + H^+ = Al(H_2O)_4(OH)_2^+$$
$$Al(OH)_3(H_2O)_3 + OH^- = Al(H_2O)_2(OH)_4^- + H_2O$$

These are only the first steps; the process can be continued until the final ions are $Al(H_2O)_3^{+3}$ and $Al(OH)_6^{-3}$, respectively. Compounds exist for each stage, for instance, $Ca_3[Al(OH)_6]_2$, calcium hydroxyaluminate.

This idea of amphoterism is related to the Brønsted theory of acids. We could say (although we do not often do so) that HSO_4^- or even H_2O is "amphoteric." Each can act as an acid or base.

The distribution of amphoteric behavior of hydroxides in aqueous solution is shown by the following portion of the periodic table.

Amphoteric Behavior of Hydroxides

		Al good	Si none	P none	S none
Cu poor	Zn good	Ga good	Ge fair	As fair	Sc none (?)
Ag poor	Cd poor	In fair	Sn good	Sb fair	Te none (?)
Au poor	Hg none	Te none	Pb good	Bi none (?)	Po (?)

Nor are the amphoteric qualities of these elements restricted to aqueous systems.

Complexes Found in Nature (22-2.5)

Many reactions in plant and animal chemistry involve complex ions, but the examples given are probably enough for the student at this stage.

Finally, the *Background Discussion* contains some remarks about amphoteric behavior that will be helpful. Amphoteric behavior and the CO poisoning example on pp. 396 and 398 of the Textbook provide a good opportunity to review equilibrium principles.

SPECIFIC PROPERTIES OF FOURTH-ROW TRANSITION ELEMENTS (22-3)

Tables 22-I and 22-II give some selected data for the transition elements in the fifth and sixth rows of the periodic table, and provide a chance for you to test the student's skill; correlations between members of a column can be readily noted.

The orbital board can be used to relate the trends in ionization energy and atomic radius to electronic configuration. The "contraction" of atomic radius results from the action of an increasing number of protons on the electrons in orbitals of fixed size (more or less). Ionic radii show the same trend but to a reduced extent.

Films, VANADIUM, A TRANSITION ELEMENT
or HIGH TEMPERATURE RESEARCH,
can be shown any time after this. See p. 723 for summary.

Table 22-I. **Some Properties of the Fifth-row Transition Elements**

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic no.	39	40	41	42	43	44	45	46	47	48
Atomic radius* (Å)	1.80	1.57	1.47	1.40	1.36	1.33	1.34	1.37	1.44	1.48
Ionization potential (kcal/mole)	149	159	—	169	—	177	177	191	173	206
Density (g/cm^3)	4.34	6.54	8.58	10.2	11.50	12.30	12.42	12.03	10.50	8.64
m.p. (°C)	1500	2100	1950	2600	2140	2400	1966	1555	960	324
b.p. (°C)	—	3600	5100	4800	—	4200	3900	3170	1980	767
Ionic radius of M^{+4} (Å)	1.06(+3)	0.87	0.69	0.68	—	0.63	0.68(+3)	—	1.13(+1)	1.03(+2)
E° (volts) $M \longrightarrow M^{+2} + 2e^-$	—	—	~1.1(+3)	~0.2(+3)	—	—	~−0.8(+3)	−0.987†	−1.389	+0.40

Note: The E° values (in acid solution) are from W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs (1952).

* For coordination number 12 (a few are corrected to this condition).

† 4 *M* $HClO_4$.

Individual Elements Scandium to Zinc (22-3.1 to 22-3.10)

These sections discuss some transition elements. Sections 22-3.1, 22-3.2, 22-3.3, 22-3.5, 22-3.7, and 22-3.10 are very short and probably merit no further discussion. The film VANADIUM, A TRANSITION ELEMENT shows this element specifically.

Chromium (22-3.4)

Sometimes students are confused or startled to find that we cannot write a formula for some compounds. The gelatinous $Cr(OH)_3 \cdot nH_2O$ is an example of a fairly frequently encountered situation. The composition is not fixed, or perhaps more precisely, the composition is so sensitive to preparation conditions and treatment that we cannot get consistent samples. Silica and alumina gels give the same difficulty.

Compounds like $KCr(SO_4)_2$, containing more than one kind of cation, may appear strange. But recall sodium bicarbonate, $NaHCO_3$, and the complex ions that have two (or more) kinds of anions.

Iron (22-3.6)

This section deals with such an important metal that it is worth more effort than the others. You should use the preparation of iron as an example of a common method of freeing metals from their oxide ores. The first step is chemical reduction, giving the metal, which is then purified of reducing agent and any unwanted "slag" that formed. Finally, the pure form is made impure in a controlled way to produce desired properties—it is alloyed.

Rusting of iron is not a simple reaction of iron plus oxygen to give iron oxide. It is best to follow the Textbook's lead and avoid writing an equation. Just describe what happens and how these observations can be explained. In case you do write an equation, make sure you explain that it does not show mechanism.

Nickel (22-3.8)

The Edison cell is covered in this section. Along with the more common lead storage cell, the Edison cell gives a brief view of how chemical *and* economical factors sometimes conflict. Present this as a case in which we examine many sides of a problem.

Table 22-11. **Some Properties of the Sixth-row Transition Elements**

Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic no.	57	72	73	74	75	76	77	78	79	80
Atomic radius (Å)	1.86	1.57	1.47	1.40	1.38	1.35	1.35	1.37	1.44	1.60
Ionization potential (kcal/mole)	129	—	—	186	—	200	207	204	211	238
Density (g/cm^3)	6.18	13.31	16.69	19.1	20.9	22.7	22.65	21.45	19.3	13.5
m.p. (°C)	826	2300	3010	3400	3150	2700	2454	1774	1063	−39
b.p. (°C)	—	5200	6000	5700	—	4600	4500	3800	2700	357
Ionic radius of M^{+4} (Å)	1.04(+3)	0.84	0.68(+5)	0.68	—	0.63	0.63	—	—	1.12(+2)
$E°$ (volts) $M \longrightarrow M^{+2} + 2e^-$	2.52(+3)	—	—	0.11(+3)	∼−0.3	∼−0.85	<−1.1	∼−1.2	−1.50(+3)	−0.79

Note: The $E°$ values (in acid solution) are from W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs (1952).

OPTIONAL EXPERIMENTS

The following experiments can be used for student projects or class laboratory work as desired.

Experiment 38: Some investigations into the corrosion of iron
Experiment 40: Preparation of potassium dichromate
Experiment 41: The preparation of chrome alum

They are not integral parts of the chapter but do apply to the material covered. See pp. 709, 716, and 720 for guides.

EXPERIMENT 37 THE SEPARATION OF SOME TRANSITION METAL IONS WITH AN ANION EXCHANGE RESIN

PURPOSE. To illustrate a modern method for separation and analysis of ions in a solution and to give an opportunity for the discussion of some complex ions.

PRELAB DISCUSSION. The use of an ion exchange resin for separating and identifying the transuranium elements is similar to what is done in this experiment and may interest the students. Such resins are a useful tool in research. Make it clear that we only appear to be separating cations; actually an anion exchange is being used, since negative chloride complexes are involved. The sample is converted to a maximum concentration of these anionic complexes by addition of a high concentration of the anion that forms the complex (in this experiment, Cl^-). Then as the concentration is gradually decreased the complexes dissociate (the weakest one first) to give the hydrated metal cations which are no longer retained by the resin.

The colors of the hydrated ions being eluted will be too faint to be noticeable in the tube leading from the column, but will probably show up in the collecting tubes if viewed, as suggested, against a white paper background.

TIMING. The experiment can be done any time during Chapter 22, but it is best to wait until after you have discussed the particular elements used (p. 408).

MATERIALS NEEDED (PER STUDENT OR PAIR)
(*see note under Time Required*)

2 ml test solution containing Fe^{+3}, Co^{+2}, and Ni^{+2} (see lab hint 2)

One sample each of Fe^{+3}, Co^{+2}, and Ni^{+2} solution for color comparison (see lab hint 3)

About 1 ml each of the following solutions

0.1 *M* KSCN (0.97 g/100 ml)
15 *M* $NH_3(aq)$ (conc. reagent)

1% dimethylglyoxime in ethanol (1 g/100 ml 95% ethanol)
10% NH_4SCN in acetone (10 g/100 ml)

50 ml 9 *M* HCl
ion exchange column (see lab hint 1)
  10 cm column in a 10–12 mm tube 20–30 cm long so that the space above the resin can act as a liquid reservoir
  stopper for column, rubber connector, pinch or screw clamp, and 2 short lengths of glass tubing (each about 5 cm long)

ring stand, buret clamp
glass plate (approx. 10 × 10 cm)
3 small (50–100 ml) beakers or other containers for acid
12–15 small (13 × 100 mm) test tubes
test tube rack

PRECAUTIONS. Observe the usual laboratory precautions, particularly with concentrated HCl and $NH_3(aq)$.

TIME REQUIRED. If the columns are prepared beforehand and students work in pairs, one period is sufficient.

LABORATORY HINTS

1. Preparation of the column:
   Analytical grade (AG2-X8) resin is recommended.

This is Dowex anion resin No. 2, which has been carefully washed and sized. A mesh of 50–100 is convenient for this experiment. This resin is available from Bio-Rad Laboratories, 32nd and Griffin, Richmond, California. It is shipped slightly moist.

Caution: If dry resin is used, take care not to breathe any of the powder.

(i) Use 10–12 mm tubing about 20 cm long. Ten grams of resin will occupy half the tube, leaving a reservoir space for solutions. Insert an exit tube into a small stopper, and clamp it as in Figure 37-1; have another stopper available to close the top when the column is left overnight. You can pull the tubing down to a small diameter and avoid the trouble of putting a tube through the small stopper.

(ii) Make a slurry of resin in 2 *M* HCl, and have extra acid available.

(iii) Insert a glass wool plug just above the stopper (see Figure 37-1).

(iv) Pour approximately the correct amount of slurry into a test tube and then into the column. The extra acid will flow out quickly.

(v) Insert another glass wool plug.

(vi) Close the exit tube, and add enough acid to cover the resin and the upper plug. The columns may be stored from one year to the next if kept moist. The best method is to wash the columns with water and place them (with clamp removed but top stopper in place) in a jar of water. A one-gallon wide-mouth jar (mayonnaise or pickle jars are available from school cafeterias) will hold a number of columns. One day before the next use, recondition the tubes by running 2 *M* HCl through them.

In such a tube the flow rate will probably need to be adjusted slightly by cutting down the opening with a pinch clamp. A rate of 2.5 ml per minute is adequate for washing, and allows enough time to record details. If by any chance the rate is too slow, aspirators may be used, or you may have the student attach a rubber squeeze bulb to apply pressure.

2. Preparation of test solution:
Under good conditions the analytical grade resin will hold 1.4 milliequivalents/ml [$(1.4 \times 10^{-3})(0.33)$ mole Fe^{+3} or $(1.4 \times 10^{-3})(0.5)$ mole Co^{+2} or Ni^{+2}], but there is no point in loading it completely for this experiment. The experiment has been designed for the use of 2 ml of solution containing 0.05 *M* Fe^{+3}, 0.1 *M* Co^{+2}, or 0.1 *M* Ni^{+2}. Add 2.7 grams of $FeCl_3 \cdot 6H_2O$, 2.4 grams of $CoCl_2 \cdot 6H_2O$, and 2.4 grams of $NiCl_2 \cdot 6H_2O$ to 100 ml of 9 *M* HCl, or add 10 ml each of 1 *M* $CoCl_2$ and 1 *M* $NiCl_2$ plus 5 ml of 1 *M* $FeCl_3$ to 75 ml of 12 *M* (conc. reagent) HCl.
3. Since 2 ml of solution of each ion are diluted to about 10 ml in the process of elution, the 0.005 *M* Fe^{+3}, 0.01 *M* Co^{+2}, and 0.01 *M* Ni^{+2} that result are reasonable concentrations for color comparison solutions. The Co^{+2} should be shown also in 9 *M* and in 5 *M* (or less) HCl to show the contrasting blue and pink solutions when the degree of aquation varies.

RESULTS. Ten ml of the 9 *M* acid are used to wash the column in step (c). The third 5 ml portion in step (e) will almost certainly be colorless, but if not, any remaining Ni^{+2} will come off with the first of the 5 *M* portions. After adding four 5 ml portions of 5 *M* acid in (f), any Co^{+2} left (shown by a green color on the column) will wash off with the first of the 1 *M* rinsings.

If a trace of Fe^{+3} is left on the column after four or five portions of 1 *M* acid have been used, this will not interfere with further use of the column. You should make one or two test runs before assigning this experiment to the class, since samples of resin differ considerably.

The following data were obtained with 10 cm of AG2-X8 resin in a 10 mm diameter tube. Five ml aliquots were collected and tested as described in the Laboratory Manual. The flow rate was 2.5 ml/minute.

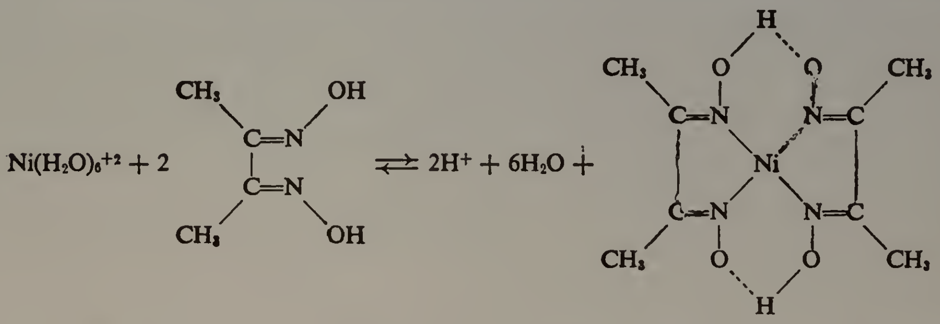
Eluate Tube No.	Acid	Color of Eluate	Result of Chemical Test for		
	9 *M* HCl		Ni^{+2}	Co^{+2}	Fe^{+3}
e-1		green	+	–	–
e-2		green	+	–	–
e-3		none	–	–	–
	5 *M* HCl				
f-1		none	–	–	–
f-2		blue	–	+	–
f-3		pink	–	+	–
f-4		pale pink	–	+	–
	1 *M* HCl				
g-1		none	–	sl+*	sl+*
g-2		yellow	–	–	+
g-3		yellow	–	–	+
g-4		pale yellow	–	–	+
g-5		none	–	–	sl+

* The KSCN gave a pale red color; the NH_4SCN, a gray color.

The qualitative tests for the various ions are as follows:

(j-1) $Fe^{+3}(aq)$ with KSCN gives blood-red $FeSCN^{+2}$ and probably some higher complexes [see *J. Chem. Education*, 30, 445 (1953)].

(j-2) $Ni^{+2}(aq)$ produces a brilliant red precipitate with dimethylglyoxime in alkaline solution.



(j-3) $Co^{+2}(aq)$ with NH_4SCN gives a blue color, probably $Co(SCN)_4^{-2}$. It is pink when hydrated to $Co(SCN)_4(H_2O)_2$. The function of the acetone is to lower the water concentration enough to stabilize the blue tetrahedral complex.

QUESTIONS

1. One of the metallic ions was eluted with 9 *M* HCl. It would also have been eluted with the 5 *M* or 1 *M* HCl solutions. Which one was it? Give a reason for this ease of elution in terms of the stability of its complex chloride anions.

   Answer: The Ni^{+2} does not form a complex chloride anion that is stable enough to be held on the column by the resin. The student may suggest the possible formation of $NiCl_4^{-2}$, but this complex has not been specifically reported.

2. The color of some of the ions on the column was different from the color of the final eluate. Explain this in terms of the composition of the complex ions.

   Answer: For the metallic ions to be held by the resin, a complex chloride ion must be formed. The complex may differ in color from the aquated ion. For cobalt, the chloride complex on the column seems to be green, although this may be due to the mixture of a blue complex with the yellow Fe^{+3} complex. In the concentrated acid the cobalt complex contains chloride and is blue in color. This complex is probably a mixture of $CoCl_4^{-2}$ and $CoCl_3(H_2O)^-$. [See Cotton and Goodgaine, *J. Am. Chem. Soc.*, 83, 4690 (1961).] The species for the iron complex is $FeCl_6^{-3}$, which is yellow.

3. What are the conditions which favor the release of ions from the column?

   Answer: The ions are released from the column when the concentration of chloride ion is too low for the complex to be stable.

4. Recalling that the resin used is an anion exchange type, which of the metallic ions in this experiment forms the most stable complex chloride anion?

   Answer: The $Fe(Cl)_6^{-3}$ is the most stable complex chloride used in this experiment.

POSTLAB DISCUSSION. A discussion of complex ions is appropriate as a follow-up of this experiment. Students may also be interested in knowing that chloride complexes of elements from Mn through Zn may be separated in a similar manner. [See Kraus and Moore, *J. Am. Chem. Soc.*, **75**, 1460 (1953).]

EXPERIMENT 38 SOME INVESTIGATIONS INTO THE CORROSION OF IRON

PURPOSE. To give more examples of oxidation and reduction, related to one of the transition elements.

PRELAB DISCUSSION. Very little is needed. Be sure the students realize that they will investigate some behavior but will not be "finding answers."

TIMING. Assign this experiment near the end of Chapter 22.

EQUIPMENT NEEDED (PER STUDENT OR PAIR)

9 clean iron nails (size not important but depends somewhat upon test tube size. Be sure these are not specially treated corrosion-resistant nails)
thin strip of zinc, about 8 cm long and 2 mm wide (see lab hint 2)
10 cm bare copper wire (B and S gauge 14–20)
2 g powdered agar-agar
1 ml 0.1 *M* ferrous sulfate (2.8 g $FeSO_4 \cdot 7H_2O$/100 ml)
2 ml 0.1 *M* potassium ferricyanide (3.3 g $K_3Fe(CN)_6$/100 ml)
0.5 ml 1% phenolphthalein (1 g/100 ml 50% ethanol)

5 ml each from one group of the following (see lab hint 1):

GROUP A
- 0.1 *M* $NaOH$ (0.4 g/100 ml)
- 0.1 *M* $Na_2Cr_2O_7$ (3 g $Na_2Cr_2O_7 \cdot 2H_2O$/100 ml)
- 0.1 *M* $NaCl$ (0.6 g/100 ml)
- 0.1 *M* HCl (8.6 ml conc. reagent/100 ml)

GROUP B
- 0.1 *M* KOH (0.6 g/100 ml)
- 0.1 *M* Na_2CO_3 (1.2 g $Na_2CO_3 \cdot H_2O$/100 ml)
- 0.1 *M* KNO_3 (1 g/100 ml)
- 0.1 *M* HNO_3 (6.4 ml conc. reagent/100 ml)

GROUP C
- 0.1 *M* Na_3PO_4 (3.8 g $Na_3PO_4 \cdot 12H_2O$/100 ml)
- 0.1 *M* $Na_2C_2O_4$ (1.3 g/100 ml)
- 0.1 *M* $NaSCN$ (0.8 g/100 ml)
- 0.1 *M* H_2SO_4 (0.5 ml conc. reagent/100 ml)

5 test tubes (need not be hard glass; may be any size)
litmus, Hydrion, or other acid–base indicator
250 ml beaker
ring stand, ring, gauze, and burner or hot plate
2 petri dishes (covers not essential) (see lab hint 3)
distilled water (if deionized water is used, it should be boiled to reduce the acidity caused by dissolved CO_2).

TIME REQUIRED. Allow 1½ periods for this experiment. Do Parts I a–I d and Parts II a through part of e on the first day.

LABORATORY HINTS

1. Solutions may be stored conveniently in squeeze bottles. Prepare three sets, but assign only one to each student. Comparison with data of other students is asked for in Part I d.

2. As suggested in Part II c, mossy zinc may be used.
3. If petri dishes are not available, use beakers.

NOTE ON CORROSION. The nature of corrosion is almost always the same—a flow of electrons between certain areas of a metal surface or between different metals. This action causes metallic ions to be produced at areas that are anodes. If the metal is in water, the ions formed are carried away; the ions in the solution also aid in the transfer of electrons, increasing the corrosive activity. In the process, hydrogen is given off from the areas that are cathodes. Since hydroxide accumulates in the solution, it is not surprising that hydroxide ions already in solution might inhibit this reaction. The accumulation of hydrogen gas at the cathode (polarization) may also inhibit the reaction (this also occurs in neutral solutions). But dissolved oxygen often combines with the hydrogen, depolarizing the electrode and allowing the corrosion to proceed. Other secondary reactions also take place, such as the oxidation of ferrous hydroxide to ferric hydroxide in the corrosion of iron.

RESULTS

	Acidity as Indicated by Litmus	Rust Evident	Other Change	Result of Test for Fe^{+3}	Appearance When Dried
NaOH	basic	no	none	negative	shiny
$Na_2Cr_2O_7$	neutral	no	none	negative	shiny
NaCl	neutral	very slight	none	blue*	corrosion, especially on head
HCl	acidic	no	bubbles	deep blue	corrosion
KOH	basic	no	none	negative	shiny
Na_2CO_3	basic	no	none	negative	slightly dull
KNO_3	neutral	on bottom of tube	none	some blue on head	quite corroded, especially on head
HNO_3	acidic	no	bubbles	deep blue	corrosion
Na_3PO_4	basic	no	nail less shiny	negative	very slightly tarnished
$Na_2C_2O_4$	neutral	no	none	negative	slightly tarnished
NaSCN	neutral	on bottom of tube	none	some blue on head	very rusted
H_2SO_4	acidic	no	bubbles	deep blue	much corrosion
distilled H_2O	slightly acidic	on bottom of tube	none	negative	considerable corrosion

* This occurred in two out of three trials.

QUESTIONS AND EXERCISES

1. List the reagents in Part I where no indication of corrosion was observed.

   Answer: None was observed for NaOH, $Na_2Cr_2O_7$, KOH; a little was observed for Na_2CO_3, Na_3PO_4, $Na_2C_2O_4$.

2. List the reagents in Part I in which there was an indication of corrosion.

   Answer: Acids (all), NaCl, KNO_3, NaSCN, distilled water.

