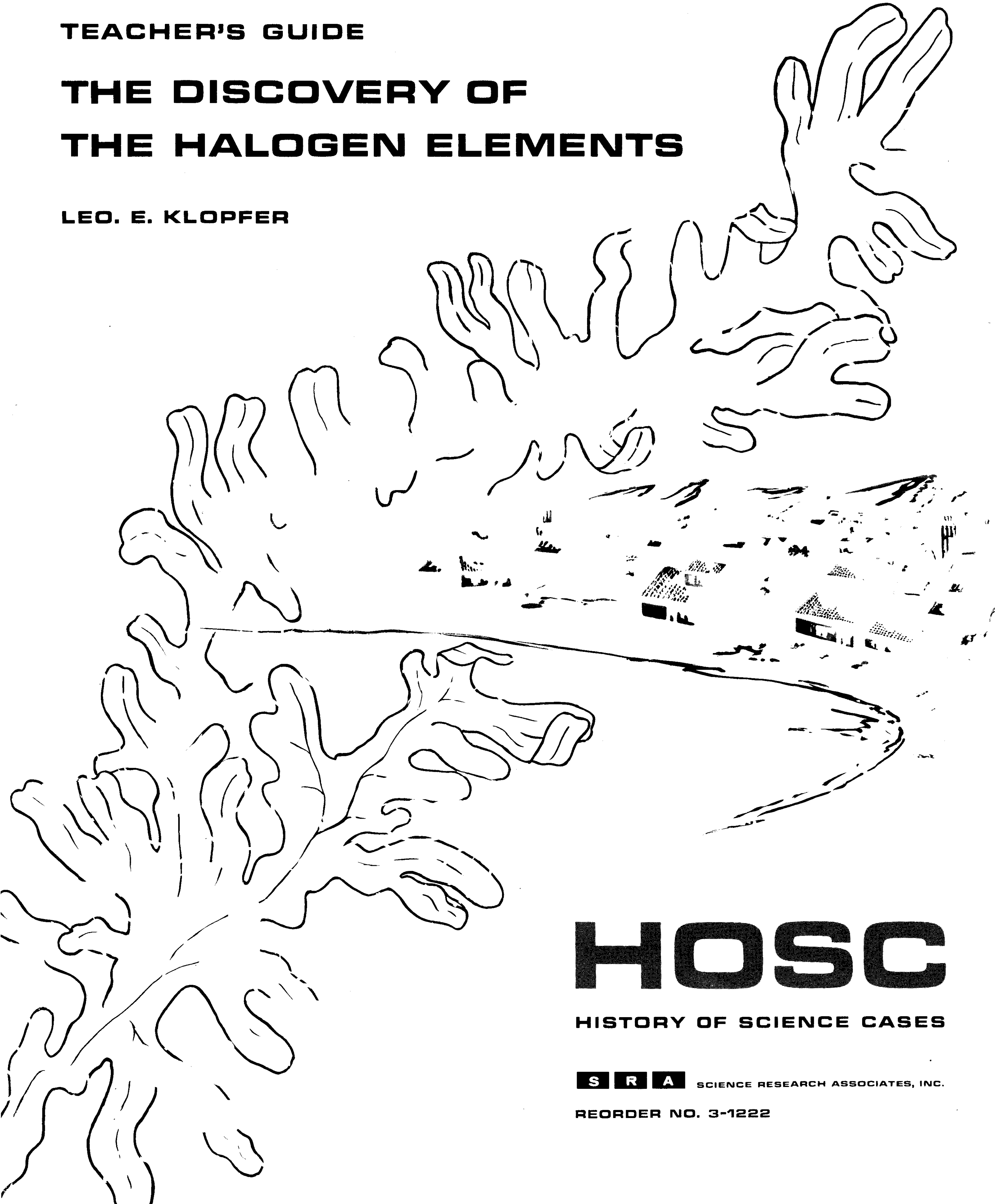
TEACHER'S GUIDE

THE DISCOVERY OF THE HALOGEN ELEMENTS

LEO. E. KLOPFER



HOSC

HISTORY OF SCIENCE CASES

S R A SCIENCE RESEARCH ASSOCIATES, INC.

REORDER NO. 3-1222

MATERIALS NEEDED FOR TEACHING THE DISCOVERY OF THE HALOGEN ELEMENTS

PRINTED MATERIALS FOR STUDENTS

Case booklet – 1 copy per student (SRA Order Number 3-1221)
Student reference books – as available (see Reading Suggestions on the inside back cover of the case booklet)
Chemistry textbooks – any standard text containing one or more chapters on the halogen elements.