3. Are any regularities in evidence? What is the evidence? How do you account for the regularity?

   Possible Answers: A basic condition inhibits action; acid and other ions favor it. Some students may answer "no" to the first question; tell them not to get discouraged. Point out that much variation exists between nails; in addition, other conditions are seldom controlled.

4. What did you observe regarding the reactions at the head, the pointed end, or at the sharp bend of the nail which were different from the rest of the nail? Account for this in terms of the mechanical treatment of the nail during its manufacture.

Answer: In the solutions in Part I, rusting was usually most evident on the head. In the agar plates, rusting was clearly most evident on the head, and sometimes also on the tip. Sometimes only the head or tip was involved; sometimes both. During manufacture the head and tip have been subjected to more stress than the shaft of the nail. Forming the sharp bend also introduces stress, and corrosion may be more evident there also.

5. Why is it that a nail can stand for many days on the shelf in a hardware store and not rust, but when placed in tap water it quickly rusts?

Answer: In water ions are present, and frequently acid. In Part I the presence of ions, especially $H^+(aq)$, seemed to speed up the reaction.

6. Ferrous ions react with potassium ferricyanide to form a colored precipitate. Write the equation for the reaction.

Answer

$$Fe^{+2}(aq) + K^+(aq) + Fe(CN)_6^{-3}(aq) = \underset{\text{(deep blue)}}{KFeFe(CN)_6(s)}$$

7. Which color in Part II indicates the site of the oxidation reaction? Which the site of the reduction? Account for the formation of each color.

Answer: The blue color (see answer to question 6) indicates formation of Fe^{+2}, and hence oxidation. The pink color of the phenolphthalein indicates formation of OH^-, and hence the site of the reduction.

8. Write the oxidation and reduction reactions for each case in which you observed a reaction in Part II.

Answer:

$$\begin{aligned} Fe &= Fe^{+2}(aq) + 2e^- && \text{(oxidation)} \\ 2e^- + 2H_2O &= H_2(g) + 2OH^-(aq) && \text{(reduction)} \end{aligned}$$

These are the reactions for the nail alone and for the nail with the copper strip. No bubbles of hydrogen will be evident because the reaction is slow. With the zinc strip the reactions are

$$\begin{aligned} Zn &= Zn^{+2}(aq) + 2e^- && \text{(oxidation)} \\ 2e^- + H_2O &= H_2(g) + 2OH^-(aq) && \text{(reduction)} \end{aligned}$$

Some solid $Zn(OH)_2$ may form and show up as a white cloudiness in the agar. Zinc ferricyanide is also a white solid.

9. Consult the E° table in Appendix 8, and predict another metal that is more readily oxidized than iron and will protect it from corrosion. Test your prediction by an experiment.

Answer: Any metal with a higher E° than $Fe = Fe^{+2} + 2e^-$ ($E^\circ = 0.44$ volt) can protect iron. Examples are Mg ($E^\circ = 2.37$) or Al ($E^\circ = 1.66$). The student will surely know by this time that metals such as Na and K will be too reactive to be practical and that many of the others will not be available. When tested by experiment the Mg works well, but Al (both foil and wire were tried) does not. Probably the oxide coating prevents contact between the metals, hence a metal–metal couple is not produced.

10. How does a coating of zinc on iron (galvanized iron) protect iron from corrosion?

Answer: Zinc serves as an anode and protects the iron by keeping it reduced to Fe. It also is limited in its oxidation, since the zinc oxide bonds tightly to the surface and serves as protection.

11. Magnesium metal rods are sometimes placed in hot water heaters. Why?

Answer: This question implies an iron heater. The Mg is oxidized more easily than Fe, hence serves as the anode. Metals are referred to as "sacrificial" metals when used in this way.

POSTLAB DISCUSSION. This experiment opens up an area in which there are many unanswered questions. Probably the students will not all observe the same behavior because there are a number of factors involved that are not controlled. Some of these factors are impurities in the water, gases dissolving from the air, condition of the nails, temperature, etc.

EXPERIMENT 39 PREPARATION OF A COMPLEX SALT AND A DOUBLE SALT

PURPOSE. To give experience with double and complex salts and with crystallization.

PRELAB DISCUSSION. None is needed.

TIMING. Assign this experiment any time during Chapter 22. It is especially related to pp. 392–396.

MATERIALS NEEDED (PER STUDENT OR PAIR)

Chemicals

10 g cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$)
2.6 g ammonium sulfate
15 ml 15 *M* ammonia solution (conc. reagent) (7 ml to make a mixture of ammonia and alcohol in part II d)
15 ml ethanol (7 ml to make mixture above)
0.1 g anhydrous copper sulfate (student may prepare this)
5 ml 6 *M* ammonia solution (40 ml conc. reagent/100 ml)

Equipment

3 large test tubes (18 × 150 mm)
250 ml beaker (for water bath)
100 ml beaker
filter paper
mortar and pestle
balance
graduate
watch glass
funnel
3 small hard glass test tubes (13 × 100 mm)
aspirator

TIME REQUIRED. Allow 1½ periods. As directed in the Laboratory Manual the student is to go on with Part II after I b (15 minutes). In the first period he should either stop after Part I b or do Part II, through (f) (25–30 minutes).

DISCUSSION OF PROCEDURE.

PART I

(a) 0.02 mole of $CuSO_4 \cdot 5H_2O = 5.0$ g
0.02 mole of $(NH_4)_2SO_4 = 2.6$ g
If large crystals are present each should be ground in a mortar and pestle before weighing.
(e) 0.02 mole (8.0 g) could be formed if practically all the reactants reacted. A 75–80% yield is to be expected. If the crystals are not dry, a higher yield will be reported.

PART II

(b) The $CuSO_4 \cdot 5H_2O$ should be pulverized for more rapid solution.
(c) If the alcohol mixes too quickly, the solid will be a mass of tiny crystals that are slow to settle and difficult to separate from the liquid.
(f) Drying over night will ensure more complete removal of excess water.
(g) 0.02 mole of this complex (mol wt = 246) is 4.92 grams. A yield of 80% is reasonable. 0.08 mole of ammonia would have been used.

PART III

(a) The blue color typical of the aquated Cu^{+2} ion is seen when water is added to the anhydrous salt. When ammonia solution is added, a deep blue color is produced. If he adds the $NH_3(aq)$

too rapidly the student may see the interim production of white copper hydroxide before the complex is formed.

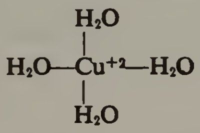
(b) The double salt is very light aqua blue (typical of hydrated Cu^{+2}), and the complex salt is a royal blue. When diluted, the color of the first almost disappears. The second may become milky and lose the deep blue color. Whether this happens depends upon the amount of salt used, and, since the amount is not specified, different students will undoubtedly get different results. A reasonable explanation is that the $Cu(H_2O)_4^{+2}(aq)$ ions are too pale in color to be seen when diluted and that the $Cu(NH_3)_4^{+2}(aq)$ ions change to $Cu(H_2O)_4^{+2}(aq)$ upon addition of more water. The milkiness that may be observed is probably $Cu(OH)_2(s)$.

(c) When heated gently the double salt loses water and becomes white. If heated strongly some decomposition occurs, and a brown solid is produced. The gas is $H_2O(g)$. The complex salt decomposes very easily to leave a red-brown solid. The odor of ammonia is clearly evident, as is that of SO_2 (see question 4 for equation). $H_2O(g)$ is also given off.

QUESTIONS

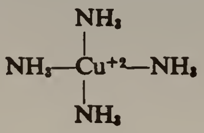
1. In Part III a, account for the successive color changes noted in terms of the structure of the ion containing copper.

Answer: The first aqua blue will be attributed to aquated copper(II) ions,



$$\begin{array}{c} H_2O \\ | \\ H_2O—Cu^{+2}—H_2O \\ | \\ H_2O \end{array}$$

although the ions in the solution are not necessarily those in the hydrate. The deeper blue is due to the formation of tetraamminecopper(II) ions,



$$\begin{array}{c} NH_3 \\ | \\ NH_3—Cu^{+2}—NH_3 \\ | \\ NH_3 \end{array}$$

which are also aquated.

2. What are the ionic species present when the double salt cupric ammonium sulfate dissolves in water?

Answer: The ionic species present in the solution are $Cu^{+2}(aq)$, $NH_4^{+}(aq)$, and $SO_4^{-}(aq)$.

3. What are the ionic species present when the complex salt tetraamminecopper(II) sulfate dissolves in a small quantity of water? Give a reasonable explanation of the changes which took place as more water was added.

Answer: The ionic species present in the crystal are $Cu(NH_3)_4^{+2}$ and $SO_4(H_2O)^{-2}$. In water these become further aquated. The changes in color as water is added are due, at first, to aquation and, as still more is added, to H_2O replacement of NH_3 in association with the copper. The reaction

$$Cu^{+2}(aq) + 2OH^{-}(aq) \rightleftarrows Cu(OH)_2(s)$$

shifts the equilibrium of the reaction

$$NH_3(aq) + H_2O \rightleftarrows NH_4^{+}(aq) + OH^{-}(aq)$$

to the right; as a result, less NH_3 is available for complex ion formation. Thus as more $Cu(OH)_2(s)$ is formed, more $NH_4^{+}(aq)$ will also be formed.

4. Account for the changes you noted when each salt was heated.

Answer: The change to a white substance when the double salt is heated is due to the loss of water. Only the hydrated Cu^{+2} ion is blue; anhydrous copper sulfate is white. If the salt is heated strongly copper oxides and SO_2 may be produced.

When the tetraamminecopper(II) sulfate is heated the student will notice some condensation of moisture and the strong odor of ammonia. He may check for ammonia by holding moist litmus at the mouth of the test tube. Even with gentle heating he will note that the solid becomes red or black. In addition to the odor of ammonia he will detect the strong odor of SO_2. The odor of NO_2 would be obscured; if only a little is produced the color might not be noticeable. The red solid is probably copper(I) oxide and the black one, copper(II) oxide. A suggested equation is

$$2NH_3 + 5Cu^{+2} + 5SO_4^{-2} \rightleftharpoons 5CuO + 5SO_2 + 2NO + 3H_2O$$

5. From the evidence obtained in this experiment, list the ionic species which constitute the fundamental building blocks in crystals of:
   (a) cupric sulfate (anhydrous),
   (b) cupric sulfate pentahydrate,
   (c) cupric ammonium sulfate hexahydrate,
   (d) tetraamminecopper(II) sulfate monohydrate.

Answer: Again it is important to emphasize that the species present in solution are not those present as building blocks in the crystals. The evidence of the experiment indicates that:

(a) $CuSO_4$ (anhydrous) is Cu^{+2} and SO_4^{-2}, since when water is added its appearance is the same as with the hydrate.

(b) $CuSO_4 \cdot 5H_2O$ is somehow hydrated, but the color is different in solution than in the crystal, hence the student has no basis for knowing that, in the crystal, each Cu^{+2} is associated with $4H_2O$ and is also adjacent to an oxygen of each of two SO_4^{-2} ions. Each SO_4^{-2} ion in the crystal is also associated with an H_2O.

(c) It is shown that $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ becomes aquated in the same way that $CuSO_4 \cdot 5H_2O$ does and that, when heated, it forms a white solid like $CuSO_4$. This suggests a different structure than in (d), where NH_3 rather than NH_4^+ is present.

(d) $Cu(NH_3)_4SO_4 \cdot H_2O$ is shown to give the same colored ion as when $NH_3(aq)$ is added to hydrated Cu^{+2}, hence there is evidence for a close association of Cu^{+2} and NH_3 in this crystal. Moreover, the products of decomposition are not the same, indicating a difference, but not the nature of the difference. Very probably the student answer to this question will be the following, and you should explain that he is answering from the formulas given, not from experimental evidence.

   (a) Cu^{+2} and SO_4^{-2}
   (b) $Cu(H_2O)_4^{+2}$, $SO_4(H_2O)^{-2}$
   (c) $Cu(H_2O)_4^{+2}$, $2NH_4^+$, $2SO_4(H_2O)^{-2}$
   (d) $Cu(NH_3)_4^{+2}$, $SO_4(H_2O)^{-2}$

6. Why was a yield of 0.02 mole expected for each of the salts you prepared?

Answer: Since 0.02 mole of each of the single salts was used, the yield for the others would be 0.02 mole. The equations are as follows:

$$CuSO_4 \cdot 5H_2O + (NH_4)_2SO_4 + H_2O \rightleftharpoons CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$$

$$CuSO_4 \cdot 5H_2O + 4NH_3 \rightleftharpoons Cu(NH_3)_4SO_4 \cdot H_2O + 4H_2O$$

EXPERIMENT 40 PREPARATION OF POTASSIUM DICHROMATE

PURPOSE. To make use of oxidation-reduction reactions in an inorganic preparation and to illustrate some of the reactions of a transition metal.

PRELAB DISCUSSION. Remind the students of their previous observations of $K_2Cr_2O_7$–K_2CrO_4 in Expt. 19 and in Part II of Expt. 22.

TIMING. This experiment could be given at any time during or preceding Chapter 22. The chemistry involved has been covered in previous chapters (Chapter 12 especially).

EQUIPMENT (PER STUDENT OR PAIR)

2.5 g chromium(III) acetate (see lab hint 1)
25 ml 6 *M* KOH (33.6 g/100 ml) (see lab hint 2)
50–60 ml H_2O_2 (3% made by diluting 30% commercial; see lab hint 3)
3 ml 18 *M* acetic acid (glacial)
10 ml ethanol
100 ml beaker
250 ml Erlenmeyer flask
ring stand, ring, gauze, and burner or hot plate
medicine dropper
ice and container (1000 ml beaker or substitute)
1 or 2 boiling chips
balance (±0.01 g)

PRECAUTIONS. Chromium compounds are poisonous, but since they are being handled as solutions, there seems to be no danger. With 3% H_2O_2 there is no danger, but higher concentrations cause severe burns. If higher concentrations are to be diluted by the student, he should wear safety glasses. Glasses should also be worn when handling glacial acetic acid. Caution student to boil *gently* in Part (d), to avoid spattering.

TIME REQUIRED. One period is sufficient if it is spread over three days to allow an evaporating period after procedure (d) and again after (g). Procedures (a)–(d) require about 30 minutes, with an additional 20–30 minutes needed to reduce the volume to 30 ml; (e) and (f) require 15 minutes; and (g), 10 minutes.

LABORATORY HINTS

1. Chromium(III) acetate is sold as $Cr(CH_3COO)_3 \cdot xH_2O$, with an assay of 23–25% Cr. This indicates an average of about one molecule of H_2O for each molecule of $Cr(CH_3COO)_3$. The monohydrate formula is given in the Laboratory Manual.
2. KOH absorbs CO_2 readily; the $[OH^-]$ of the solution should be checked before being used in this experiment.
3. Stabilized hydrogen peroxide (30%) keeps well in the stockroom and may be conveniently diluted for student use, providing all glassware has been scrupulously cleaned (detergent, H_2O rinse, dilute acid rinse, additional H_2O rinses) (almost everything acts as a catalyst for H_2O_2 decomposition). The student will find that 17 ml of 3% H_2O_2 is sufficient, but he should use about 50 ml initially. See the answer to question 1.
4. In procedure (d) the excess H_2O_2 is boiled off. If it is not, Cr^{+3} is formed instead of $Cr_2O_7^{-2}(Cr^{+6})$ when acid is added. If the solution turns green upon addition of acid, add more KOH and H_2O_2, and reheat for 10 minutes.

The solution must be *gently* boiled, since there is danger of spattering, even when a 250 ml Erlenmeyer flask is used. But if an overnight period is available, the solution may be concentrated by heating in a drying oven at 30–50°C.

QUESTIONS AND EXERCISES

1. Write the equations for the reactions involved in each of the steps used in the preparation of $K_2Cr_2O_7$. Show your calculations for the amount of H_2O_2 required and for the expected yield of $K_2Cr_2O_7$.

Answer: The balanced equations are:

STEP I: $Cr(H_2O)_6^{+3} + 4OH^- = Cr(H_2O)_2(OH)_4^- + 4H_2O$
See Textbook p. 394 for a discussion of this complex ion and Textbook p. 396 for a discussion of this reaction.

STEP II: The equation is:

$$Cr(OH)_4^- + 4OH^- = CrO_4^{-2} + 4H_2O + 3e^- \qquad E^\circ = 0.13 \text{ volt} \qquad (1)$$

A footnote informs the student that $Cr(OH)_4^-$ is the same as $Cr(H_2O)_2(OH)_4^-$, shown in the introduction, except that the water of aquation is omitted.

$$3OH^- = HO_2^- + H_2O + 2e^- \qquad E^\circ = -0.88 \text{ volt} \qquad (2)$$

Using (*1*) and (*2*) he will get the net equation

$$2Cr(OH)_4^- + 3HO_2^- = 2CrO_4^{-2} + 5H_2O + OH^- \qquad E^\circ = 1.01 \text{ volts}$$

STEP III: $2CrO_4^{-2} + 2H^+ = Cr_2O_7^{-2} + H_2O$
For 0.01 mole of chromium acetate, 0.015 mole of H_2O_2 will be needed, since 2 moles of $Cr(OH)_4^-$ require $3HO_2^-$ (Step II).

$$(0.015 \text{ mole})(34 \text{ g/mole}) = 0.51 \text{ g}$$

Since a 3% H_2O_2 solution contains 0.03 g H_2O_2/ml,

$$\frac{0.51 \text{ g}}{0.03 \text{ g/ml}} = 17 \text{ ml}$$

Each mole of chromium acetate yields $\frac{1}{2}$ mole of $K_2Cr_2O_7$, hence 0.01 mole of chromium acetate is produced from 0.005 mole of dichromate. This is (0.005 mole) (294 g/mole) = 1.47 g.

2. What ionic species were present in the final acidic solution before it was cooled? What equilibria are present?

Answer: The ionic species were $CH_3COO^-(aq)$, $H^+(aq)$, $K^+(aq)$, $Cr_2O_7^{-2}(aq)$, and a small amount of $CrO_4^{-2}(aq)$;

$$2CrO_4^{-2}(aq) + 2H^+(aq) = Cr_2O_7^{-2}(aq) + H_2O$$

and

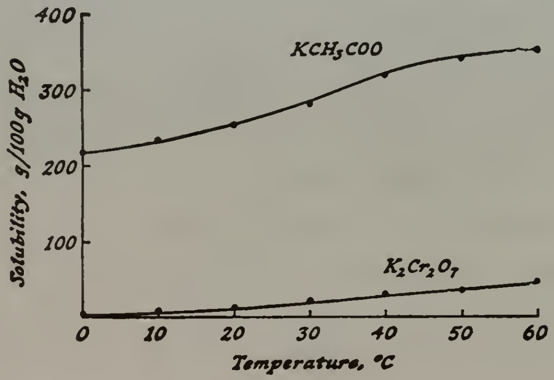
$$H^+(aq) + OH^-(aq) = H_2O$$

In both these equations, equilibrium strongly favors the products. Recall Expt. 19.

3. Considering the following solubility data, would you expect your sample of $K_2Cr_2O_7$ to be relatively pure? Why?

Temperature (°C)	Solubility in g/100 g H_2O KCH_3COO	 $K_2Cr_2O_7$
0	217	5
20	256	12
40	323	26
60	350	43
80	380	61
100	—	80

Answer: The sample should be quite pure. KCH_3COO is quite soluble and will stay in solution. The data for the solubilities of these two compounds gives the following curves:



At 10°C almost 2 grams of $K_2Cr_2O_7$ would dissolve in 25 ml water. In this experiment 0.005 moles of $K_2Cr_2O_7$ may be produced, which is 1.5 grams (0.005 mole × 294 g/mole). However, only 0.01 mole of K^+ is required and 0.15 mole was added (0.025 liter × 6 moles/liter). This large excess of K^+ will result in the crystallization of considerable $K_2Cr_2O_7$ from this solution.

At 10°C the K_{sp} of $K_2Cr_2O_7 = \sim 5 \times 10^{-2}$. If the concentration of K^+ is 0.15 mole in 25 ml, or 6 *M*, the amount of $Cr_2O_7^{-2}$ remaining in the solution is only about 0.01 gram. This is consistent with the percent yield (nearly 100%) actually obtained in two trial runs of this experiment.

4. Compare the $E°$ values of the half-reactions for the oxidation of Cr(III) to Cr(VI) in a basic solution with that for the oxidation in an acidic solution. See the introductory section of this experiment for the former value and Appendix 8 for the latter value. Which oxidation is potentially the more spontaneous?

Answer: The reaction in basic solution is spontaneous, whereas in the acidic solutions, it is not. For equations in basic solution, see Step II above.

$$2Cr(OH)_4^- + 3HO_2^- = 2CrO_4^{-2} + 5H_2O + OH^- \qquad E° = 1.01 \text{ volts}$$

The products are favored.

In acid solution

$$2Cr^{+3} + 7H_2O = 6e^- + Cr_2O_7^{-2} + 14H^+ \qquad E° = -1.33 \text{ volts}$$

Therefore

$$2Cr^{+3} + 3HO_2^- + H_2O = Cr_2O_7^{-2} + 5H^+ \qquad E° = -0.45 \text{ volt}$$

The reactants are favored. In fact, with H_2O_2 in acid solution,

$$H_2O_2 = O_2(g) + 2H^+ + 2e^- \qquad E° = -0.68 \text{ volt}$$

hence the spontaneous reaction would be

$$3H_2O_2 + Cr_2O_7^{-2} + 8H^+ = 3O_2 + 2Cr^{+3} + 7H_2O \qquad E° = +0.65 \text{ volt}$$

rather than the oxidation of Cr^{+3} to Cr^{+6}.

5. Note the half-reaction for the oxidation of H_2O_2, for which the $E°$ value is −0.68 volt (Appendix 8). Can you now suggest a reason for decomposing the excess H_2O_2 in Step d before the solution was acidified to convert CrO_4^{-2} to $Cr_2O_7^{-2}$?

   Answer: See the answer to question 4. If excess H_2O_2 were left, the CrO_4^{-2} or $Cr_2O_7^{-2}$ would be reduced to Cr^{+3} when the solution was acidified.