SUGGESTED TEACHER REFERENCE BOOKS

(The books marked with an asterisk are frequently cited by authors' last names in the commentary of this guide.)

BEVERIDGE, W.I.B. *The Art of Scientific Investigation.* New York: Norton, 1957 (or paperbound, Vintage V129. New York: Random House, 1960).
*CALDER, RITCHIE. *Science in Our Lives.* Signet P2124. New York: New American Library, 1962.
CONANT, JAMES B. *On Understanding Science.* New Haven, Conn.: Yale Univ. Press, 1947 (or paperbound, Mentor MD68. New York: New American Library, 1951).
——. *Science and Common Sense.* New Haven, Conn.: Yale Univ. Press, 1951 (or paperbound, Yale Paperbounds Y32. Yale Univ. Press, 1960).
*DAVIS, HELEN M. *The Chemical Elements.* 2d ed. Revisions by GLENN T. SEABORG. BSF320. New York: Ballantine Books, 1959.
FARBER, EDUARD. *The Evolution of Chemistry.* New York: Ronald Press, 1952.
*GOLDSTEIN, PHILIP. *How to Do an Experiment.* New York: Harcourt, Brace, 1957.
HALL, A. RUPERT, and HALL, MARIE BOAS. *A Brief History of Science.* Signet T2524. New York: New American Library, 1964.
LACHMAN, SHELDON. J. *The Foundations of Science.* 2d ed. New York: Vantage Press, 1960.
NASH, LEONARD K. *The Nature of the Natural Sciences.* Boston: Little, Brown, 1963.
PARTINGTON, J.R. *A History of Chemistry,* Vol. IV. London: Macmillan; and New York: St. Martin's Press, 1964. Extensive, scholarly work, but quite expensive.
*——. *A Short History of Chemistry.* 3d ed. New York: Macmillan, 1959 (or paperbound, Torchbook TB522. New York: Harper, 1960).
TATON, R. *Reason and Chance in Scientific Discovery.* Translated by A.J. POMERANS. New York: Philosophical Library, 1957 (or paperbound, 775-S. New York: Science Editions, 1962).
WALKER, MARSHALL. *The Nature of Scientific Thought.* Englewood Cliffs, N.J.: Prentice-Hall, 1963.
*WEEKS, MARY E. *Discovery of the Elements.* 6th ed. Easton, Pa.: Chemical Education Publishing Co., 1956.
WIGHTMAN, WILLIAM P.D. *The Growth of Scientific Ideas.* New Haven, Conn.: Yale Univ. Press, 1950.

LABORATORY EQUIPMENT AND SUPPLIES

beakers, test tubes, gas-collection bottles, pipettes, droppers, glass tubing and rods, 150-ml flasks, assorted stoppers and corks, ring stands, clamps, rings, filter paper, litmus paper, Bunsen burners, dilute hydrochloric acid, dilute sulfuric acid, chlorine water, carbon tetrachloride, manganese dioxide, starch solution, glass retort, chlorine gas, glass wool, iron filings	various experiments and activities
iodine crystals, potassium iodide solution, ethyl alcohol	Activity 2
diethyl ether, distilling flasks, thermometers, mother liquors from Kreuznach salt springs (see page 18 of this guide)	Experiment 1 Experiment 2
sodium iodide, potassium iodide, washings from *Fucus* (see page 20 of this guide)	Experiment 3
potassium bromide, ammonium hydroxide	Experiment 4
hydrogen gas, bromine water, ammonia, phosphorus, lighted taper or red-hot wire	Experiment 5
sodium bromine, sodium iodide, large-diameter hard-glass tube	Experiment 6
seaweed, large crucible or frying pan	Activity 1
powdered antimony, copper leaves, mercury (II) sulfide, iron (II) sulfate, ammonium chloride, sodium carbonate, candles, butter, margarine, turpentine	Activity 2
1-liter round-bottom flasks with two-hole rubber stoppers, hydrogen bromide gas, hydrogen chloride gas	Activity 3
samples of sea, river, or lake water	Activity 4

(See also the notes on the experiments and additional activities in the commentary of this guide for further suggestions of materials you may wish to use.)

Printed in U.S.A. Reorder No. 3-1222

TEACHER'S GUIDE

THE DISCOVERY OF THE HALOGEN ELEMENTS

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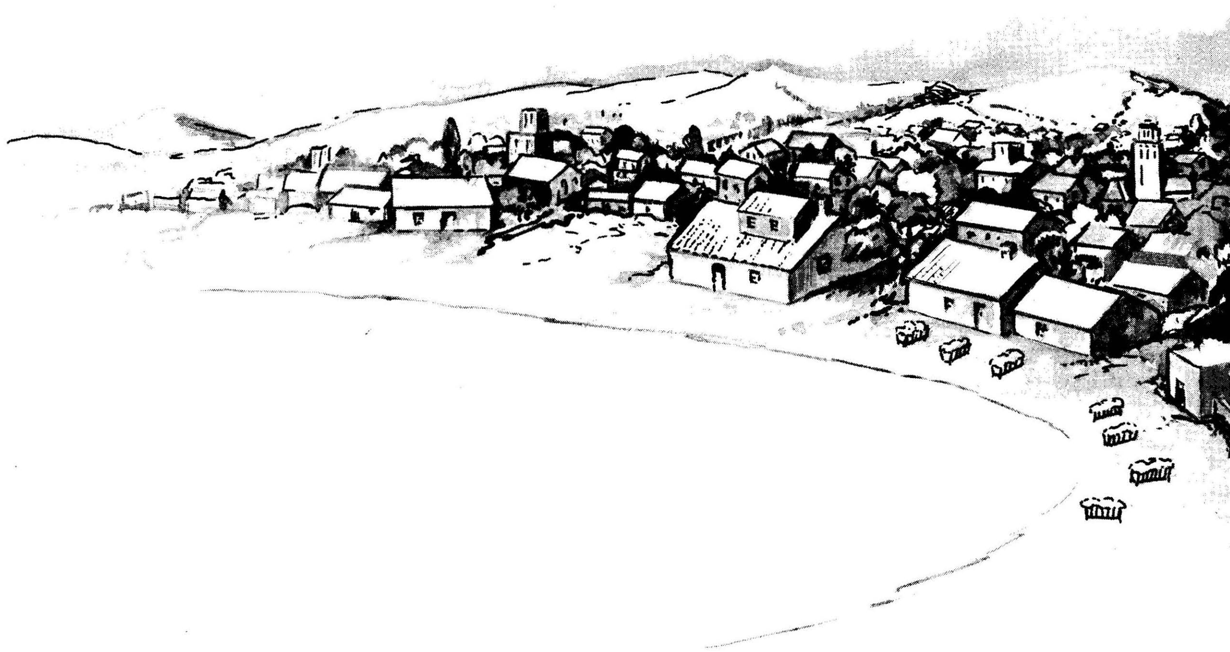


HOSC

HISTORY OF SCIENCE CASES

SRA SCIENCE RESEARCH ASSOCIATES, INC.

ACKNOWLEDGMENTS

The HISTORY OF SCIENCE CASES were developed, beginning in 1956, at the Harvard Graduate School of Education. The two persons who, more than any others, inspired the development of these new instructional materials were Fletcher G. Watson, professor of education, and James B. Conant, the former president of Harvard who pioneered the use of case histories in collegiate science teaching and edited the series of *Harvard Case Histories in Experimental Science.* Invaluable encouragement and assistance were also generously given by I. Bernard Cohen, professor of the history of science, Harvard; William W. Cooley, assistant professor of education, Harvard; Leonard K. Nash, professor of chemistry, Harvard; and Derek J. de Solla Price, professor of the history of science and medicine, Yale University.

The experimental editions of the HISTORY OF SCIENCE CASES were published in 1960 by the Department of School Services and Publications of Wesleyan University, Middletown, Connecticut. More than one hundred high school science classes in twenty-six states participated in the experimental evaluation of the HISTORY OF SCIENCE CASES during the school year 1960–61. A report of the results of this study can be found in the *Journal of Research in Science Teaching,* Vol. 1 (1963), pages 35–47.

The Teacher's Guides accompanying the HISTORY OF SCIENCE CASES were prepared with the assistance of a group of teachers including Maurice Belanger, Elba O. Carrier, Abraham Flexer, Roberta Flexer, Allan Furber, Nancy Klabunde, Uhlrich Klabunde, Eugene C. Lee, James W. Miller, Muriel B. Niles, Bernard O'Donnell, and John J. Seiler. The notes and comments for the Teacher's Guide to accompany *The Discovery of the Halogen Elements* were compiled principally by Allan Furber.

TABLE OF CONTENTS

SUGGESTED SCHEDULE

The outline in this table may be useful if you wish to teach this HOSC unit in 12 lessons, with class periods between 40 and 50 minutes long and double periods for student laboratory work, plus one period for the Unit Test.