6. Is the conversion of chromate ion to dichromate ion an oxidation reaction? Explain.

   Answer: In both CrO_4^{-2} and $Cr_2O_7^{-2}$ the oxidation number of Cr is +6, hence this conversion is not an oxidation-reduction reaction.

EXPERIMENT 41 THE PREPARATION OF CHROME ALUM

PURPOSE. To give further experience with oxidation-reduction reactions and with crystallization.

PRELAB DISCUSSION. None is needed.

TIMING. This experiment may be done any time during Chapter 22, since a transition element is used as an example. The oxidation-reduction reactions have been covered in Chapter 12.

MATERIALS NEEDED (PER STUDENT OR PAIR)

- 15 g potassium dichromate
- 30 g sodium metabisulfite ($Na_2S_2O_5$), sometimes called sodium hydrogen sulfite
- 30 ml 6 *M* sulfuric acid (340 ml conc. reagent/liter)
- 60 ml 3 *M* sulfuric acid (170 ml conc. reagent/liter)
- ice (about 250 g)
- balance (±0.01 g)
- graduate (25 or 100 ml)
- 250 ml erlenmeyer flask
- 125 ml flask or a second 250 ml flask
- evaporating dish and watch glass
- 400 ml beaker or other container for ice bath
- delivery tube (30–40 cm, 6 mm inner diameter)
- glass bend and glass tube (6 mm tubing, each about 10 cm long)
- #6 two-hole stopper
- thistle or funnel tube
- ring stand, ring, gauze, clamp for flask
- burner
- thermometer
- medicine dropper (pipet)
- filter paper
- funnel

TIME REQUIRED. The student will need $1\frac{1}{2}$ periods. Procedure (a) (10 minutes) may be done on the first day; (b) through the first part of (g), on the second day (45 minutes); and the rest of (g) and (h) on the third day, a week or so later (20 minutes).

PRECAUTIONS. Emphasize the importance of handling sulfuric acid correctly and of thorough clean-up if any is spilled. The generation of SO_2 must be carried on in a well-ventilated room or under a hood. Take care that the gas is thoroughly reacted with the solution through which it is being bubbled and that it is not produced too rapidly. When disposing of the generator after the reaction is complete, do not breathe the fumes.

PROCEDURE. Before coming to the laboratory, the student should have worked out the following equations and amounts of reactants:

$$\begin{aligned}
& 3[SO_2(g) + 2H_2O = SO_4^{-2} + 4H^+ + 2e^-] && E^\circ = -0.17 \text{ volt} \\
& Cr_2O_7^{-2} + 14H^+ + 6e^- = 2Cr^{+3} + 7H_2O && E^\circ = +1.33 \text{ volts} \\
\textit{Net:}\ & Cr_2O_7^{-2} + 2H^+ + 3SO_2(g) = 2Cr^{+3} + H_2O + 3SO_4^{-2} && E^\circ = +1.16 \text{ volts}
\end{aligned}$$

(a) 0.05 mole of $K_2Cr_2O_7$ is (0.05 mole)(294 g/mole) = 14.7 grams.

(b) From the equations above we see that three moles of SO_2 are needed per mole of $K_2Cr_2O_7$, hence 0.15 mole SO_2 is needed for 0.05 mole $K_2Cr_2O_7$. The equations for the production of SO_2 are

$$\begin{aligned}
Na_2S_2O_5(s) + H_2O &= 2HSO_3^-(aq) + 2Na^+(aq) \\
HSO_3^-(aq) + H^+(aq) &= H_2O + SO_2(g)
\end{aligned}$$

Therefore one mole of $Na_2S_2O_5$ will produce two moles of SO_2, and since 0.15 mole SO_2 is needed, 0.075 mole of $Na_2S_2O_5$ will be needed.

$$(0.075 \text{ mole})(190 \text{ g/mole}) = 14.25 \text{ g } Na_2S_2O_5$$

The student should use about 30 grams of $Na_2S_2O_5$ because the yield is not 100%.

When heated, the hydrated violet chromium sulfate, $[Cr(H_2O)_6]_2(SO_4)_3 \cdot nH_2O$, forms green chromium(III) sulfates called sulfato-complex compounds. Most of these complex compounds have a very poor ability to crystallize. It is, therefore, extremely important that the temperature be controlled here to prevent the formation of these troublesome compounds, which tend to inhibit crystallization of the chrome alum.

(e)–(f) Two moles of $H^+(aq)$ are required for one mole of $Na_2S_2O_5$, therefore 0.15 mole will be required for 0.075 mole. Since 6 M H_2SO_4 is being used, there are available two H^+ per mole, or 0.012 mole H^+/ml. To obtain 0.15 mole of H^+ we need 0.15 mole/0.012 mole/ml = 12.5 ml. Thus 12 to 13 ml of H_2SO_4 would be sufficient, but owing to dilution, slightly more than this will be needed. Two or three 10 ml portions should be sufficient.

The student will need to watch this reaction carefully. Very little heating of the generator is needed to maintain the production of SO_2 so that it will enter the solution only as fast as it can react. If allowed to cool too much, however, liquid from the reaction flask will be forced back. The time needed will vary considerably, but 30 minutes seems a good average. The test with a drop on some filter paper works very well and is clear-cut.

(g) It may occur to the student to reduce the volume somewhat here, but if he does, the solution will become quite viscous and form a syrupy mixture which will not crystallize, therefore we suggest that he be told not to do this. It is probably best to assign this experiment far enough from the end of the semester so that the crystals have plenty of time to develop; otherwise you will have to be satisfied with very small ones. Since the solution contains enough acid to react with the string, we advise against suspending a string on which crystals may grow.

(h) The maximum possible yield is 0.1 mole, since one mole of $K_2Cr_2O_7$ will produce two moles of chrome alum if one considers the ionic species present in the crystal lattice to be $Cr(H_2O)_6^{+3}$, $K(H_2O)_6^{+}$ and SO_4^{-2}. Thus (0.1 mole)(499 g/mole) = 50 grams. At room temperature 24 grams of chrome alum dissolve in 100 grams of water. When poured into the evaporating dish, there will be about 50–60 ml of solution, so one may expect to obtain 30–35 grams of crystals. There is, however, a great tendency for a supersaturated solution to form, and the actual yield is more likely to be 20–25 grams.

QUESTIONS AND EXERCISES

1. Write the equations for the reactions involved in the experiment as requested in the introduction. Include the reaction for the production of sulfur dioxide.

Answer: See the discussion of procedure for details.

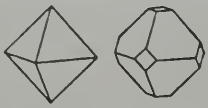
$$Cr_2O_7^{-2} + H^+ + 3SO_2 = 2Cr^{+3} + H_2O + 3SO_4^{-2}$$
$$Na_2S_2O_5 + 2H^+ = 2Na^+ + 2SO_2 + H_2O$$

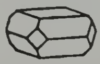
2. Under what conditions could you grow large crystals of chrome alum?

Answer: The student will suggest slow evaporation or gradual cooling to get large crystals. He may know about the method of "seeding" with a small well-formed crystal. If any students are particularly interested, a good reference is Holden and Singer, *Crystals and Crystal Growing*, Doubleday (an Anchor Book) (1960).

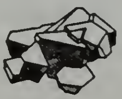
3. Examine one of the larger crystals you prepared. Note any outstanding features of its geometric symmetry, and prepare a sketch showing these.

Answer: He may observe that the crystal is octahedral. He will certainly note that most of the crystals show a distinct triangular face, but some rectangular faces. Many will be pyramids.





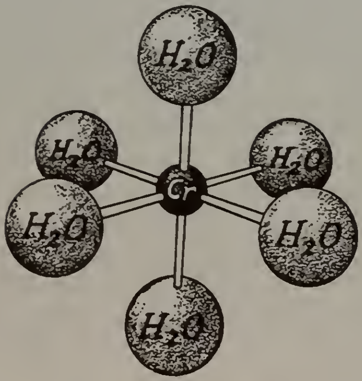
"Tablet" growing on bottom of container



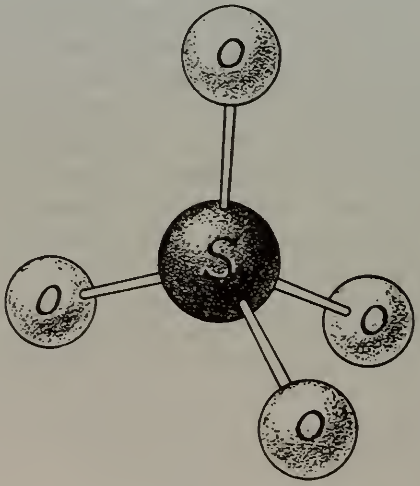
"Sketch" of crystals produced on trial run of experiment

4. What are the building blocks of the chrome alum crystal? Draw a three-dimensional structural formula for each of the ionic species involved.

   Answer: The building blocks of the crystal are Cr^{+3} ions, each hydrated with six molecules of water, similarly hydrated potassium ions, again with six molecules of H_2O, and SO_4^{-2} ions.



$Cr(H_2O)_6^{+3}$



SO_4^{-2}

5. Show calculations of the amounts of reactants required and the theoretical yield expected.

   Answer: See the discussion of procedure (a) for amount of $K_2Cr_2O_7$, (b) for amount of $Na_2S_2O_5$, (e)–(f) for amount of H_2SO_4, and (h) for theoretical yield.

Supplementary Material

Articles

G. A. W. Boehm, "Titanium: a new metal," *Scientific American*, April 1949, pp. 48–51 (Offprint 258).*

H. F. Walton, "Ion exchange," *Scientific American*, November 1950, pp. 48–51.

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

VANADIUM, A TRANSITION ELEMENT

A CHEM Study film
Running Time: 22 minutes

The collaborator, Professor Robert Brasted, University of Minnesota, shows vanadium as a typical transition element. The different oxidation states and their colors are identified via titration with cerium solution. The oxidation states and the observed colors are correlated with the electronic structures using an orbital board. The formation of complex ions containing vanadium in various oxidation states is demonstrated. The variations in properties are discussed in terms of ion size and charge density.

HIGH TEMPERATURE RESEARCH

A CHEM Study film
Running Time: 19 minutes

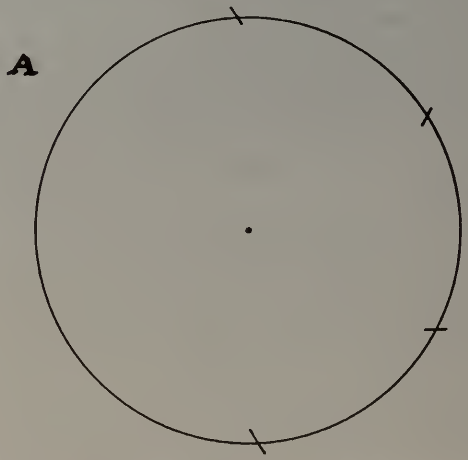
A high-temperature laboratory, its instruments and furnaces are shown by the collaborator, Professor Paul Gilles of the University of Kansas. He does experiments with titanium sulfide and uses a crystal model of TiS to explain the purpose of high-temperature research. From the mass spectrum of TiS vapor and from vapor pressure data at various temperatures, he derives the bond energy in the gas species. This film points out the challenge of high-temperature research and its possible applications.

How to Make a Tetrahedron and an Octahedron

These solid figures are quite useful for illustrating some of the geometrical forms exhibited by molecules.

Tetrahedron

Choose the length of side desired; 4–6 inches is best. Use cardboard or showcard for durability. Draw a circle having a radius equal to the side chosen, and lay off the same radius three times around the circle, as shown in (A).



Connect the points, and center with light lines to give (B). Then extend the lines as in (C), and add gluing tabs as shown.

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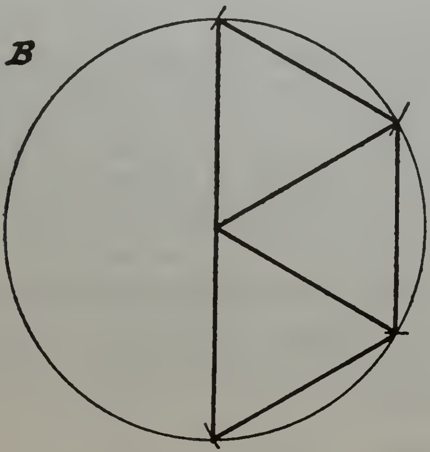
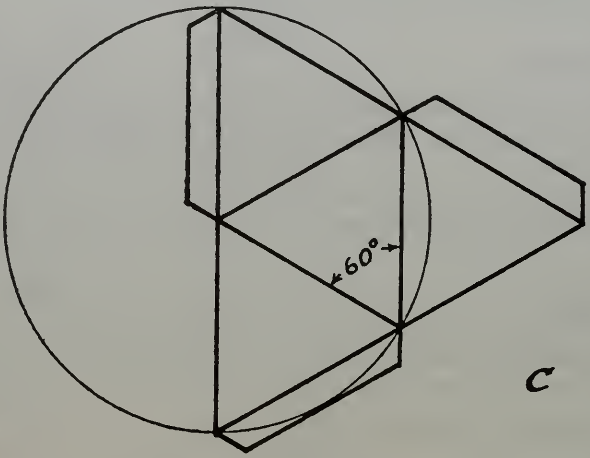
* Available from W. H. Freeman and Co., San Francisco. Order by number.



B



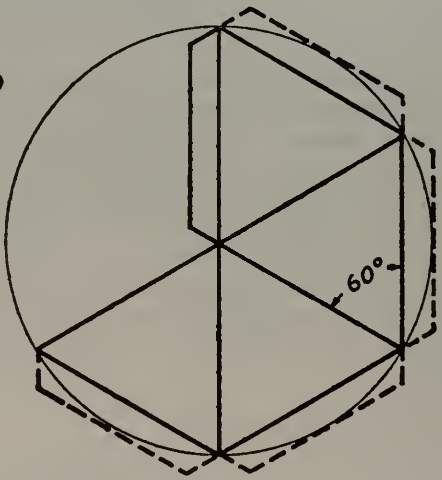
C

Cut around the outer edges, score the inner lines (with the back of a scissors blade), fold along the lines, and glue together. Regular tetrahedra are made of equilateral triangles having three 60° angles.

Octahedron (one half)

Start as for the tetrahedron, but lay off four radii around the circle. Connect the radii, and add tabs as shown in (D). Make a second half *without* the dotted tabs, then glue the halves together.

D



Note: This is just one form of the octahedron—flatter or taller ones result when the angle varies between 45 and 90°.

A coat of lacquer (airplane dope) will make the figures more attractive and durable.

Background Discussion

The discussion of this chapter is presented in four sections. The order is:

Complexes—Definition and Detection
d Orbitals
Models of Complex Ions
Ion Exchange

COMPLEXES—DEFINITION AND DETECTION

For most purposes it is sufficient to define a complex ion as *an ion containing a central atom*[*] *to which others are joined.* Most commonly, the central atom is from a metallic element. If this definition is mentioned after Sec. 22-2.1 (on geometry). then the meaning of "in the center" will be clear. Do not attempt to make a rigid definition, because there is no universally accepted one. Common occurrence and usage have taken sulfate, nitrate, and a few other ions out of the complex class, although they could well be included.

Following the identification of complex ions, special forces were invented to explain them. The then current bonding theories could not account for them. Additional structural information and advances in bond theory have erased this need. Bonds in complexes are explained by the same kind of orbital overlap and electron pairing that has been used in this course for simpler compounds (Chapters 16 and 17).

Complexes can be detected in a number of ways, although the convincing proof is much harder to give. The following list touches briefly on some methods.

X-Ray Diffraction	For solids this is the most convincing test. It is complicated and tells nothing about what exists in solution. But it does give quite specific information about structure. It is the source of the dimensions for models such as those discussed on p. 726.
Ion Integrity	Complex ions have "integrity" in reactions, just as organic groups have skeletal integrity.
Colligative Properties	Conductivity, osmotic pressure, freezing point, and so on can provide evidence of the number of particles obtained from a unit.
Electrolysis	If an element which normally forms a positive ion is concentrated around the positive (instead of negative) electrode, one possibility is that it is part of a complex anion.
Color Change	The usual example is white $CuSO_4$, which turns blue when water is added. The water-copper complex gives the color. This method is a useful, although rough, guide once other, more positive proof has been provided for the presence of a complex.

d ORBITALS

The bonding exhibited by transition elements requires the use of *d* orbitals. Like *s* and *p* orbitals, these represent volumes in which electrons are most likely to occur. A bond can be represented by an overlap of two orbitals (as in Chapter 16). This overlap produces a region of high electron density, and consequently, a region to which nuclei are attracted.

We commonly represent *d* orbitals as shown in the five diagrams of Figure 22-1.

Note: Each diagram shows *one d* orbital, which has a capacity of only two electrons. Some of the diagrams can be confused as showing two *p* orbitals, especially the $d_{x^2-y^2}$ orbital. Refer to the papers by DeVault (mentioned on p. 485) and to Figure 15-2 (p. 499) for information about the energy of 3*d* orbitals and how the energy changes with atomic number.

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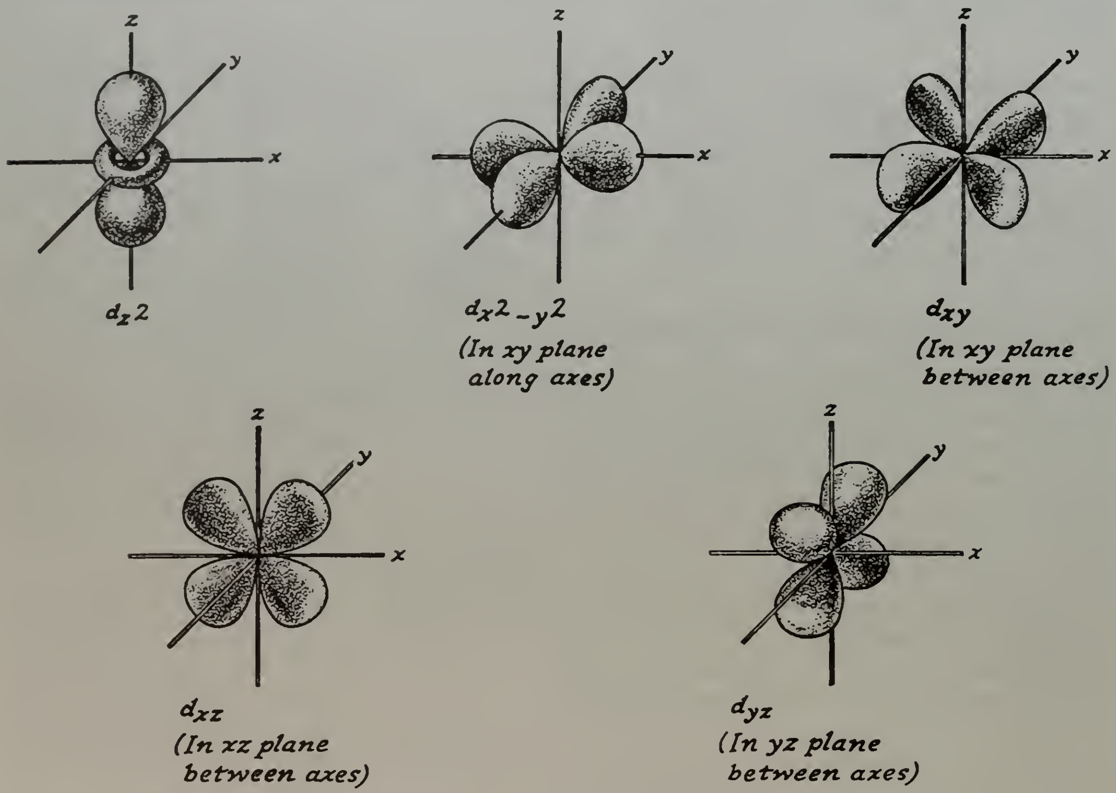
[*] Remember, an atom can be either charged or neutral. Using this convention, one can refer to the Mn *atom* in $KMnO_4$ without specifying whether it is neutral or charged.



d_{z^2}

$d_{x^2-y^2}$
(In xy plane along axes)

d_{xy}
(In xy plane between axes)

d_{xz}
(In xz plane between axes)

d_{yz}
(In yz plane between axes)

Fig. 22-1 **Schematic diagrams of *d* orbitals.**

MODELS OF COMPLEX IONS

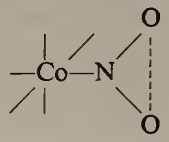
Some students may express interest in the size and appearance of these complex substances. A good source of information, from which the following examples are taken, is *Interatomic Distances*, edited by L. E. Sutton, The Chemical Society, London (1958). Others are A. F. Wells, *Structural Inorganic Chemistry*, Oxford, at the Clarendon Press (1962), the L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press (1960). The atomic radii are from Pauling.

I. $(AlF_6)^{-3}$ Al—F distance; center to center = 1.81 Å
Occurs in Na_3AlF_6 [trisodium hexafluoroaluminum(III)]
Radii: Al^{+3} = 0.50 Å; F^- = 1.36 Å

II. $(VO_4)^{-3}$ V—O = 1.86 Å (tetrahedral)
Occurs in $BiVO_4$ (bismuth vanadate)
Radii: V^{+5} = 0.59; O^{-2} = 1.40

III. $[Co(NO_2)_6]^{-3}$ (octahedral)
Occurs in $K_3Co(NO_2)_6$ [tripotassium hexanitrocobalt(III)]; referred to in questions as cobaltinitrite

Co—N = 2.03 A
N—O = 1.1
O···O = 2.1



Radii: Co^{+3} ~ 0.7; N = 0.74; O = 1.40

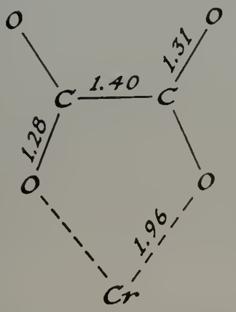
IV. $Ni(CN)_4$ tetracyanonickel(IV) (square planar)
Ni—C = 1.95 Å; C—N = 1.30
Radii: Ni^{+4} ~ 0.5; C = 0.77; N = 0.74

V. $[PtBr_4(NH_3)_2]^0$ [tetrabromodiammineplatinum(IV)] (octahedral)
Pt—N = 2.01 Å
Pt—Br = 2.44

N—H = 1.01 (∠H—N—H = 107°)
Radii: Pt^{+4} = 1 (est.); Br^- = 1.85;
N = 0.74; H = 0.34

VI. $[Pd(NO_2)_4]^{-2}$
[tetranitropalladium(II) ion]
(square planar)
Pd—N = 2.10 Å (∠N—Pd—N = 90°;
∠Pd—N—O = 112°)
N—O = 1.14 (∠O—N—O = 136°)
Radii: Pd^{+2} = 0.86; N = 0.74; O = 1.40

VII. $[Cr(C_2O_4)_3]^{-3}$
[*tris*(oxalato)chromium(III) ion]
(octahedral)
The oxalate group is planar, and has the dimensions shown.



	Radii
Cr^{+3}	0.65
C	0.77
O	1.40

This complex illustrates a "bidentate" (two-tooth) complexing group. Organic molecules with three, four, and six complexing groups are known.

ION EXCHANGE

Ion exchange is a process of considerable commercial value. Its name is self-explanatory. Ions from a solution are exchanged (adsorbed) for other ions from the exchange medium. This medium is most commonly a solid polymer containing polar groups which act as exchange sites.

Some exchange polymers (resins) are organic—either natural ones (cellulose, polyamides from silk, or carbonaceous matter from coal), which have been treated to give (or increase) ion adsorption, or synthetic polymers made from monomers containing the desired groups. Some exchangers are inorganic—usually silicate or aluminate minerals (clays and zeolites are the best examples).

The polymer can be regarded as a huge ion of one type (cation or anion) with many small, soluble ions of the other type on its surface. The classifications *anionic resin* and *cationic resin* are determined by the nature of the small, soluble ion. Anionic resins exchange anions. This exchange is an equilibrium process—one that is subject to the equilibrium principles described in Chapter 9. The regeneration of resins involves changing the environment so as to favor one equilibrium state over another. To illustrate this, let us consider the cationic resin H*R* where *R* is a site on the resin which releases a proton. The exchange of Ca^{+2} is then written

$$2HR + Ca^{+2} = Ca(R)_2 + 2H^+$$

With a "good" resin, the removal of Ca^{+2} will be essentially complete, and the equilibrium constant for the above reaction will be large. But by increasing H^+ ion concentration (by "backwashing" with acid), the reaction is reversed, the original state of the exchanger is restored, and the Ca^{+2} is discarded in the wash solution.

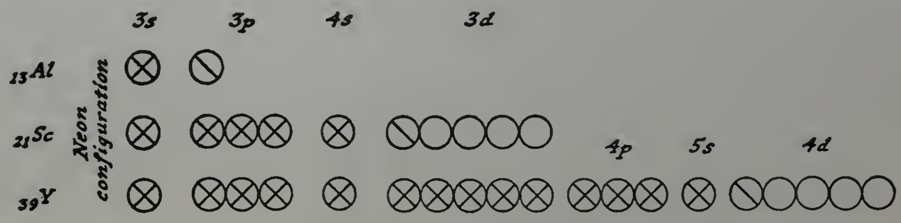
The main use of ion exchange resins is in the treatment of water. On a commercial scale, water softening (exchanging Na^+ for Ca^{+2} and Mg^{+2}) is the major example. In the laboratory, it is more usual to find mixed resins used to demineralize water. In this case all cations are replaced by H^+, and all anions by OH^-, so that the result is extremely pure water. The purification of sea water by this technique is possible, but it is still prohibitively expensive.

Other uses include the purification of many products—sugar, milk, beer, and pharmaceutical products. The commercial separation of rare earths (similar to Expt. 37 on Fe, Co, and Ni) is made practical by ion exchange resins.

Answers to Exercises and Problems

Ex. 22-1. Draw on one line a set of orbitals from 1*s* through 4*d*. Under this give the orbital occupancy for Al, Sc, and Y. Account for the fact that yttrium is much more like scandium than is aluminum.

Answer



Both Sc and Y show the s^2d^1 arrangement. Since a large amount of the chemistry that elements exhibit can be explained in terms of outer electron population, we expect Sc and Y to have similar chemistries. Aluminum's outer electrons have the s^2p^1 arrangement. These three valence electrons cause Al to have some chemistry common to that of Sc and Y but to differ in detail.

Ex. 22-2. Again using Figure 22-1, decide which orbital would next be used after the five 3*d* orbitals have been filled. What orbital would next be used after the 4*d* set has been filled? What element does this correspond to in the periodic table?

Answer

The electrons will go into the 4*p* orbitals after the 3*d* orbitals have been filled, giving gallium, and will go into the 5*p* after the 4*d* have been filled, producing element 49, indium.

Ex. 22-3. Make an electron configuration table like Table 22-II for the fifth-row transition elements—yttrium ($Z = 39$) through cadmium ($Z = 48$). In elements 41 through 45, one of the 5*s* electrons moves over to a 4*d* orbital. In element 46, two electrons do this.

Answer

See the table in the next column.

These configurations are not easy to assign, and some authors give slightly different ones. The real point is that the 4*d* level is generally gaining the incoming electrons. The point could be made that the filled *d* shell apparently has special stability (as does the half-filled shell, not evident here).

Element	Symbol	Atomic number	Outer electron configuration	
Yttrium	Y	39	$4d^1$	$5s^2$
Zirconium	Zr	40	$4d^2$	$5s^2$
Niobium	Nb	41	$4d^4$	$5s^1$
Molybdenum	Mo	42	$4d^5$	$5s^1$
Technetium	Tc	43	$4d^6$	$5s^1$
Ruthenium	Ru	44	$4d^7$	$5s^1$
Rhodium	Rh	45	$4d^8$	$5s^1$
Palladium	Pd	46	$4d^{10}$	
Silver	Ag	47	$4d^{10}$	$5s^1$
Cadmium	Cd	48	$4d^{10}$	$5s^2$

Ex. 22-4. What is the oxidation number of chromium in each of the following compounds: $Cr_2O_7^{-2}$, CrO_4^{-2}, $Cr(OH)_3$, CrO_2Cl_2?

Answer

The oxidation number of chromium in

$Cr_2O_7^{-2}$ is $+6$;
CrO_4^{-2} is $+6$;
$Cr(OH)_3$ is $+3$;
CrO_2Cl_2 is $+6$.

Ex. 22-5. Look through a handbook of chemistry, and find one *other* compound of each oxidation state given for the elements in Table 22-II.

Answer: See the table on the next page.

Ex. 22-6. If you wish to prepare some chlorophyll, grind up some fresh leaves and extract with alcohol. The alcohol dissolves the chlorophyll as shown by the solution color.

OXIDATION NUMBER

I	II	III	IV	V	VI	VII
		$ScBr_3$ $ScCl_3$ $Sc(NO_3)_3$				
	$TiCl_2$	$TiCl_3$ TiF_3	$Ti_2(SO_4)_3$ $TiBr_4$ $TiCl_4$ TiF_4 TiI_4			
	VCl_2 V_2Si V_2O_2	VCl_3 VF_3 V_2O_3	VCl_4 V_2O_4	VF_5 V_2O_5 $VOBr_3$		
	$CrCl_2$ CrF_2 CrI_2	$CrCl_3$ CrF_3 $CrBr_3$ Cr_2O_3	CrO_2		CrO_2Cl_2 CrO_3	
	$MnBr_2$ $MnCl_2$ MnI_2	MnF_3 $MnPO_4$	$MnCl_4$ $Mn(SO_4)_2$		Na_2MnO_4	Mn_2O_7
	FeF_2 $FeBr_2$ $FeCl_2$	FeF_3 $FeBr_3$ $FeCl_3$				
	$CoBr_2$ $CoCl_2$ CoI_2	$CoCl_3$ $Co(OH)_3$				
	$NiBr_2$ $NiCl_2$ NiF_2	K_3NiF_6				
Cu_2S $CuCl$ $CuBr$	CuS $CuCl_2$ $CuBr_2$					
	$ZnCl_2$ $ZnSO_4$					

Answer

This suggested experiment does not require an answer.

Ex. 22-7. If a typical plant leaf yields 40.0 mg of chlorophyll A, how many milligrams of this will be magnesium? The molecular weight of chlorophyll A is 893.

Answer

For the questioning student, the molecular formula of chlorophyll A is $C_{55}H_{72}MgN_4O_5$, from which the molecular weight is obtained.

$$\begin{array}{rcrcr} 12.0 & \times & 55 & = & 660 \\ 1.01 & \times & 72 & = & 73 \\ 24.3 & \times & 1 & = & 24.3 \\ 14.0 & \times & 4 & = & 56 \\ 16.0 & \times & 5 & = & \underline{80} \\ & & & & 893.3 \end{array}$$

The following procedure can be used to determine the milligrams of Mg.

$$(\text{mg chlorophyll A})\left(\frac{\text{g}}{\text{mg}}\right)\left(\frac{1}{\text{g/mole}}\right)$$

$$\times\left(\frac{\text{mg Mg}}{\text{mole chlorophyll A}}\right) = \text{mg Mg}$$

$$(40)\left(\frac{1}{10^3}\right)\left(\frac{1}{893}\right)\left(\frac{24.3 \times 10^3}{1}\right) = 1.1 \text{ mg Mg}$$

Ex. 22-8. Write the equation for the reduction of Cr_2O_3 by Al. If it takes 399 kcal/mole to decompose Al_2O_3 into the elements and 270 kcal/mole to decompose Cr_2O_3, what will be the net heat liberated in the reaction you have just written?

Answer

(1) $Cr_2O_3 + 2Al = Al_2O_3 + 2Cr$

(2) $Al_2O_3 + 399 \text{ kcal} = 2Al + 1\frac{1}{2}O_2$

(3) $Cr_2O_3 + 270 \text{ kcal} = 2Cr + 1\frac{1}{2}O_2$

(4) $\underline{2Al + 1\frac{1}{2}O_2 = Al_2O_3 + 399 \text{ kcal}}$

(3) + (4)

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr + 129 \text{ kcal}$$

$$\Delta H = -129 \text{ kcal/mole } Cr_2O_3$$

Therefore 129 kcal will be liberated for each mole of Cr_2O_3 reacted.

$$\frac{104 \text{ g}}{206 \text{ g}} \times 100 = 50.5\% \text{ Cr}$$

Pr. 1. Why are the elements with atomic numbers 21 to 30 placed in a group and considered together in this chapter?

Answer

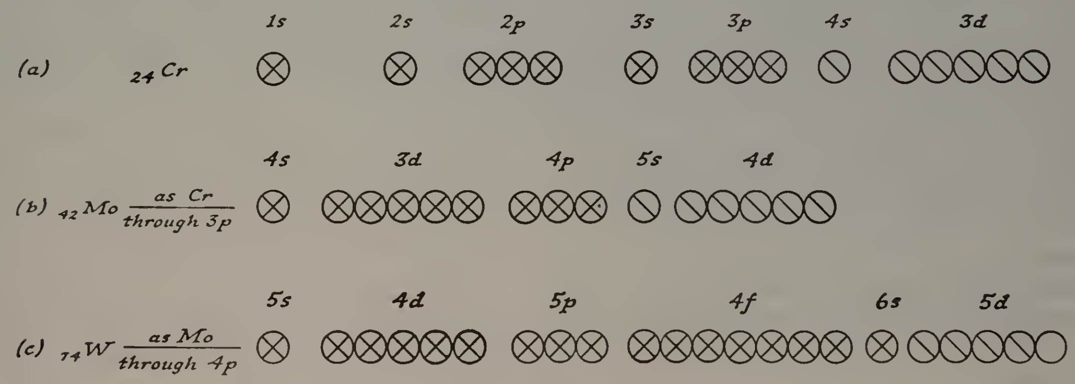
The valence electrons of all these elements are in 4*s* and 3*d* orbitals. This makes their chemical behavior similar. They are grouped together because, by noting the generalities of the group, we are able to express a great deal of information in a few statements.

Pr. 2. Write the orbital representation for

(a) chromium,
(b) molybdenum,
(c) tungsten.

Answer

The student may assume that the sd^5 electron pattern of Cr holds throughout. Actually it does not. It does for Mo, but apparently the energy of the 6*s* orbital is sufficiently less than that of a 5*d* orbital such that the 6*s* orbital remains filled rather than require an electron shift to half-fill the five 5*d* orbitals.



Ex. 22-9. Calculate the percent chromium in $Cr(OH)_3$ and in $Cr_2O_3 \cdot 3H_2O$.

Answer

$$\text{wt/mole } Cr(OH)_3 = 52.0 + 3(17.0) = 103 \text{ g}$$

$$\frac{52.0 \text{ g}}{103 \text{ g}} \times 100 = 50.5\% \text{ Cr}$$

$$\text{wt/mole } Cr_2O_3 \cdot 3H_2O = 104 + 3(16.0) + 3(18.0) = 206 \text{ g}$$

Pr. 3. What properties of the transition elements are consistent with their being classified as metals?

Answer

The following properties are consistent with the classification of transition elements as metals:

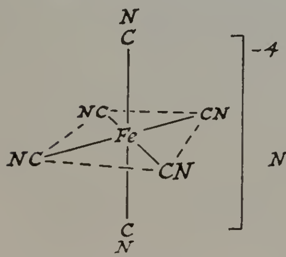
(a) They are good electrical and thermal conductors.

(b) They are lustrous and have high tensile strength.

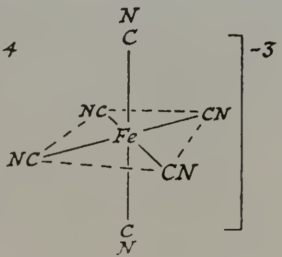
(c) They have many orbitals available for bonding. Note also that the ionization energies given later in the chapter (in Textbook Table 22-III) are relatively low.

Pr. 4. Ferrous ion, iron(II), forms a complex with six cyanide ions, CN^-; the octahedral complex is called ferrocyanide. Ferric ion, iron(III), forms a complex with six cyanide ions; the octahedral complex is called ferricyanide. Write the structural formulas for the ferrocyanide and the ferricyanide complex ions.

Answer



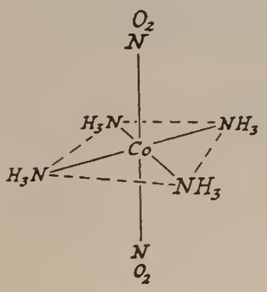
$Fe(CN)_6^{-4}$
ferrocyanide ion

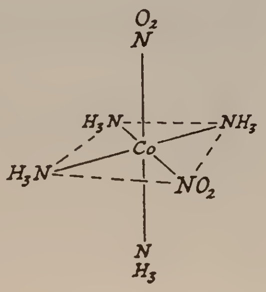


$Fe(CN)_6^{-3}$
ferricyanide ion

Pr. 5. Draw the different structures for an octahedral cobalt complex containing four NH_3 and two NO_2 groups.

Answer





These are the only two unique forms. That is, it is not possible to make them exactly the same (superimposable). Students often draw others which can be rotated into one of these. The most common flaw is that the octahedron is not kept symmetrical. The NO_2 groups will be either opposite or adjacent. No other possibilities exist that have regular octahedral symmetry. The use of a ball-and-stick model will clarify this.

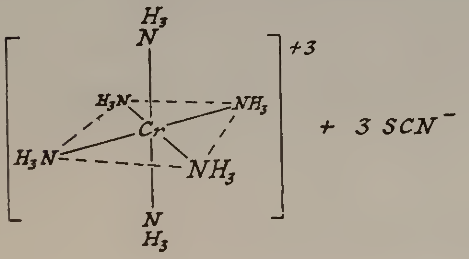
Pr. 6. Draw the structures of the compounds

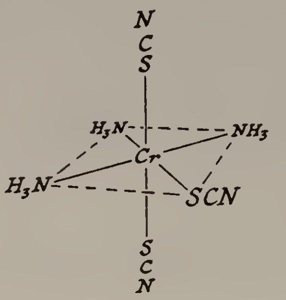
$Cr(NH_3)_6(SCN)_3$ and $Cr(NH_3)_3(SCN)_3$

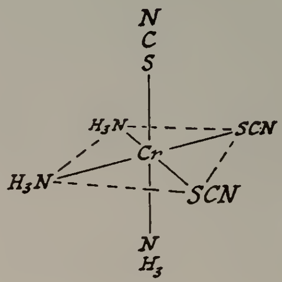
(SCN^- is the thiocyanate ion). Consider the oxidation number of chromium to be +3 and the coordination number to be 6 in both compounds. Estimate

(a) the solubility of these compounds in water;
(b) their relative melting points;
(c) the relative conductivity of the liquid phases.

Answer



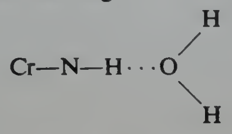




Note that the two structures given for $Cr(NH_3)_3(SCN)_3$ are position isomers. There are no others as long as the complex has perfect octahedral symmetry. With a given coordination number of 6 for Cr, it is easy to suggest that $Cr(NH_3)_6(SCN)_3$, hexaamminechromium(III) thiocyanate, is an ionic substance;

$$Cr(NH_3)_6(SCN)_3 = Cr(NH_3)_6^{+3}(aq) + 3SCN^-(aq)$$

Solubility will depend upon a balance of two factors: the energy required to tear the ions from the crystal and the energy released when the ions become hydrated. The opportunities for hydrogen bonding,



will add to the energy released.

With a coordination number of 6 for Cr, $Cr(NH_3)_3(SCN)_3$, triamminetrithiocyanatochromium(III) will form a molecular solid. Solubility will depend upon the same factors as given above. The weak van der Waals forces between molecules will be easy to overcome, but the solvation energy might not be so high. There are fewer opportunities for hydrogen bonding.

Pr. 7. Why does NH_3 readily form complexes, but NH_4^+ does not?

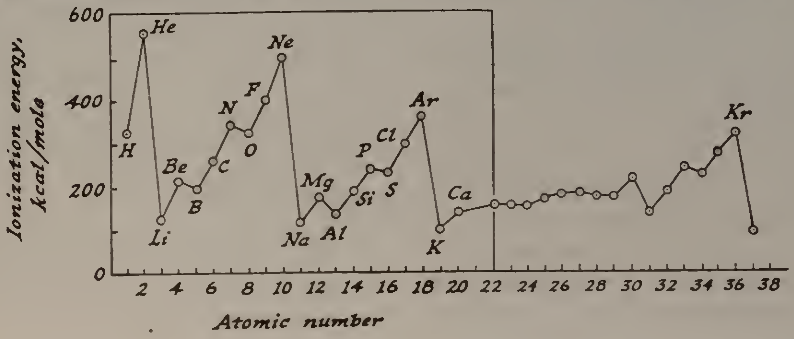
Answer

Recall that NH_3 has a pair of electrons that is not used in bonding but which can be if suitable orbitals are available on another particle. The ion NH_4^+ has neither unused electrons nor unused orbitals. It can attract negative particles, but its one plus charge is spread over such a large surface that the attraction is not strong enough to withstand much thermal agitation. No stable complex is formed.

Pr. 8. Place a piece of paper over Figure 15-13, and trace it. Extend the abscissa, and add the ionization energies of the transition elements. Complete the row with the following ionization energies: Ga, 138; Ge, 187; As, 242; Se, 225; Br, 273; Kr, 322; Rb, 96 kcal/mole.

Answer

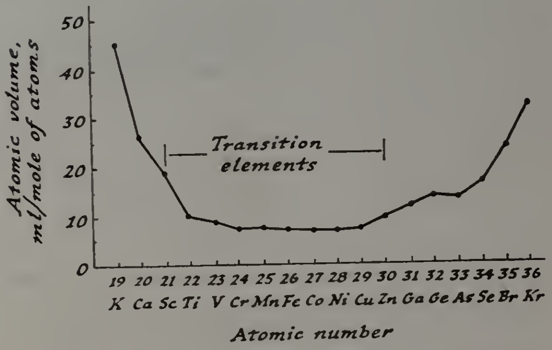
Contrast between ionization energy of the fourth-row transition elements and the first twenty elements.



The point of making this plot is to show the constancy of the first ionization energies of the transition metals. The characteristic rise of E_1 across the first three rows is interrupted as the *d* orbitals fill. The same phenomenon occurs in the lower transition series. This constancy of E_1 is an important basis for explaining the similar properties of the transition metals.

Pr. 9. The volume per mole of atoms of some fourth-row elements (in the solid state) are as follows: K, 45.3; Ca, 25.9; Sc, 18.0; Br, 23.5; and Kr, 32.2 ml/mole of atoms. Calculate the atomic volumes (volume per mole of atoms) for each of the fourth-row transition metals. Plot these atomic volumes and those of the elements given above against atomic numbers.

Answer



Variation of molar volume *for fourth-row transition elements.*

The constancy of the atomic volume across the transition elements again provides a basis for establishing the similarity of these elements.

Pr. 10. Chromic oxide, Cr_2O_3, is used as a green pigment and is often made by the reaction between $Na_2Cr_2O_7(s)$

and $NH_4Cl(s)$ to give $Cr_2O_3(s)$, $NaCl(s)$, $N_2(g)$ and $H_2O(g)$. Write a balanced equation, and calculate how much pigment can be made from 1.0×10^2 kg of sodium dichromate.

Answer

The balanced equation is

$$Na_2Cr_2O_7(s) + 2NH_4Cl(s) \longrightarrow Cr_2O_3(s) + 2NaCl(s) + N_2(g) + 4H_2O(g)$$

(Cr changes from oxidation number +6 to +3. N changes from oxidation number −3 to 0.)

STEP I

$$(g)\left(\frac{\text{moles}}{g}\right)$$

$$(1.0 \times 10^5)(\tfrac{1}{262}) = 3.8 \times 10^2 \text{ moles}$$

STEP II

$$(\text{moles } Na_2Cr_2O_7)\left(\frac{\text{moles } Cr_2O_3}{\text{mole } Na_2Cr_2O_7}\right)$$

$$(3.8 \times 10^2)(\tfrac{1}{1}) = 3.8 \times 10^2 \text{ moles } Cr_2O_3$$

STEP III

$$(\text{moles})\left(\frac{g}{\text{mole}}\right) = g$$

$$(3.8 \times 10^2)(152) = 5.8 \times 10^4 \text{ g or 58 kg}$$

Pr. 11. Chromic hydroxide, $Cr(OH)_3$, is a compound with low solubility in water. It is usually hydrated and does not have the definite composition represented by the formula. It is quite soluble either in strong acid or strong base.

(a) Write an equation showing the ions produced by the small amount of $Cr(OH)_3$ that dissolves.

(b) Explain, using Le Chatelier's Principle, why $Cr(OH)_3$ is more soluble in strong acid than in water.

(c) What is the significance of the fact that $Cr(OH)_3$ dissolves in base, as well as in acid.

Answer

(a) Either

$$Cr(OH)_3(s) \rightleftharpoons Cr^{+3}(aq) + 3OH^-(aq)$$

or

$$Cr(OH)_3(s) + 6H_2O \rightleftharpoons Cr(H_2O)_6^{+3} + 3OH^-(aq)$$

(b) The addition of $H^+(aq)$ causes the removal of the product $OH^-(aq)$, hence equilibrium conditions shift to replace, in part, the removed $OH^-(aq)$. More solid must dissolve for this to happen.

(c) $Cr(OH)_3$ is called amphoteric because it dissolves in both acid and base. The reaction can be written

$$Cr(OH)_3(s) + OH^- \longrightarrow Cr(OH)_4^-(aq)$$

Pr. 12. What is the oxidation number of manganese in each of the following: $MnO_4^-(aq)$; $Mn^{+2}(aq)$; $Mn_3O_4(s)$; $MnO_2(s)$; $Mn(OH)_2(s)$; $MnCl_2(s)$; $MnF_3(s)$?

Answer

The oxidation number of manganese in

$MnO_4^-(aq)$ is +7;

$Mn^{+2}(aq)$ is +2;

$Mn_3O_4(s)$ is $+\frac{8}{3}$ (or, perhaps, +3 for two Mn atoms and +2 for one Mn atom, averaging $\frac{8}{3}$);

$MnO_2(s)$ is +4;

$Mn(OH)_2(s)$ is +2;

$MnCl_2(s)$ is +2;

$MnF_3(s)$ is +3.

Pr. 13. Manganese(III), $Mn^{+3}(aq)$, spontaneously disproportionates to $Mn^{+2}(aq)$ and $MnO_2(s)$. Balance the equation for the reaction.

Answer

$$2Mn^{+3}(aq) + 2H_2O \rightleftharpoons Mn^{+2}(aq) + MnO_2(s) + 4H^+(aq)$$

Pr. 14. Use the $E°$ values in Table 22-III to predict what might happen if a piece of iron is placed in a 1 M solution of Mn^{+2} and if a piece of manganese is placed in a 1 M solution of Fe^{+2}. Balance the equation for any reaction that you feel would occur to an appreciable extent.

Answer

$$Mn \longrightarrow Mn^{+2} + 2e^- \qquad E° = +1.18 \text{ volts}$$

$$Fe \longrightarrow Fe^{+2} + 2e^- \qquad E° = +0.44 \text{ volt}$$

Manganese will react with Fe^{+2}, producing Mn^{+2} and coating the Mn with metallic iron:

$$Mn(s) + Fe^{+2}(aq) \longrightarrow Fe(s) + Mn^{+2}(aq)$$

Since $E°$ is less positive, $Fe(s)$ will not react with Mn^{+2}.

Pr. 15. Iron exists in one cubic crystalline form at 20°C (body-centered cubic, with cube edge length 2.86 A) and in another form at 1100°C (face-centered cubic, with cube edge length 3.63 Å).

(a) Draw a picture of each unit cell, showing the nine atoms involved in a body-centered cubic cell and the fourteen atoms involved in a face-centered cubic cell. (See Figure 21-2.)

(b) Decide the number of unit cells with which each atom is involved (in each structure).

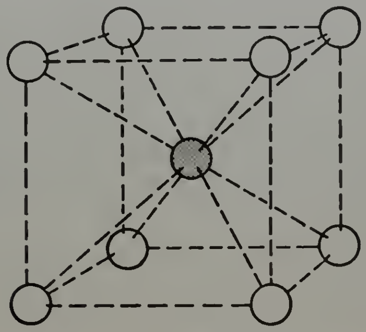
(c) How many atoms are in each unit cell if we take into account that some atoms are shared by two or more adjoining unit cells?

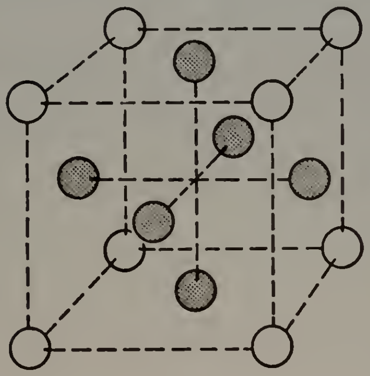
(d) Calculate the volume of the unit cell and, with your answer to part c, the volume per atom (for each structure).

(e) What conclusion can be drawn about the "effective size" of an iron atom?

Answer

(a)





(b) See answer to (a).

(c) Body-centered: $8(\frac{1}{8}) + 1(1) = 2$.

Face-centered: $8(\frac{1}{8}) + 6(\frac{1}{2}) = 4$.

(d) Body-centered: $(2.86 \times 10^{-8})^3$

$$= 2.34 \times 10^{-23}\ \text{cm}^3$$

$$\text{volume per atom} = \frac{2.34 \times 10^{-23}}{2}$$

$$= 1.17 \times 10^{-23}\ \text{cm}^3$$

Face-centered: $(3.63 \times 10^{-8})^3$

$$= 4.80 \times 10^{-23}\ \text{cm}^3$$

$$\text{volume per atom} = \frac{4.80 \times 10^{-23}}{4}$$

$$= 1.20 \times 10^{-23}\ \text{cm}^3$$

(e) The "size" of an iron atom is fairly independent of the type of packing.

Note: The May 1961 issue of *J. Chem. Education*, p. A357, gives the details of a demonstration involving this change of form.

Pr. 16. One of the important cobalt ores is

$$Co_3(AsO_4)_2 \cdot 8H_2O$$

How much of this ore is needed to make 1.0 kg of Co?

Answer

$$(\text{kg Co})\left(\frac{\text{moles Co}}{\text{kg Co}}\right)$$

$$(1.0)\left(\frac{1}{59 \times 10^{-3}}\right) = 17 \text{ moles Co wanted}$$

$$(\text{moles Co})\left(\frac{\text{moles ore}}{\text{moles Co}}\right)$$

$$17 \times \tfrac{1}{3} = 5.7 \text{ moles ore}$$

$$(\text{moles ore})\left(\frac{\text{kg ore}}{\text{mole ore}}\right)$$

$$5.7 \times \frac{0.460}{1} = 2.6 \text{ kg ore needed}$$

Pr. 17. Nickel carbonyl, $Ni(CO)_4$, boils at 43°C, and uses the sp^3 orbitals of Ni for bonding. Give reasons to justify the following:

(a) it forms a molecular solid;
(b) the molecule is tetrahedral;
(c) bonding to other molecules is of the van der Waals type;
(d) the liquid is a nonconductor of electricity;
(e) it is not soluble in water.

Answer

(a) The low boiling point is consistent with a molecular solid structure.

(b) The use of sp^3 orbitals in bonding results in tetrahedral geometry.

(c) Again, the low boiling point suggests a molecular solid in which van der Waals forces are the main ones between molecules.

(d) Bonding involving sp^3 orbitals is highly directive and largely covalent. Therefore ionization in the liquid is unlikely, and a nonconductor is expected.

(e) The lack of water solubility is consistent with the lack of polarity of the symmetrical tetrahedral molecule.

Pr. 18. Write balanced equations to show the dissolving of $Cu(OH)_2(s)$ on the addition of $NH_3(aq)$, and also the reprecipitation caused by the addition of an acid.

Answer

$$Cu(OH)_2(s) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4^{+2}(aq) + 2OH^-(aq)$$

$$Cu(NH_3)_4^{+2}(aq) + 2OH^-(aq) + 4H^+(aq) \longrightarrow Cu(OH)_2(s) + 4NH_4^+(aq)$$

Pr. 19. Cupric sulfide, copper(II) sulfide, reacts with hot nitric acid to produce nitric oxide gas, NO, and elemental sulfur. Only the oxidation numbers of S and N change. Write the balanced equation for the reaction.

Answer

$$3CuS(s) + 2NO_3^- + 8H^+ \rightleftarrows 3Cu^{+2} + 3S(s) + 2NO(g) + 4H_2O$$

Using oxidation numbers, we have

$$S^{-2} \xrightarrow{+2} S^0$$

$$N^{+5} \xrightarrow{-3} N^{+2}$$

Therefore three S atoms must change for every two N atoms that change. Now we need only balance the number of atoms on each side.

Pr. 20. The solubility of copper(II) iodide, CuI_2, is 0.004 g/liter. Determine the value of the solubility product.

Answer

$$CuI_2(s) = Cu^{+2}(aq) + 2I^-(aq)$$

$$K_{sp} = [Cu^{+2}][I^-]^2$$

$$\left(\frac{\text{g}}{\text{liter}}\right)\left(\frac{\text{moles}}{\text{g}}\right) = \frac{\text{moles}}{\text{liter}}$$

$$0.004 \times \frac{1}{320} = 1.3 \times 10^{-5}\,\frac{\text{mole}}{\text{liter}}$$

$$Cu^{+2}] = 1.3 \times 10^{-5}\,\frac{\text{mole}}{\text{liter}}$$

$$[I^-] = 2.6 \times 10^{-5}\,\frac{\text{mole}}{\text{liter}}$$

$$K_{sp} = [1.3 \times 10^{-5}][2.6 \times 10^{-5}]^2 = 8.8 \times 10^{-15}$$

For less able students, present the problem as follows. The solubility of CuI_2 is 0.004 g/liter at 18°C.

(a) What is the solubility in moles/liter?
(b) What is the equation representing the equilibrium between the dissolved and undissolved substances?
(c) What is the molarity of the Cu^{+2}?
(d) What is the molarity of the I^-?
(e) What is the solubility product expression for (b)?
(f) What is the numerical value of solubility product?

CHAPTER
23

SOME SIXTH- AND SEVENTH-ROW ELEMENTS

Intent and Approach

This chapter uses the sixth- and seventh-row elements to lead into a group of topics relating to unstable nuclei. The approach is essentially an empirical one, since the make-up of the nucleus is not yet well understood. One important point of view to express is that the chemistry in this region of the periodic table is not *unusual.* There is currently great glamour to the production of synthetic elements and nuclear energy, but it doesn't derive from the chemical behavior that is known at this time. In fact, much of the study of these new elements has depended upon carrier experiments in which the new unknown "follows" (i.e., behaves like) a naturally occurring lower-atomic-weight element.

Outline

1. The lanthanides are discussed briefly, mainly in terms of radii and E° values (23-1.1), with some comments on occurrence and preparation (23-1.2).
2. The seventh-row elements are treated similarly (23-2.1, 23-2.2).
3. Nuclear stability is examined in the light of the neutron/proton ratio (23-2.3).
4. Several types of radioactive behavior are considered—α and β decay and electron capture (23-2.4).
5. Nuclear energy, from both fusion and fission, is covered (23-2.5).

New Concepts

1. The neutron/proton ratio and its importance.
2. Nuclear binding energy.

Development

THE SIXTH ROW OF THE PERIODIC TABLE (23-1)

The Lanthanides, or Rare Earths (23-1.1)

The student will almost certainly never have heard of these elements. There is little reason to make a point about their individual properties. The main purpose in presenting them is to show the effect of filling a new type of orbital, the 4*f* orbitals. In the lanthanides the *f* orbital is so deeply buried that the electrons there have relatively little effect on the chemistry of the elements; as a result, they are almost exactly alike.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*	*Topic*
S 23-1/23-2.1 (pp. 411–414)	1	Discussion	1, 2	None	Sixth- and seventh-row elements
S 23-2.2 (pp. 414–416)	2	Discussion Film: TRANSURANIUM ELEMENTS	3–5		Elements following actinium
S 23-2.3/23-2.5 (pp. 416–419)	3	Discussion			Nuclear stability, Radioactivity, Nuclear energy

Occurrence and Preparation (23-1.2)

These elements have been called the rare earth elements. Their "rarity" is more a result of the difficulty involved in their separation than of a scarcity of ore. For instance, the elements rank from 28th (Ce) to 60th (Tm) in abundance in the earth's crust. All these are more abundant than the "common" elements, mercury (62nd), iodine (64th), bismuth (66th), silver (69th), and gold (74th).

THE SEVENTH ROW OF THE PERIODIC TABLE (23-2)

The Occurrence of the Seventh-row Elements (23-2.1)

The Elements Following Actinium (23-2.2)

The naturally occurring seventh-row elements vary from moderately abundant (thorium, 36th) to very rare (actinium, 86th), and even some francium is found, about $10^{-22}\%$! Thorium occurs with rare earth oxides in monazite sand. It has few uses, but these include catalysts and electric heater alloys. The element almost always has oxidation number +4, and most of its salts dissolve to give colorless solutions.

Uranium is found in nature in pitchblende, a heavy, dark-gray or black ore resembling pitch. This element assumed crucial importance when Hahn and Meitner discovered nuclear fission (1939). It can be prepared by reduction of the fluoride with calcium:

$$UF_4 + 2Ca = U + 2CaF_2 + 134 \text{ kcal}$$

The metal is quite reactive, especially when warmed. It burns readily in air and combines rapidly with F_2 and S_8 (at 500°C). Uranium powder reacts with water and dilute acids to give H_2. Other than their use in atomic piles, uranium compounds have only a few applications, including use in photography as "toners" and "intensifiers" and also as analytical reagents.

Actinium, radium, and protoactinium are also found in quite small amounts in pitchblende, from which they were separated by elaborate concentration methods. They can now be prepared by nuclear reactions.

Beyond uranium are the man-made elements, now numbering ten. Plutonium is perhaps the best known. The chemistry of these is complicated for several reasons: (1) their high level of radioactivity often requires remote handling, (2) the same factor decomposes water to H_2O_2, therefore aqueous chemistry is always done in H_2O_2 solution, (3) for elements beyond plutonium only minute amounts are available. In spite of these problems, enough has been learned to show that the synthetic elements do not have a unique chemistry. For instance, plutonium is known in +3, +4, and +6 oxidation states. Changes between these states are effected by common agents, oxygen and permanganate changing Pu^{+3} to Pu^{+4}. Hot $KMnO_4$ (above 60°C) gives Pu^{+6}. Complex ions are formed, especially with Pu^{+4}, for which $Pu(H_2O)_6^{+2}$ (pale red) and $Pu(NO_3)_6^{-2}$ (green) are examples. Ammonia precipitates blue $Pu(OH)_3$ and pale-green $Pu(OH)_4$, which on strong heating give the oxides PuO, Pu_2O_3, Pu_4O_7, and PuO_2. The oxide PuO has the NaCl structure.

The halides are also well characterized. The fluoride PuF_4 (yellow) was the first plutonium compound separated free of other metallic compounds. It and PuF_3 (purple) result from the action of F^- on Pu^{+4} or Pu^{+3} solutions. Similar chlorides and bromides are known, although they are not equally stable, $PuCl_4$ being obtained only in solution. These and other salts behave according to the solubility rules given in Chapter 10. The sulfate $Pu_2(SO_4)_3$ is fairly soluble; the sulfide, Pu_2S_3, and the hydroxides are not very soluble. The problem of how close a correspondence exists between the lanthanides and the elements of row 7 is currently a matter of active research effort.

Nuclear Stability and Radioactivity (23-2.3)

The subject of nuclear structure and stability can hardly be discussed at the high school level. Intensive research, both practical and theoretical, is in progress. As of mid-1963 the results have not been sufficiently agreed upon or codified to allow presentation. There are these difficulties:

1. The internuclear attractive forces are not understood.
2. The list of "fundamental" particles is not complete, or rather, not decided.
3. The arrangement of the particles in the nucleus is largely unknown.

In spite of the lack of generally accepted theories, the experimental evidence so far available has made possible some progress. The shape of the stability belt in Textbook Figure 23-1 (p. 417) tells us that the optimum ratio of neutrons to protons is 1 for light elements and increases to about 1.6 for the heaviest. This is related to our ideas of nuclear forces in the following way. We postulate an attraction between a neutron and proton. This is a new kind of attractive force. It is not electrostatic. Electrostatic repulsion between the protons still exists, and is quite large, as the calculation on Textbook p. 416 shows. The new attractive force must be even larger because nucleons do stay together in the nucleus.

As the nucleus (and the number of protons) becomes larger for the heavier elements, the number of proton–proton repulsions goes up, and more neutrons are required to provide sufficient attractive force. This view of the nucleus also explains why there are relatively few isotopes for a given element. The n/p ratio must have a rather specific value and cannot deviate much.

Types of Radioactivity (23-2.4)

There are a few types of nuclear decay other than those given. These are neutron emission, positron emission, and loss of energy (without change of mass or charge). These modes of activity, however, are fairly rare and are omitted here.

Nuclear Energy (23-2.5)

The technical use of nuclear energy from fission reactions is an accomplished fact. Several reactors have been built and are generating electrical power. Certain economic factors still argue against a rapid and complete changeover to a nuclear source of power.

Fusion reactions are not so well developed. Some short-time reactions have been carried out, but a whole new technology must be perfected. Both the fission and the fusion reaction are the subject of articles in *Scientific American* and other publications.

Supplementary Materials

Films

FOR ORDERING INFORMATION SEE THE *List of Film Sources* AT THE BACK OF THE TEACHERS GUIDE

TRANSURANIUM ELEMENTS

A CHEM Study film
Running Time: 23 minutes

This film, produced in the Lawrence Radiation Laboratory at Berkeley, California, features four chemists who were principals in the actual discovery and identification of the transuranium elements. The collaborator, Dr. Glenn Seaborg, reviews the historical problem of the placement of the transuranium elements in the periodic table, and emphasizes that the new elements must be synthesized and identified. Dr. Burris Cunningham shows in experiments that neptunium, plutonium, and americium can behave like uranium but that curium behaves like its rare earth homolog, gadolinium. Dr. Stanley Thompson demonstrates how the ion-exchange separation technique aids in identification, using actual solutions of curium, berkelium, californium, and einsteinium. Albert Ghiorso demonstrates the Hilac, an instrument used in making elements of very high atomic number. He discusses the methods which helped lead to the discovery of elements 102 and 103 and proposes a similar type of reaction which may lead to the discovery of element 104.

Books

1. G. T. Seaborg, *Man-made Transuranium Elements*, Prentice-Hall, Englewood Cliffs (1963). A description, aimed at the able student, of the discovery, electronic structure, chemical properties, and nuclear reactions of elements 93 to 103.
2. T. Moeller, *The Chemistry of the Lanthanides*, Reinhold, New York (1963). Good supplementary reading for teachers and able students.
3. R. T. Overman, *Basic Concepts of Nuclear Chemistry*, Reinhold, New York (1963). Good supplementary reading for teachers and able students.

Answers to Exercises

Ex. 23-1. (a) Balance the equation for the reaction between neodymium metal and chlorine gas.

(b) At 0°C and one atmosphere pressure, how many liters of chlorine gas would react with 14.4 grams of the metal?

Answer

(a) $Nd(s) + \frac{3}{2}Cl_2(g) \rightleftharpoons NdCl_3(s)$

(b) $$\text{moles Nd} = \frac{14.4 \text{ grams}}{144.3 \text{ grams/mole}} = 0.100 \text{ mole}$$

$$\text{moles } Cl_2 \text{ required} = \tfrac{3}{2} \times 0.100 = 0.150 \text{ mole}$$

volume occupied

$$= (0.150 \text{ mole})\left(22.4 \frac{\text{liters}}{\text{mole}}\right) = 3.36 \text{ liters } (0°\text{C and 1 atm})$$

Ex. 23-2. To a solution containing "tracer" amounts of radioactive gadolinium, $Gd^{+3}(aq)$ (concentration less than $10^{-12}\ M$) is added 0.01 M lanthanum chloride, $LaCl_3$, and then 0.1 M hydrogen fluoride, HF. A precipitate of lanthanum fluoride forms and it contains most of the radioactive gadolinium. Explain in terms of the similarity of lanthanum and gadolinium ions.

Answer

The chemistries of La^{+3} and Gd^{+3} are practically identical. Since LaF_3 has low solubility, GdF_3 should also have low solubility. Furthermore, since Gd^{+3} and La^{+3} have practically the same size, the Gd^{+3} ions fit into the LaF_3 solid lattice. Hence LaF_3 carries the GdF_3 into the solid state.

Ex. 23-3. Two half-reactions involving neptunium are

$$Np^{+3} \longrightarrow Np^{+4} + e^- \qquad E° = -0.147 \text{ volt}$$
$$Np^{+4} + 2H_2O \longrightarrow NpO_2^+ + 4H^+ + e^- \qquad E° = -0.75 \text{ volt}$$

Find an oxidizing agent in Appendix 3 that could oxidize $Np^{+3}(aq)$ to $Np^{+4}(aq)$ but not to $NpO_2^+(aq)$.

Answer

We are interested in a half-reaction with $E°$ less than $E° = -0.15$ volt but greater than $E° = -0.75$ volt. The most reasonable choice in Appendix 3 is the I^--I_2 half-reaction.

$$2I^- \longrightarrow I_2 + 2e^- \qquad E° = -0.53 \text{ volt}$$

The oxidizing agent is I_2 for this half-reaction.

Ex. 23-4. Balance the equation for the reaction between permanganate, $MnO_4^-(aq)$, and plutonium(III), $Pu^{+3}(aq)$, to form manganous, $Mn^{+2}(aq)$, and plutonyl ion, $PuO_2^{+2}(aq)$, in acid solution.

Answer

	MnO_4^- +	Pu^{+3} gives	Mn^{+2} +	PuO_2^{+2}
oxid. no.	+7	+3	+2	+6

The changes in oxid. no. for Mn and Pu are:

$$\text{Mn} \quad +7 \xrightarrow{-5} +2$$
$$\text{Pu} \quad +3 \xrightarrow{+3} +6$$

$3MnO_4^- + 5Pu^{+3}$ gives $3Mn^{+2} + 5PuO_2^{+2}$

$3MnO_4^- + 5Pu^{+3}$ gives $3Mn^{+2} + 5PuO_2^{+2} + 2H_2O$

$$3MnO_4^- + 5Pu^{+3} + 4H^+ \longrightarrow 3Mn^{+2} + 5PuO_2^{+2} + 2H_2O$$

Ex. 23-5. Plutonium(IV), $Pu^{+4}(aq)$, forms a complex ion with fluoride ion, PuF^{+3}:

$$PuF^{+3} \rightleftharpoons Pu^{+4} + F^- \qquad K = 1.6 \times 10^{-7}$$

If the F^- concentration is adjusted to 0.10 M in a solution containing $1.0 \times 10^{-3}\ M$ Pu^{+4}, calculate the ratio of the concentration of Pu^{+4} to PuF^{+3}. What is the equilibrium concentration of Pu^{+4}?

Answer

$$\frac{[Pu^{+4}][F^-]}{[PuF^{+3}]} = 1.6 \times 10^{-7}$$

$$\frac{[Pu^{+4}]}{[PuF^{+3}]} = \frac{1.6 \times 10^{-7}}{[F^-]} = \frac{1.6 \times 10^{-7}}{0.10} = 1.6 \times 10^{-6}$$

Since $[Pu^{+4}] = (1.6 \times 10^{-6})[PuF^{+3}]$, most of the plutonium is in the form of the complex ion PuF^{+3}. Hence

$$[PuF^{+3}] \cong 1.0 \times 10^{-3}\ M$$

and

$$[Pu^{+4}] = (1.6 \times 10^{-6})(1.0 \times 10^{-3}) = 1.6 \times 10^{-9}\ M$$

CHAPTER

24

SOME ASPECTS OF BIOCHEMISTRY: AN APPLICATION OF CHEMISTRY

Intent and Approach

The chapter title is a capsule description of the philosophy desired in this chapter. The student has covered the important principles of chemistry. This chapter should show him that these principles are applicable to all chemistry. Biochemistry is often presented as something of a mystery that is more to be memorized than understood. There is no theoretical justification for this, although the molecular systems are many times beyond the reach of our mathematical models.

You will find that the examples in this chapter do not pretend to cover biochemistry. They are chosen to illustrate that molecular composition, reaction energy effects, and molecular structure can be applied to biochemical substances and that they have the same importance they do for simpler compounds. It is not intended that the student be confronted with many complex cycles or with multitudes of huge molecules. The study of heredity, RNA, DNA, and "high energy" phosphate chemistry are best reserved for more advanced courses.

Outline

1. Sugars (24-1.1)—glucose, fructose, and sucrose; cellulose and starch (24-1.2), and fats (24-1.3) are discussed and their reactions compared to simpler organic compounds.
2. The metabolism of glucose is explored (24-2.1) and the oxidation cycle of acetic acid given (24-2.2).
3. Photosynthesis is treated briefly (24-2.3).
4. Simplified versions of the starch, cellulose (24-3.1), and protein polymers (24-3.2) are given.
5. Enzymes are treated (24-3.3), but rather lightly.

New Concepts

The chapter is not designed to introduce new concepts. These few are important.

1. The chemistry in the body is fundamentally no different from that in a test tube.
2. Specific arrangements in polymers have an effect on their properties.
3. Cyclic systems of reactions are prominent in living systems.

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*	*Topic*
S 24-1/24-1.1 (pp. 422–425)	1	Discussion	1–4	None	Sugars
S 24-1.2/24-1.3 (pp. 425–426)	2	Discussion	5, 6		Cellulose, Starch, Fats
S 24-2 (pp. 426–431)	3	Discussion	7–10		Energy sources in Nature
S 24-3 (pp. 431–434)	4	Discussion			
	5	Review or discuss topics of your choice Film: BIOCHEMISTRY AND MOLECULAR STRUCTURE			

Development

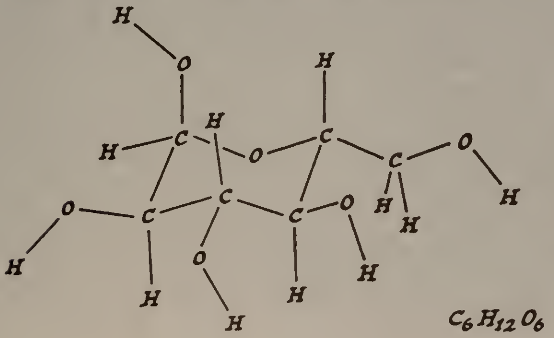
It will become clear from the many references in the Textbook that this chapter is closely related to Chapter 18 on organic chemistry. There is some need for you to recall the principles being used from earlier chapters—equilibrium, structure, acid–base relations, oxidation and reduction, catalysis, and energy considerations. The exercises are designed to emphasize this dependence, but mention of it is also desirable.

MOLECULAR COMPOSITION OF LIVING SYSTEMS (24-1)

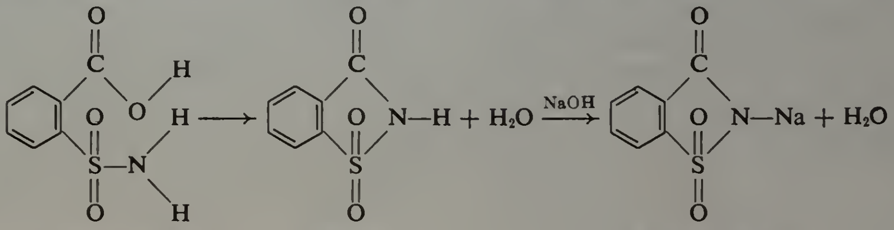
Sugars (24-1.1)

You will notice that the structural formula given in the Textbook for the glucose chain does not show the asymmetric carbon feature. That feature makes up a whole field of chemistry and is not, at this point, needed by a beginner. A careful observer may see in the ring form, equation (*2*), the placement of some OH groups above the ring, and others, below the ring. Such a student can be told that different isomers result from the different arrangements. He is not likely to benefit much from a discussion of polarized light, since he probably hasn't studied ordinary light yet.

The ring structure does not give all details. Glucose actually has a "chair" configuration (below), not the planar configuration used throughout this chapter. Again, the use of the more complicated formula is unwarranted.



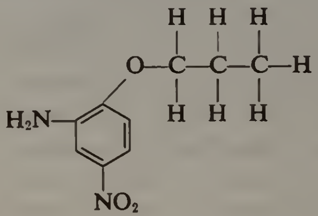
The word *saccharide* may seem strange, but most pupils know saccharin and its use as a sugar substitute. Saccharin is a good compound to use to show that sweetness is not unique to the sugar structure.


o-sulfonamidobenzoic acid

saccharin

soluble saccharin (the form usually used)

Note that saccharin is an "inner" amide—that is, an amine group combined with an acid group of the same molecule. This material is about 500 times as sweet as sucrose. Another, even sweeter, substance (4000 times sucrose) is *n*-propoxy-2-amino-4-nitrobenzene:



Equation (*4*) in the Textbook shows the oxidation of an aldehyde group by Fehling's solution. This test works for many sugars. Sometimes sugars that have no aldehyde group will also be oxidized by Fehling's solution. These complications need not be mentioned.

Cellulose and Starch (24-1.2)

These substances are given mainly as examples of polysaccharides and to set up their use in showing the importance of structure. It is best not to go deeply into their chemistry (for instance, the production of rayon is too complicated).

Fats (24-1.3)

The "fats" that the student is familiar with are not very pure. They do not consist of single chemical compounds. The result is that you cannot cite the behavior of "bacon fat" as showing what is characteristic of the group of compounds called fats.

ENERGY SOURCES IN NATURE (24-2)

Some Fundamental Biochemical Processes (24-2.1)

The reactions represented by equations (*9*)–(*15*) are known to be considerably more complex than shown. At least eighteen steps are known, involving thirteen enzymes (see Sec. 24-3.3). The simpler version serves our needs. The student should realize these reactions do not violate the conservation of energy law. Some reactions serve to store energy that is liberated by other reactions. There is no creation of energy by the plant.

Oxidative Metabolism (24-2.2)

This section discusses the only example of a cycle that we present. (It is a short version of the Krebs cycle.) Cycle is not a perfect name, since it implies a succession of steps. Actually, we have a set of concurrent equilibrium reactions which continue to operate because some of the products (CO_2 and H_2O) are removed. The figure on the opposite page is Textbook Figure 24-1, p. 428, with the names in the double boxes added.

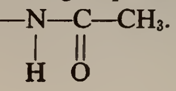
Photosynthesis (24-2.3)

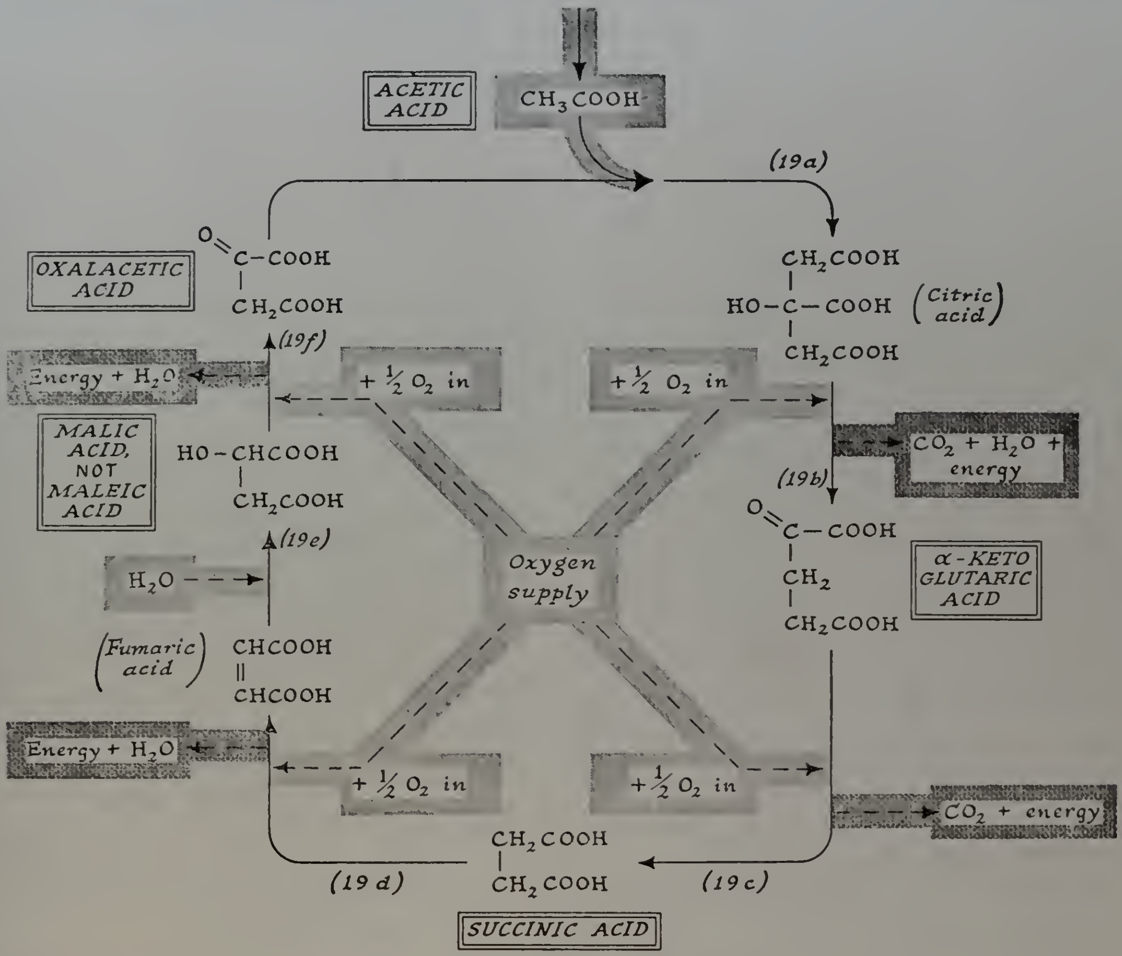
MOLECULAR STRUCTURES IN BIOCHEMISTRY (24-3)

The Structure of Starch and Cellulose (24-3.1)

The soluble portion of natural starch is called amylose (mol wt = 10,000–50,000) and makes up 10–20% of the material. The slightly soluble portion is amylopectin. It is much larger than the soluble part (mol wt $\approx$ 50,000–100,000). Branching is detected by reactions that occur only at glucose units that terminate a chain. One "end" is found for each 25–30 glucose units. Since amylopectin consists of about 500 of these units, branching must exist. The amylose polymer is shown on Textbook p. 432. Amylopectin is made of the same monomer, but branching occurs from some of the carbons that are not part of the ring.

The cellulose polymer is shown on p. 432 of the Textbook. Current evidence suggests that this is a completely linear polymer (mol wt = 300,000–500,000). The determination of the molecular weight of a polymer is very difficult. Consequently, published values are frequently given as a range rather than as a specific number. Large molecular weights and moderate solubility render freezing point determinations of little value. For example, one gram of polymer having a molecular weight of 100,000 when dissolved in 100 grams of benzene would lower the freezing point only 5×10^{-4}°C. Measurement of osmotic pressure is much more useful. The presence of a solute makes the vapor pressure of a solution lower than that of the solvent. If solution and solvent are separated by a membrane which is not permeable to the solute, then at equilibrium a hydrostatic head will exist on the solution side.

The hard shell on crustaceans (shrimp, lobster) and insects (beetles) is made of a polysaccharide called chitin (hardened with $CaCO_3$). Chitin has a structure like starch and cellulose except that in each glucose one —OH group has been replaced by an amide group,  $-\underset{\displaystyle H}{\underset{|}{N}}-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$.



Proteins (24-3.2)

Proteins are the first class of compounds whose structure was explained on the basis of a helical molecular form. The idea has been well proved by X-ray analysis of natural proteins and of similar, synthetic polyamides. The same idea is now being used for nucleic acids. Unfortunately, however, they seem to have a complex double helix that is beyond our ability to fruitfully discuss in this course.

Hydrogen bonds are quite important in explaining the properties of polyamides (and of the polysaccharides, too, although this was not brought out when they were discussed). The previous comments (p. 573) about the effect of hydrogen bonds on molecular properties apply to these more complex polymeric substances, but they are more difficult to demonstrate.

Enzymes (24-3.3)

This section deals with the importance of limited parts of big molecules. The entire "lock and key" theory of enzyme action requires that there be certain areas to which the substrate molecule fits particularly well. This theory explains many of the observed facts. Until recently, not much else was possible, because the structure of enzymes was not known, but this is changing now.

All the enzymes are proteins, hence they probably have structures like the helix shown in Textbook Figure 24-2. A single molecule may have more than one helix joined together. These helixes are thought to be joined side by side through covalent bonds, probably —S—S— bridges.

Supplementary Material

Articles

The articles listed below are the latest ones in *Scientific American*. Numerous older ones are not listed.

Subject	Date		Page	Offprint No.*
Sugar metabolism	December	1948	28	
Cellulose	September	1957	156	
Photosynthesis	November	1953	80	
	November	1960	104	75
Protein structure	September	1957	173, 204	7
	December	1961	96	
	February	1961	81	80
Krebs cycle	September	1949	48	
Enzymes—chemistry	March	1956	42	
—functions	December	1956	126	
—substrate complex	August	1959	119	
Chemotherapy	November	1956	135	
Fats	February	1960	46	67
Hormones	March	1957	76	
	May	1958	99	
Nucleic acids	September	1957	188	54
	December	1959	55	68

* Available from W. H. Freeman and Co., San Francisco. About 250 other articles are also available in this form.

Films

BIOCHEMISTRY AND MOLECULAR STRUCTURE

A CHEM Study film
Running Time: About 20 minutes

The collaborator, Dr. Donald E. Rounds, Pasadena Foundation for Medical Research, Pasadena, California, demonstrates the role of molecular structure in determining biological activity. Correlation of the structure and biological activity of sulfanilamide with a vitamin essential for bacterial growth leads to a more general investigation of the biochemical nature of growth. Paper chromatography is used to separate some of the compounds which make up human cells. It is proposed that compounds similar to those found in cell chromosomes may stop cell growth and thus be useful in controlling cancer. The technique of time-lapse microphotography is used to demonstrate the effect of one such compound, 5-fluorouracil, on cancer cells.

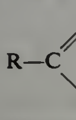
Answers to Exercises

Ex. 24-1. Glucose, a sugar simpler than sucrose, has a molecular weight of 180 and empirical formula CH_2O. What is its molecular formula?

Answer

The empirical formula weight of CH_2O is 30. Thus the glucose formula contains $\frac{180}{30}$, or 6 empirical formulas. The glucose formula is $C_6H_{12}O_6$.

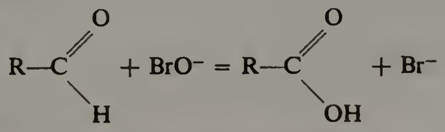
Ex. 24-2. Write the equation for the oxidation of



by hypobromite ion, BrO^-, to produce Br^-.

What are the oxidation numbers of carbon and bromine before and after reaction? Which element is oxidized? Which is reduced?

Answer



The change in oxidation number is

$$\text{bromine } +1 \xrightarrow{-2} -1$$

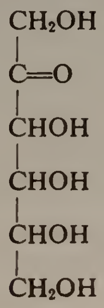
Carbon is oxidized; bromine, reduced. The alkyl group R is usually assigned a zero oxidation number. Hence, for carbon, we have

$$+1 \xrightarrow{+2} +3$$

Be sure to call attention to the fact that it doesn't matter what number is assigned to R as long as it doesn't change.

Ex. 24-3. Draw a structural formula for the fructose molecule (remember that fructose is an isomer of glucose). Explain why fructose cannot be oxidized to a six-carbon acid.

Answer:



$$\begin{array}{l} CH_2OH \\ | \\ C{=}O \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

fructose

Fructose cannot be oxidized to a six-carbon acid because the carbonyl group can be oxidized to an acid only if it is placed at the end of the chain. Oxidation of a ketone must break the chain; it then produces CO_2 and H_2O.

Ex. 24-4. At equilibrium in a 0.1 M solution of glucose in water, only 1% of the glucose is in the straight-chain form. What is K for reaction (2)?

Answer

The equilibrium reaction can be expressed

$$\text{chain} \rightleftharpoons \text{ring}$$

$$K = \frac{[\text{ring}]}{[\text{chain}]} = \frac{0.099}{0.001} = 99$$

The ring form is favored.

Ex. 24-5. The monomer unit in starch and that in cellulose each has the empirical formula $C_6H_{10}O_5$. These units are about 5.0 Å long. Approximately how many units occur and how long are the molecules of cellulose and of the soluble starch?

Answer

The empirical formula weight $C_6H_{10}O_5$ is 162.

For starch,

$$\frac{4000}{162} = 25 \text{ glucose units}$$

For cellulose,

$$\frac{600{,}000}{162} = 3700 \text{ glucose units}$$

length of starch molecule:

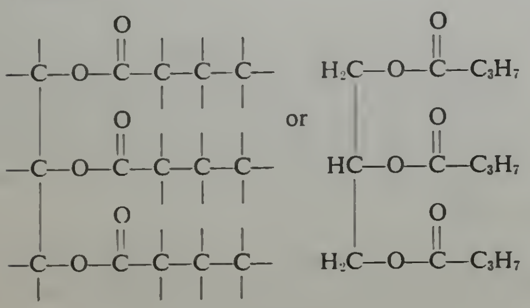
$$25 \text{ unit} \times 5 \text{ Å/unit} = 125 \text{ Å}$$

length of cellulose molecule:

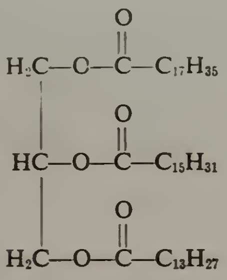
$$3700 \text{ unit} \times 5 \text{ Å/unit} = 19{,}000 \text{ Å}$$

Ex. 24-6. Write the formula for glycerol tributyrate, and then write the formula of the fat made from glycerol and one molecule each of stearic ($C_{17}H_{35}COOH$), palmitic ($C_{15}H_{31}COOH$), and myristic ($C_{13}H_{27}COOH$) acids. How many isomers are possible for the last fat? How many would be possible if all possible combinations of the three acids were used? Compare your answer with that for Exercise 18-15, p. 349.

Answer

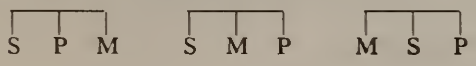


glycerol tributyrate

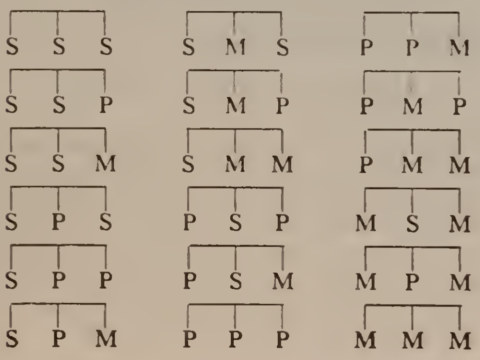


mixed fat

This mixed fat is named α-stearo-β-palmito-γ-myristin. If named from the other end, it then becomes α-myristo-β-palmito-γ-stearin. This fat has only three isomers (when we specify that three different acids are to be used per molecule of fat). Using S, P, and M for the acids, and a line for glycerol, the isomers are



If all possible combinations of the three acids are used, eighteen isomers of this fat can be obtained. The eighteen combinations are shown below.



In Ex. 18-15 there were 27 combinations, but only 18 of these are different for a free molecule. Combinations such as ABC and CBA are distinct when hooked into a chain because the two groups to the left and right of the two may not be identical. For a free molecule, however, ABC and CBA are the same. One is just rotated in space by 180°.

Ex. 24-7. Write a balanced equation for the oxidation of pyruvic acid to CO_2 and H_2O.

Answer

$$CH_3COCOOH + 2\tfrac{1}{2}O_2 = 3CO_2 + 2H_2O$$

Ex. 24-8. The sun provides about 0.50 calorie on each square centimeter of the earth's surface every minute. How long would it take ten leaves to make 1.8 g of glucose if the area of each leaf is 10 cm² and if only 10% of the energy is used in the reaction?

Answer

$$(1.8 \text{ g glucose})\left(\frac{1}{180 \text{ g glucose/mole}}\right) = 0.010 \text{ mole glucose}$$

$$(0.010 \text{ mole glucose})\left(\frac{673 \text{ kcal}}{\text{mole}}\right) = 6.7 \text{ kcal needed}$$

energy taken in

$$= \left(0.50 \frac{\text{cal}}{\text{min-cm}^2}\right)\left(10 \frac{\text{cm}^2}{\text{leaf}}\right)(10 \text{ leaves}) = \frac{50 \text{ cal}}{\text{min}}$$

Since only 10% of the energy is used, there will be available 5.0 cal/minute. The time required to provide 6700 calories will be

$$\frac{6700 \text{ cal}}{5.0 \text{ cal/min}} = 1.3 \times 10^3 \text{ minutes}$$

or

22 hours

Ex. 24-9. Normally about 0.03% of the molecules in air are carbon dioxide molecules. How many liters of air (STP) are needed to provide enough CO_2 to form 1.8 g of glucose in reaction (*20*)?

Answer

$$(1.8 \text{ g glucose})\left(\frac{1}{180 \text{ g glucose/mole}}\right) = 0.010 \text{ mole glucose}$$

$$(0.010 \text{ mole glucose})\left(\frac{6 \text{ moles } CO_2}{1 \text{ mole glucose}}\right) = 0.060 \text{ mole glucose}$$

We need

$$\frac{0.060 \text{ mole } CO_2}{0.0003 \text{ mole } CO_2} \times 22.4 \text{ liters} = 4500 \text{ liters air}$$

Notice that 4500 liters is about 160 cubic feet, the volume of a cube $5\frac{1}{2}$ feet on a side, very roughly the volume of an automobile. The 1.8 g of glucose is about equivalent to one-half a sugar cube.

Ex. 24-10. Suppose red light of wavelength 6700 A is absorbed by chlorophyll.

(a) Show that the frequency of this light is 4.5×10^{14} cycles per second.

(b) How much energy is absorbed per mole of photons absorbed? (See Sec. 15-1.1; $h = 9.5 \times 10^{-14}$ kcal-sec/mole.)

(c) How many moles of photons would be needed to provide enough energy to produce one mole of glucose by reaction (*20*) if all of the energy were provided by red light?

Answer

(a)
$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{10} \text{ cm/second}}{6700 \times 10^{-8} \text{ cm/cycle}}$$
$$= \frac{3.0}{0.67} \times 10^{14}$$
$$= 4.5 \times 10^{14} \text{ cycles/second}$$

(b)
$$E = h\nu$$
$$= \left(9.5 \times 10^{-14} \frac{\text{kcal sec}}{\text{mole}}\right) \left(4.5 \times 10^{14} \frac{\text{cycles}}{\text{sec}}\right)$$
$$= 43 \frac{\text{kcal}}{\text{mole photon}}$$

(c) One mole of glucose requires 673 kcal of energy input.

$$\text{moles of photons required} = \frac{673}{43} = 15.6.$$

CHAPTER

25

THE CHEMISTRY OF EARTH, THE PLANETS, AND THE STARS

Intent and Approach

In this chapter we wish to show that the chemistry of the entire universe can be understood in terms of the student's experience. The same principles apply whether the sample is a test-tube-full or the entire atmosphere of Jupiter. The time scale is perhaps the most important difference. We can see, in planetary chemistry and in geochemistry, the results of very slow processes acting for millions of years, whereas the student has studied reactions with much faster rates.

Outline

1. The earth is discussed first (25-1.1) as comprising the atmosphere (25-1.2), the hydrosphere (25-1.3), and the lithosphere (25-1.4).
2. The practical sources of elements receive some remarks (25-1.5 and 25-1.6).
3. The age of the earth (25-1.7) and ways to determine it are reviewed.
4. The planets are treated next, with sections on meteorites (25-2.1), the atmospheres and lithospheres of planets (25-2.2 and 25-2.3), and the sun (25-2.4).
5. Finally, the atmospheres around and between the stars are discussed (25-3.1 and 25-3.2).

New Concepts

Three spheres constitute the earth, and correspond to the gas, liquid, and solid phases which have been under discussion throughout the course.

The use of spectroscopic methods for identifying the chemical constituents of the sun and stars is new.

Development

THE CHEMISTRY OF OUR PLANET, EARTH (25-1)

The Parts of the Earth (25-1.1)

The parts of the earth could be studied under the names "solid part," "liquid part," and "gaseous part." It is intended that the student realize that what he knows about these phases applies to this new, relatively large sample he is now studying. Stick to this three-phase division. There is little to gain by dwelling on the

Schedule and Related Material

Assignment Prior to Period	*Period*	*Class Work*	*Ex.*	*Problems*	*Topic*
S 25-1/25-1.3 (pp. 437–440)	1	S 25-1/25-1.3	1, 2	None	Parts of the earth, Composition
S 25-1.4/25-1.7 (pp. 440–444)	2	S 25-1.4/25-1.7	3		Availability of elements, Age of the earth
S 25-2 (pp. 444–447)	3	S 25-2	4		Chemistry of the planets
S 25-3 (pp. 447–448)	4	S 25-3 Review	5		The stars

geologist's division of the solid portion into several zones according to seismic behavior and supposed composition.

This and the following sections provide a feeling for the distribution of the elements among the three parts of the earth. In addition, you can comment on the relative uniformity, or lack of it, along the following lines. Although the individual molecules in the atmosphere are constantly changing, the overall composition is quite homogeneous (see Landsberg's article cited in *Supplementary Material* for information about the various stages of our atmosphere within the various geological time periods). This homogeneity is due to the low percentage of total molecules engaged in chemical change at any one time. Some chemicals (CO, CO_2, H_2O) vary in *local* concentration because of man's activities. Such changes are so small and limited in number that they do not affect the total atmosphere. A possible exception is the increase in CO_2 that has occurred during the industrial revolution as a result of the heavy use of fossil fuels. In 1961 the level of CO_2 was about 310 parts per million (ppm) and was increasing at about 0.7 ppm/yr. Moreover, the hydrosphere is homogeneous in content, although subject to continual change of individual molecules, especially through the processes of evaporation, condensation, and solution. The concentration of ocean salt is gradually building up through a process of leaching.

The lithosphere, by contrast, is heterogeneous. Its content is uncertain. Even geochemists, as experts, have given only educated guesses. The deepest man-made penetration is five miles, 0.00062 of the earth's diameter. Such holes are made at very infrequent intervals. Thus knowledge about the earth, most of which comes from seismic experiments, is incomplete.

A current research study is underway with the intent to drill through the earth's crust to obtain a direct sampling. This project is called the "Mohole," a nickname derived from the geologists' name for the earth's crust, the "moho." Moho is an abbreviation of Mohorovicic, the name of the Croatian scientist who discovered the seismological basis for defining the thickness of the earth's crust. This project is described in *Scientific American*, April 1959, pp. 41–49.

Composition and Properties of the Atmosphere (25-1.2)

Water vapor is the exception to the remarks about constancy in the atmosphere, since it varies quite markedly in a local way. A short discussion of relative humidity as related to vapor pressure data is desirable at this point as an example of one kind of formal chemical information found in the newspaper weather reports. Relative humidity multiplied by vapor pressure of water at the given temperature is equal to the existent vapor pressure.

It is interesting to indicate that only about 0.01% of the earth's water is in vapor form; yet this is an impressive figure in tons, being several trillion tons. This fraction is rather important, since it is one of the stages in our supply of fresh water.

Composition of the Hydrosphere (25-1.3)

The hydrosphere is mostly liquid water in the oceans and lakes. About 99% of our total of 3.5×10^8 cubic miles of water is liquid. Only a tiny fraction is gaseous, and about 1% is solid. The solid portion exists mainly in the form of huge ice sheets in Greenland and Antarctica.

Ice ages are well known in geology. At the peak of an ice age about one third of the land surface is ice-covered, and the oceans are low (as much as 300 feet below present levels). During nonglacial periods the ice is almost all melted, and low areas are flooded. At present, the earth is at an intermediate stage; 10% of the land area is ice-covered, with a general recession of ice underway. The oceans are presently rising at about 6 cm per century.

Water is unique in that it is the only major component of the earth's surface that exists in all three physical states. This fact, combined with its prevalence and its relatively high heat of vaporization, explains its important influence on our weather.

The dynamic change between liquid and gaseous water is an example of equilibrium. All natural water surfaces, rivers, lakes, and ocean, are subject to evaporation. They display a dynamic disequilibrium because the space above them does not readily become saturated with water vapor. Therefore the rate of vaporization will usually exceed the rate of condensation. During rains these rates are reversed, with the result that, over a long period, complete evaporation does not occur. If your school is located near a body of salt water, the analysis of its dissolved constituents would be a pertinent experimental project.

Composition and Properties of the Lithosphere (25-1.4)

In discussing the earth's crust you can consider whether it is composed of network, ionic, molecular, or metallic solids. The majority of minerals and soils are network solids of silicon, aluminum, and oxygen. The other types of solids occur as ores and mineral deposits but make up a very small fraction of the total lithosphere. A discussion of each type of solid could be used to review the principles studied earlier in the course.

Availability of Elements (25-1.5)

The Air as a Source of Elements (25-1.6)

These sections are intended to make the point that percent composition does not give all the important facts. Physical accessibility and the chemical means to convert ores to usable compounds are also required. For example, aluminum is an abundant element. It also exists in massive deposits of high quality. Until the late nineteenth century, however, it was a chemical curiosity; no economical method of extraction had been found. Titanium is an element currently undergoing a shift from laboratory chemical to commercial material.

Melting, crystallization, solution, and precipitation are mentioned as natural processes that have led to concentrated deposits of minerals. Suggest that the student review the solubility table and relate it to the common occurrence of oxide, sulfide, carbonate, and sulfate deposits. Also discuss why large deposits of sodium chloride and $NaNO_3$ are found.

The student may not think of the air as a source of chemicals. He may have heard of "liquid air," although, if he has, it is very likely that liquid nitrogen was meant. Both $N_2(l)$ and $O_2(l)$ are made by compressing air and then letting it expand. The Joule-Thomson cooling effect (discussed on p. 137) eventually causes some of the sample to liquefy. The pure components are separated by distillation, the entire operation being relatively simple. Liquid N_2 costs about the same as milk. Argon is separated from air in the same way, but costs much more.

The Age of the Earth (25-1.7)

This section should draw attention to the fact that the earth has a finite age. We have emphasized the uranium decay scheme because radioactive decay is not covered elsewhere in the Textbook. Two other decay schemes produce lead isotopes, ^{207}Pb from ^{235}U, and ^{208}Pb from ^{232}Th.

THE CHEMISTRY OF THE PLANETS (25-2)

All four sections of this main topic are really directed toward the idea that there is no fundamental distinction between "earth" chemistry and "space" chemistry. These sections will probably be most useful if you initiate a discussion of absorption spectra and the attendant spectroscopy. Remark that a spectral study of sunlight and starlight supplies the clues upon which we base our knowledge of their content. The discovery of helium in the sun is the common example. The method serves to "analyze" other stars. The information is limited to those substances and reactions emitting radiation (visible, infrared or radio).

Some student may wonder how we can observe H_2O or CO_2 on another planet through our atmosphere, since it contains these substances. Part of the answer is that the spectral lines are shifted (by the Doppler effect) as a result of the relative motion of the observer and the "sample."

THE STARS (25-3)

Supplementary Material

Articles

All of the following are in *Scientific American:*

W. A. Fowler, "The origin of the elements," September 1956, pp. 82–91.

K. E. Bullen, "The interior of the earth," September 1955, pp. 56–61.

O. F. Tuttle, "The origin of granite," April 1955, pp. 77–82.

H. Bloom and H. F. Walton, "Chemical prospecting," July 1957, pp. 41–47.

H. E. Landsberg, "The origin of the atmosphere," August 1953, pp. 82–86.

J. L. Mero, "Minerals on the ocean floor," December 1960, pp. 64–72.

H. G. Bachmann, "The origin of ores," June 1960, pp. 146–156.

"The planet earth," September 1955, entire issue.

"The universe," September 1956, entire issue.

Books

1. H. Bondi, *The Universe at Large*, The Science Study Series (PSSC), Wesleyan University Press Inc., Education Center, Columbus 16, Ohio.
2. P. M. Hurley, *How Old is the Earth ?*, The Science Study Series (PSSC), Wesleyan University Press Inc., Education Center, Columbus 16, Ohio.

Background Discussion

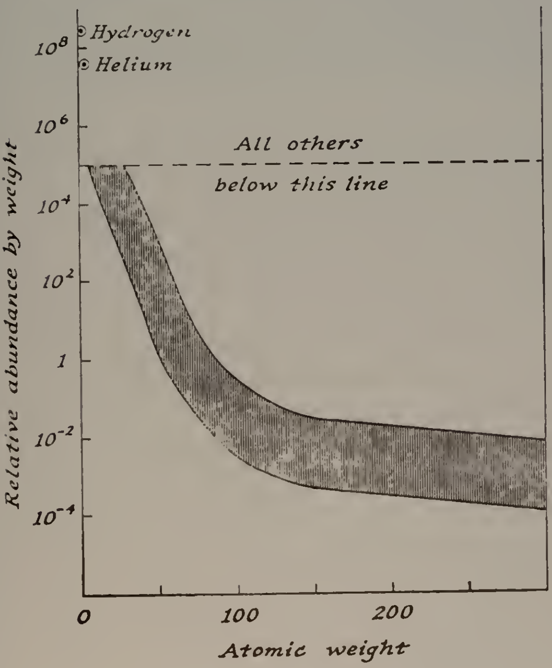
THE ORIGIN OF ELEMENTS

One question that has engaged almost every philosopher, natural or religious, is the origin of the universe. The ultimate why and where may never be known. But we do have a large number of facts that can be applied to the smaller questions, "Why are there so many elements?" and "How did they form?" The data are from a variety of scientific fields and are not highly precise, but they can be codified into a relatively simple theory.

First consider Figure 25-1, which shows in a general fashion the relative abundance of the elements. If we take elements of atomic number 50 to 85 as having unit abundance, hydrogen is 10^8 times as abundant. Other light elements are 10^3–10^5 times as abundant.

The great predominance of light elements is shown, as is the superabundance of hydrogen. This figure doesn't apply to the earth alone but to the much larger sample, including the stars. Most of the light elements are in the stars, where nuclear reactions are producing the heat and light we observe, and where heavier elements are being made from hydrogen.

Fig. 25-1. **The relative abundance of elements in the universe.**



We will discuss two theories for the origin of the elements. One is simple, elegant, and inadequate for explaining elements other than the first few. The other gives mechanisms that explain the generation of heavy elements, but it becomes complicated.

The simple theory (due to Gamow and coworkers) postulates that all elements were made in one large explosion at "the beginning." According to Gamow, a huge ball of neutrons expanded about 5 billion years ago. As the pressure was released, neutrons decayed to protons, which captured a neutron. In equations (refer to Chapter 7 on energy in the nucleus) this is written

$$^1_0n \longrightarrow {}^1_1p + {}^{\;0}_{-1}e = {}^1_1\mathrm{H}$$

$$^1_1\mathrm{H} + {}^1_0n \longrightarrow \underset{\text{deuterium}}{^2_1\mathrm{H}}$$

The deuterium again captures a neutron, then loses an electron to give a helium isotope:

$$^2_1\mathrm{H} + {}^1_0n \longrightarrow \underset{\text{tritium}}{^3_1\mathrm{H}}$$

$$^3_1\mathrm{H} \longrightarrow {}^3_2\mathrm{He} + {}^{\;0}_{-1}e$$

Processes of this type continued (taking only a few minutes, according to the theory), producing all the elements. In the process of this explosion the various stars and planets were formed. The best confirmation of this theory is the expected *and observed* relation between the distribution of elements and the tendency of a given element to capture neutrons. The elements that capture neutrons easily should disappear rapidly, hence be in minor abundance. Such is the case—the heavy elements capture neutrons better than light ones, and they are present in small proportion.

The inadequacy of this theory lies in the fact that the capture reactions cannot get past He. At least as far as we know, there are no stable isotopes of mass 5. We can form $^5_2\mathrm{He}$,

$$^{4}_{2}\text{He} + ^{1}_{0}n \longrightarrow ^{5}_{2}\text{He}$$

but this reaction only reverses. It does not lead to a lithium isotope. There is a similar impasse at atomic weight 7. That is, even if we explain the formation of Be, it decomposes to two ^{4}He atoms when it captures a neutron, therefore the progression to heavier elements stops.

The second theory (by Hoyle) postulates that the elements are made in the hot interior of stars, where nuclear fusion reactions occur. In this case we start with all matter as highly dispersed hydrogen atoms. They condense by gravity, into stars where enough pressure eventually builds up such that the interior becomes very hot. Then by fusion of protons, hydrogen isotope mass 2, and helium can occur.

$$^{1}p + ^{1}p \longrightarrow ^{2}\text{H} + \text{energy}$$
$$^{2}\text{H} + ^{1}p \longrightarrow ^{3}\text{He} + \text{energy}$$
$$^{3}\text{He} + ^{3}\text{He} \longrightarrow ^{4}\text{He} + 2(^{1}p)$$

Here we find ourselves at the same roadblock that stopped us in the neutron absorption theory. But we can now postulate a way around the difficulty. Allowing fusion instead of neutron capture, we can imagine a reaction which, first, fuses particles to give ^{8}Be and then, in another leap, produces carbon:

$$^{4}\text{He} + ^{4}\text{He} \longrightarrow ^{8}\text{Be}$$
$$^{8}\text{Be} + ^{4}\text{He} \longrightarrow ^{12}\text{C}$$

From this point on, the theory is complex, but no new aspects arise.

Besides the reactions mentioned, this proposed explanation involves a number of changes in the star—expansions and contractions, with concurrent changes in temperature. These changes can be related to the observed variety of stars so that our explanation gives a better description of the astronomer's universe, as well as a basis for the origin of elements.

The present situation seems to be that the second theory is best for roughly the first half of the elements (up to about iron, with atomic number 56). The neutron capture theory seems to explain the origin of the second half best.

Answers to Exercises

Ex. 25-1. Suppose that the photosynthesis reaction (*20*) in Chapter 24 (p. 430) could be based upon light of wavelength 2400 Å (this light is absorbed heavily by ozone). How many moles of these photons would provide the 673 kcal of energy needed to produce one mole of glucose? (Remember, $E = h\nu$, and $h = 9.5 \times 10^{-14}$ kcal sec/mole). Compare your answer with that of Exercise 24-10.

Answer

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^{10}\ \text{cm/second}}{2400 \times 10^{-8}\ \text{cm/cycle}}$$

$$E = h\nu = \left(9.5 \times 10^{-14}\ \frac{\text{kcal seconds}}{\text{mole}}\right)(1.25 \times 10^{15}\ \text{cycles/second})$$

$$= 1.2 \times 10^{2} = 120\ \text{kcal/mole}$$

Moles of photons needed per mole glucose:

$$\frac{673\ \text{kcal/mole glucose}}{120\ \text{kcal/mole light}} = 5.6\ \frac{\text{moles light}}{\text{mole glucose}}$$

In Exercise 24-10 you found that when using red light, 15.6 photons are needed, or, roughly, three times as many.

Ex. 25-2. On this planet, of what value would be an eye that is sensitive only to light in the ultraviolet spectral region? Discuss the evolutionary significance of the facts that the human eye and the photosynthesis process are both dependent upon light in the part of the spectrum called the "visible."

Answer

An eye sensitive only in the ultraviolet region would be useless, because this spectral region would always be "dark." No doubt, both the eye and the photosynthetic process evolved to be dependent upon the visible part of the spectrum because this is the part of the spectrum transmitted best by the atmosphere.

For this, and the previous exercise, you may like to know the regions of absorption. Electronic excitation in the ultraviolet region renders the earth's atmosphere opaque in the ranges 2200–2950 Å (ozone) and 1300–2400 Å (O_2). There are also opaque regions in the infrared region; completely below 400 and almost completely up to 1600 cm^{-1} (absorbed by rotation of water), there are eight regions between 1600 and 10,000 cm^{-1} (vibration of water) at 667 and 2350 (vibration of CO_2). The result is that our atmosphere has a spectral "window" between 3000 and 10,000 Å. The human eye cannot register all this range; it can register only between 4000 Å (violet) and 6500 Å (red). Hence there is both an ultraviolet and an infrared portion of light striking the earth's surface that we cannot see.

Ex. 25-3. Explain in terms of energy the significance of the fact that a piece of wood is stable in air at room temperature but if the temperature is raised, it burns and releases heat.

Answer

Since heat is released when reaction occurs, the energy of the products is lower than the energy of the reactants. But their failure to react at room temperature indicates that an activation energy barrier exists, which obstructs reaction. Only when the temperature is raised do enough molecules have the energy required to react, giving self-sustaining reaction.

Ex. 25-4. Nitrogen is considered to be a likely constituent of the atmosphere of Jupiter, though it is undetected as yet. As a chemist, would you expect oxygen also to be an important constituent of Jupiter's CH_4-NH_3 atmosphere?

Answer

Oxygen is not likely to be present in a reducing atmosphere of methane. A mixture of CH_4 and O_2 is chemically unstable and would, presumably, react explosively if reaction were ever accidentally started (e.g., by lightning) or would react slowly under the influence of ultraviolet irradiation. Remember that even a slow reaction can be important over a billion years. As regards boiling point, freezing point, and gravitational effects, oxygen could be present.

Ex. 25-5. Calculate the volume in liters of a sphere of radius 6400 kilometers (the radius of the earth). How many grams of oxygen would be needed to fill this volume to a concentration of one molecule per 1000 liters?

Answer

The volume of a sphere is $\frac{4}{3}\pi r^3$. The radius is

$$\begin{aligned} 6.4 \times 10^3 \text{ km} &= 6.4 \times 10^6 \text{ meters} \\ &= 6.4 \times 10^8 \text{ cm} \\ V &= \tfrac{4}{3}\pi(6.4 \times 10^8)^3 \text{ cm}^3 \\ &= 1.1 \times 10^{27} \text{ cm}^3 \\ V &= 1.1 \times 10^{24} \text{ liters} \end{aligned}$$

If there is one molecule per 1000 liters, we need

$$\frac{1.1 \times 10^{24}}{1000} = 1.1 \times 10^{21} \text{ molecules}$$

This is

$$\frac{1.1 \times 10^{21} \text{ molecules}}{6.0 \times 10^{23} \text{ molecules/mole}} = 1.9 \times 10^{-3} \text{ mole}$$

$$\begin{aligned} &1.9 \times 10^{-3} \text{ mole of } O_2 \\ &\quad = (1.9 \times 10^{-3} \text{ mole})(32 \text{ g/mole}) = 0.059 \text{ g} \end{aligned}$$

Chemicals and Equipment Used

The following list is divided into three main categories. **Supplies** consists of materials consumed during the school year, and include the chemicals and a few miscellaneous items. **Equipment** includes reuseable items—glassware and hardware. **Items used by the class as a whole** are fairly expensive, and normally only one or a few are needed per school. The supplies and equipment are not much different from what is normally stocked.

The list shows the amounts needed for a class of 30 students who are doing all the experiments. We have assumed that *each student works alone* except in Expts. 21, 27, 30, and 37, where, owing to your limited supply of voltmeters, polystyrene spheres, D.C. sources, and ion exchange tubes, we expect you will have to organize students into groups of 4, 2, 4, and 2, respectively. Chemicals are to be analytical grade unless otherwise specified. We have allowed a modest surplus.

The Teachers Guide contains many hints for substitutes. Check individual guides to the pertinent experiment before you decide you must purchase.

SUPPLIES (Expended during School Year)

Chemicals

Compound	*Purchased As*	*Quantity*	*Used in Experiment*
Acetic acid	glacial	1200 ml	D5,* 12, 17, 18, 19, 29, 40
Acetone		2150 ml	D1, 16, 25, 29, 29a, 37
Agar-agar	powder	60 g	38
Alizarin Yellow R		0.1 g	18
Aluminum chloride	$AlCl_3 \cdot 6H_2O$	6 g	11
Aluminum nitrate	$Al(NO_3)_3 \cdot 9H_2O$	75 g	32
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	14 g	11
Ammonia solution	conc. reagent (15 *M*)	800 ml	19, 32, 34, 35, 36, 37, 39
Ammonium carbonate	lump	210 g	22, 29, 34
Ammonium chloride		30 g	12
Ammonium dichromate		1 g	12
Ammonium nitrate		16 g	21
Ammonium oxalate	$(NH_4)_2C_2O_4 \cdot H_2O$	13 g	34
Ammonium sulfate		138 g	34, 39
Ammonium thiocyanate		3 g	37
isoAmyl alcohol		1000 ml	D1
Aniline hydrochloride		300 g	29a
Barium chloride	$BaCl_2 \cdot 2H_2O$	45 g	8b, 11
Barium hydroxide	$Ba(OH)_2 \cdot 8H_2O$	10 g	D5, 22
Barium nitrate		40 g	11, 19, 33, 34, 36
Benzene		150 ml	D3, 28
Benzoyl peroxide paste (see note, p. 611)		0.6 g	29a
Bromine		2 g	20, 28
Bromthymol blue		1 g	32
1-Butanol		150 ml	28
2-Butanol		150 ml	28
t-Butanol		150 ml	28
Calcium carbonate	marble chips	40 g	12
Calcium chloride	anhydrous, #12 mesh	100 g	29
Calcium hydroxide	powder, tech.	6 g	4, 18, 19
Calcium nitrate	$Ca(NO_3)_2 \cdot 4H_2O$	11 g	34
Calcium sulfate	$CaSO_4 \cdot 2H_2O$	15 g	8b
Carbon tetrachloride		600 ml	20, 22, 28, 30
Chlorine	bottled	lec. bot.	20, 32
Chromium(III) acetate	$Cr(CH_3COO)_3 \cdot H_2O$ 23–25% Cr	90 g	40
Chromium sulfate	$Cr_2(SO_4)_3 \cdot H_2O$ 65% $Cr_2(SO_4)_3$	12 g	22
Citric acid	monohydrate	1 g	18
Cobalt(II) chloride	$CoCl_2 \cdot 6H_2O$	31 g	11, 37
Cobalt(II) nitrate	$Co(NO_3)_2 \cdot 6H_2O$	20 g	11, 14a
Copper wire	B and S, 22 gauge	30 ft	D2, 9, 28
Copper wire	B and S, 16 gauge	1 pound (128 ft)	2, 7, 16, 25, 28, 38
Copper screen, 20 mesh		1500 cm²	25
Copper sheet, B and S 20–30 gauge		750 cm²	20, 21, 25, 28
Copper(II) nitrate	$Cu(NO_3)_2 \cdot 3H_2O$	120 g	20, 21
Copper(II) sulfate	$CuSO_4 \cdot 5H_2O$	550 g	8b, 25, 39
Copper(II) sulfate	anhydrous	3 g	39
Cyclohexane		30 ml	28
Cyclohexene		30 ml	28
*Para*dichlorobenzene		300 g	3
Dimethylglyoxime		1 g	37
Ethanol		1500 ml	D3, 10, 18, 19, 20, 28, 29, 39, 40
Ethyl acetate		300 ml	29, 29a
Ferric chloride	$FeCl_3 \cdot 6H_2O$	60 g	11, 22, 30, 37
Ferric nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	120 g	D4, 14a, 15
Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	10 g	12, 22, 38

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* The symbol D indicates demonstration.

Formaldehyde	40% Formalin	300 ml	29a
Fumaric acid		3 g	26
Glycerol		60 g	29a
Hydrochloric acid	conc. 12 *M*	3500 ml	frequent use
Hydrogen peroxide	30% stabilized	250 ml	22, 31, 40
Indigo Carmine		0.25 g	18
Iodine		35 g	20, 31
Iron nails	10 penny	270	38
Lead	sheet, $\frac{1}{32}$ inch thick	1500 cm²	2, 20, 21, 25
Lead dioxide		30 g	12
Lead nitrate		360 g	8a, 10, 12, 20, 21, 22, 35
Lucite	pellets or chips	750 g	29a
Magnesium	ribbon, 1 ounce roll	6 g	9, 26, 32
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	2 g	11
Magnesium nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	20 g	22, 34
Magnesium oxide		10 g	18, 32
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	30 g	8b
Maleic acid		270 g	26
Manganous sulfate	$MnSO_4 \cdot H_2O$	35 g	8b, 12
Mercurous nitrate	$Hg_2(NO_3)_2 \cdot 2H_2O$	1 g	35
Methanol		250 ml	D3, 28
Methylethylketone		300 ml	29a
Methyl Orange		1 g	18, 32
Methyl Red		0.3 g	32
Nickel(II) chloride	$NiCl_2 \cdot 6H_2O$	24 g	37
Nitric acid	conc. (15 *M*)	350 ml	frequent use
Oil, vegetable or silicone		2 liters	26
Orange IV		0.1 g	18, 26
Oxalic acid	$H_2C_2O_4 \cdot 2H_2O$	1 g	18
Oxygen	bottled	see p. 63	6
Paraffin (household)	m.p. 52–54°C	150 g	5
Perchloric acid	60%	30 ml	32
Phenolphthalein		2 g	frequent use, 18
Phosphorus	white	2 g	32
Phosphorus pentoxide		1g	32
Phthalic anhydride		90 g	29a
Potassium bromide		3 g	12, 22
Potassium chloride		5 g	11
Potassium chromate		65 g	11, 12, 19, 33, 34, 35
Potassium dichromate		500 g	19, 22, 41
Potassium ferricyanide	$K_3Fe(CN)_6$	2 g	38
Potassium ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$	20 g	33
Potassium hydrogen oxalate (or sodium)		20 g	23
Potassium hydrogen phthalate (or sodium)		23 g	18, 23
Potassium hydrogen sulfate (or sodium)		20 g	23
Potassium hydrogen tartrate (or sodium)		21 g	18, 23
Potassium hydroxide		450 g	11, 17, 19, 31, 38, 40
Potassium iodate		50 g	14, 31
Potassium iodide		150 g	22, 30, 31
Potassium nitrate		1 g	38
Potassium permanganate		2 g	12, 22, 28
Potassium thiocyanate		1 g	D4, 15, 37
Resin, ion exchange (reusable)	Dowex AG1-X8	120 g	37
Silicon		2 g	32
Silicon dioxide	silicic acid, hydrous	9 g	32
Silver (sheet)	B and S 20–30 gauge	165 cm² (pairs)	21
Silver acetate		30 g	16
Silver chloride		75 g	D3, 2, 25
Silver nitrate		310 g	frequent use
Sodium		3 g	28, 32
Sodium acetate	$NaCH_3COO \cdot 3H_2O$	100 g	12, 16, 18, 25
Sodium bromide		3 g	20
Sodium carbonate	$Na_2CO_3 \cdot H_2O$	70 g	8b, 18, 26, 29, 36, 38
Sodium chloride		100 g	D3, 8, 11, 12, 20, 22, 33, 36, 38
Sodium chromate		5 g	11
Sodium dichromate		1 g	38

SUPPLIES (continued)

Chemicals (continued)

Compound	*Purchased As*	*Quantity*	*Used in Experiment*
Sodium hydrogen carbonate	anhydrous	1 g	18
Sodium hydroxide	pellets	500 g	frequent use
Sodium hypochlorite	commercial bleach, 5%	950 ml	14a, 31
Sodium iodide		65 g	10, 20, 36
Sodium metabisulfite (sodium hydrogen sulfite)	$Na_2S_2O_5$	960 g	14, 25, 31, 41
Sodium monohydrogen phosphate (sodium phosphate, dibasic)	Na_2HPO_4	2 g	D4
Sodium nitrate		5 g	11
Sodium oxalate		10 g	12, 38
Sodium peroxide		6 g	32
Sodium phosphate, tribasic	$Na_3PO_4 \cdot 12H_2O$	5 g	18, 38

Compound	*Purchased As*	*Quantity*	*Used in Experiment*
Sodium sulfate	anhydrous	40 g	11, 22, 25, 33, 36
Sodium sulfide	$Na_2S \cdot 9H_2O$	30 g	21, 22
Sodium sulfite	anhydrous	9 g	12, 22
Sodium thiocyanate		1 g	38
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	170 g	25
Starch	soluble	5 g	14, 31
Strontium nitrate		17 g	11, 34
Sugar	sucrose	10 g	D3
Sulfur	roll	12 g	2, 32
Sulfuric acid	conc. reagent (18 *M*)	1250 ml	frequent use
Tin	sheet or mossy	15 g	2
Toluene		30 ml	28
Zinc	sheet, 2 × 8 cm	750 cm²	20, 21, 38
Zinc nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	150 g	20, 21, 33
Zinc sulfate	$ZnSO_4 \cdot 7H_2O$	6 g	22

Miscellaneous

Item	*Quantity*	*Used in Experiment*
Aluminum foil	1500 cm²	4a, 29a
Boiling chips	200	29, 40
Can, tin, frozen fruit juice	30	29a
soup	30	5
large fruit juice	30	5
lid, 4 inch	30	1, 2
Candle, 6 × ¾ inch diam., household	30	1, 2, 4a, 5
Emery cloth, fine, 2 × 3 inch	2 sheets	16, 20
Filter paper, 11 cm diam.	300 sheets	8, 8a, 10, 26, 31, 39, 41
Glass wool	60 small pieces	37

Item	*Quantity*	*Used in Experiment*
Indicating paper		
$CoCl_2$	2 pieces	4
litmus	300 pieces	frequent use
Hydrion	15 rolls	26, 30, 32, 38
Labels, box	30	11, 18, 28
Matches, box	30	frequent use
Pipe cleaners, 1–2 inch pieces	1800	27
Plastic bag, 1 qt., frozen food	30	6
Rubber band, small	120	6, 15, 29a
Steel wool, #00	¼ pound	2, 16, 20
Toothpicks, round, tapered	1 box	27
Wood splint	30	12

EQUIPMENT (Not Expended during School Year)

Glassware

Item	*Quantity*	*Used in Experiment*
Beaker, 100 ml	30	frequent use
250 ml	30	frequent use
400 ml	30	3, 14, 21, 41
Bottles, 4 oz., screw cap	48	for reagents
large	12	for reagents
Buret, 50 ml	30 (60 optimum)	9, 23, 26
Condenser, small	30	29
Crucible, cover, and tongs	30	8b
Dropper bottles (~50 ml)	150–300	18, 22, 28, 31, 33, 34, 35, 36
Evaporating dish, 00A, 75 mm	30	41
Flask, 125 ml	30	26, 41
250 ml	30	4, 8a, 13, 14a, 17, 23, 40, 41
Funnel, 75 mm diam., short stem	30	8, 8a, 10, 26, 31, 39, 41
thistle, 6 × 300-mm stem	30	41
separatory, 25 to 50 ml	30	D2, 29
Gas-measuring tube, 50 ml (can use buret)	30	9
Glass plate, 10 × 10 cm	30	11, 37
Glass tubing, capillary, melting point	60	26
Glass stirring rod, 6 mm, 15–20 cm long	30	frequent use

Item	*Quantity*	*Used in Experiment*
Glass tubing, 6 mm	30 4-foot lengths	5, 14a, 29, 37, 41
Glass tubing, 10 mm	25 4-foot lengths	4a, 29, 37
Graduate, 10 ml	30	8, 9, 10, 14, 15, 18, 32
25 ml	30	10, 14a, 15, 26, 41
100 ml	15	6, 13, 14a, 16, 17
Jar, baby food	30	29a
2 ounce	20	D3
half-gallon	15	6
Medicine dropper	30	4a, 6, 10, 18, 30, 40, 41
Mortar and pestle	15	29a, 39
Petri dishes, covers unnecessary	60	38
Test tubes,		
13 × 100 mm, soft glass	240	frequent use
13 × 100 mm, hard glass	120	frequent use
18 × 150 mm, hard glass	120	frequent use
soft glass	90	32
25 × 200 mm (or 50 ml flask)	30	29
U-tube, 150 mm	8	21, 30 (groups of 4)
Vial, shell form, 15 × 45 mm	30	7
Vial, ½ × 4½ inch (e.g., sample storage set)	150	15
Watch glass, 75 mm diam.	30	7, 26, 29a, 39, 41

Hardware

Item	*Quantity*	*Used in Experiment*
Alligator clamps	32	21, 25, 30
Ammeter, D.C.	8 (groups of 4)	25
Aspirator	8	26, 39
Box, shoe or cigar	30 (students bring)	27
Buret brushes	5	9, 23, 26

Item	*Quantity*	*Used in Experiment*
Burner	30	frequent use
Carbon electrodes	16	30
Clamp, utility	30	frequent use
Connecting wires, 18 inch	40	21, 25, 30
D.C. source, 12 volts	8 (group of 4)	25, 30
Electrode holder, homemade	16	25

EQUIPMENT (continued)

Hardware (continued)

Item	*Quantity*	*Used in Experiment*
Electrochemical cells		21 (groups of 4)
porous cup, 75 ml *or*	16	
U-tube salt bridge from Expt. 30	8	
D.C. voltmeter, 1000 ohm/volt, 0–5 volt	8	
Funnel rack	15	8, 8a, 10
Metric rulers, 15 cm	15	1, 9
Pinch or screw clamp	30	frequent use
Platinum wire, B and S, 20–22 gauge	150 cm	34
Resistor, variable, 18–25 ohms (from physics stockroom)	8	25
Ring stand, 18 inch	30	frequent use
Ring, support, 4 inch	30	frequent use
Rubber tubing, $\frac{3}{16}$ or $\frac{1}{4}$ inch	50 feet	6, 14a, 44
Safety glasses	30	12, 29
Spheres, styrofoam, $\frac{3}{4}$ inch	200	27 (pairs)
1 inch	200	27 (pairs)
2 inch	600	27 (pairs)
Squeeze bottles, 125 ml (dispensing bottle)	30	frequent use
250 ml (wash bottles)	30	frequent use
Stopper, cork, #3	150	10, 12, 15, 20, 22, 28
Stopper, cork, #10	30	29
Stopper, 1 hole, size #0 or #00	30	9, 37
Stopper, rubber, #6, 1 hole	30	6, 14a
Stopper, #6, 2 hole	30	14a, 26, 41
Test tube brush	30	frequent use
Test tube holder	30	common use
Test tube rack	30	10, 11, 28, 37
Thermometer, −10°C to 110°C	30	frequent use
Triangle, $1\frac{1}{2}$ inch	30	8b
Water reservoir, pneumatic trough	15	6
Water reservoir, at least 8 inches deep; can be beaker, battery jar, etc.	15	9
Wire gauze, 5 × 5 inch, with asbestos center	30	frequent use

ITEMS USED BY CLASS AS A WHOLE

Item	*Quantity*	*Used in Experiment*
Balance, centigram, ±0.01 g	15	frequent use
platform, ±0.1 g	5	5
Barometer	1	6, 9
Centrifuge	1	31, 35
Large clock, with sweep second hand	1	3, 14, 14a, 25
Conductivity apparatus (homemade)	1	demonstrations
Drying oven	1	several uses
Electrolysis apparatus	1	demonstrations
Hot plate	several	29, 29a. Helpful in 14, 35, 38, and 40, but not required.

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9 Garfield Place
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Cleveland, Ohio 44115
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(214) RI 2-4106

Denver, Colorado 80204
922 Bannock Street
(303) 244-4621

Detroit, Michigan 48203
14533 Second Avenue
(313) 883-7333

Harrisburg, Pennsylvania
928 No. Third St.
Cedar 8-8123

Honolulu, Hawaii 96813
742 Ala Moana Blvd.
99-4102

Houston 27, Texas
4084 Westheimer Rd.
Mohawk 6-2438

Indianapolis 4, Indiana
102 E. Vermont St.
Melrose 5-5331

Kansas City, Missouri 64111
3718 Broadway
(816) LO 1-1208

Los Angeles, Calif. 90057
2400 West 7th Street
(213) DU 7-7221

Memphis 4, Tennessee
214 So. Cleveland St.
Broadway 5-3187

Milwaukee 2, Wisconsin
1696 No. Astor St.
Broadway 1-0861

Minneapolis, Minnesota 55403
1114 Nicollet Avenue
(612) FE 6-2645

New Orleans 12, Louisiana
715 Girod St.
Jackson 5-9061

New York, N.Y. 10036
1212 Avenue of the Americas
(212) 765-3100

Omaha 2, Nebraska
1410 Howard St.
34-1-8476

Philadelphia, Pa. 19107
1234 Spruce Street
(215) KI 5-2500

Pittsburgh 19, Pennsylvania
210 Grant St.
Grant 1-9118

St. Louis 30, Missouri
621 No. Skinker Blvd.
Parkview 6-3333

San Francisco, Calif. 94105
16 Spear Street
(415) YU 2-1712

Seattle, Washington 98103
2100 North 45th Street
(206) ME 3-3878

Washington, D.C. 20006
927 Nineteenth Street, N.W.
(202) ST 3-6611

In Canada—Don Mills (Metro Toronto)—1875 Leslie Street, Ontario, Canada—(416) 444-7347

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INTERNATIONAL ATOMIC WEIGHTS

NAME	SYMBOL	ATOMIC NUMBER	ATOMIC WEIGHT
Actinium	Ac	89	(227)
Aluminum	Al	13	27.0
Americium	Am	95	(243)
Antimony	Sb	51	121.8
Argon	Ar	18	39.9
Arsenic	As	33	74.9
Astatine	At	85	(210)
Barium	Ba	56	137.3
Berkelium	Bk	97	245
Beryllium	Be	4	9.01
Bismuth	Bi	83	209.0
Boron	B	5	10.8
Bromine	Br	35	79.9
Cadmium	Cd	48	112.4
Calcium	Ca	20	40.1
Californium	Cf	98	(251)
Carbon	C	6	12.01
Cerium	Ce	58	140.1
Cesium	Cs	55	132.9
Chlorine	Cl	17	35.5
Chromium	Cr	24	52.0
Cobalt	Co	27	58.9
Copper	Cu	29	63.5
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.5
Einsteinium	Es	99	(254)
Erbium	Er	68	167.3
Europium	Eu	63	152.0
Fermium	Fm	100	(253)
Fluorine	F	9	19.0
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.3
Gallium	Ga	31	69.7
Germanium	Ge	32	72.6
Gold	Au	79	197.0
Hafnium	Hf	72	178.5
Helium	He	2	4.00
Holmium	Ho	67	164.9
Hydrogen	H	1	1.008
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	192.2
Iron	Fe	26	55.8
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Lutetium	Lu	71	175.0
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mendelevium	Md	101	(256)
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.2
Neon	Ne	10	20.2
Neptunium	Np	93	(237)
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.01
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	31.0
Platinum	Pt	78	195.1
Plutonium	Pu	94	(242)
Polonium	Po	84	210
Potassium	K	19	39.1
Praseodymium	Pr	59	140.9
Promethium	Pm	61	(147)
Protactinium	Pa	91	(231)
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.5
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.4
Scandium	Sc	21	45.0
Selenium	Se	34	79.0
Silicon	Si	14	28.1
Silver	Ag	47	107.9
Sodium	Na	11	23.0
Strontium	Sr	38	87.6
Sulfur	S	16	32.1
Tantalum	Ta	73	180.9
Technetium	Tc	43	(99)
Tellurium	Te	52	127.6
Terbium	Tb	65	158.9
Thallium	Tl	81	204.4
Thorium	Th	90	232.0
Thulium	Tm	69	168.9
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.9
Uranium	U	92	238.0
Vanadium	V	23	50.9
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2

Parenthetical names refer to radioactive elements; the mass number (not the atomic weight) of the isotope with largest half-life is usually given.

* *Latest values recommended by the International Union of Pure and Applied Chemistry, 1961.*

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