Lesson No.	Classwork	Assignments
		Read introduction to the case, page 3, and introductory section on the nature of elements. Write answers to Questions 1 to 5.
1	Discuss purpose of the case and briefly sketch its historical background. Discuss the meaning of "element" (Questions 1 to 4). Outline the importance of the halogen elements (Question 5).	Read beginning of Section Two (The Discovery of Chlorine and Iodine) through page 6, and read Activity 1, The Discovery of Chlorine. Write answers to Questions 6 to 11.
2	*Demonstration:* Preparation of chlorine accord- to Scheele's procedure (Activity 1). Discuss the establishment of chlorine as an element and the assigned questions. (The study of the chemistry of chlorine may be extended by one or two additional lessons at this point through student laboratory work based on Activity 1 and readings in the regular chemistry textbook.)	Read remainder of Section Two to ". . . by a new discovery," on page 12. Read Experiment 1, Preparation and Properties of Iodine. Write answers to Questions 12 to 19. Activity 2, Iodine from Seaweed, may be assigned as a project for interested students.
3	*Laboratory:* Experiment 1, Preparation and Properties of Iodine, followed by discussion with emphasis on the similarities and differences between chlorine and iodine.	Read beginning of Section Three (Löwig's and Balard's Discovery of Bromine) to ". . . with this assignment," on page 12; and read Experiment 2, Löwig's Experiment. Write answers to Questions 20 and 21. Reports of Activity 5, Scientists and Nations, assigned to individual students or to student groups.
4	Discuss assigned questions of Section Two, especially those concerning the roles of hypotheses and accidents in scientific work (Questions 6 and 15); communication between scientists (Questions 14 and 21); the place of science in society (Questions 12 and 13); and the personal characteristics of scientists (Questions 16 and 19). *Demonstration:* Experiment 2, Löwig's Experiment.	Read middle of Section Three to ". . . had taken its place," on page 14; and read Experiment 3, Balard's Discovery. Write answers to Questions 22 to 25.
5	*Laboratory or Demonstration:* Experiment 3, Balard's Discovery. Discuss Balard's hypotheses in detail, tying in the assigned questions.	Read remainder of Section Three to ". . . decolorized by it," on page 18; and read Experiment 4, Balard's Preparation of Bromine. Write answers to Questions 26 to 32.

6	*Laboratory:* Experiment 4, Balard's Preparation of Bromine, including consideration of the properties of bromine. Discuss assigned questions, especially those relating to Balard's testing of his hypotheses (Questions, 25, 29, and 32) and to the personal risks scientists sometimes take (Questions 30 and 31).	Read section on bromine and iodine in the regular chemistry textbook. Review material to date. Plan an efficient procedure for Activity 4, Bromine from Seawater, and bring in one quart of natural water.
7	Quiz – 15 to 20 minutes. *Laboratory:* Activity 4, begin extraction of bromine from seawater.	Read beginning of Section Four (Spread of Knowledge About Bromine and Its Compounds) to ". . . compounds by chlorine," on page 20. Write answers to Questions 33 to 35. Student volunteers to prepare demonstrations of Experiment 5, Preparation of Hydrogen Bromide, and/or Activity 3, Hydrogen Bromide Fountain.
8	*Laboratory:* Complete Activity 4.	Read remainder of Section Four to ". . . by unambiguous experiments," on page 22. Read Experiment 5 and Activity 3. Write answers to Questions 36 to 38.
9	Discuss assigned questions in Section Four. *Demonstrations* (by students or teacher): Experiment 5, Preparation of Hydrogen Bromide, and/or Activity 3, Hydrogen Bromide Fountain.	Read Section Five (Döbereiner's Triads) to end of the case, on page 24. Write answer to Questions 39 and 40. Read Experiment 6.
10	*Demonstration:* Experiment 6, Replacement of Bromine and Iodine, followed by discussion of observations. Discuss the idea of family relationships among chemical elements. Discuss the nature and functions of scientific theories, focusing on Question 41.	Write answers to Questions 41 to 43, and three review questions.
11	Discuss Döbereiner's paper, its impact on chemical ideas, and the assigned questions relating to it.	Complete preparation of reports on Activity 2, if carried out, and Activity 5.
12	Presentation of reports on Activity 2 (Iodine from Seaweed) and on Activity 5, Scientists and Nations. General review of the case and the ideas developed in it.	Study for unit test.
13	*Unit test:* Allow one period.	

TO THE TEACHER

It is essential that our students, the citizens of tomorrow, attain a clear and realistic understanding of the nature of the scientific enterprise, of the aims and processes of science, and of the people who are scientists. The HISTORY OF SCIENCE CASES (HOSC) have been prepared to provide you, the science teacher, with a means of guiding your students toward these understandings of science and scientists.

Understandings Developed

In the HOSC unit that you are about to teach, understandings are developed through a critical study of some significant investigations of the halogen elements that were conducted by Antoine Jérôme Balard and other scientists. As your students study this unit, they will witness (and participate in) the struggle to identify chemical substances, the difficult task of interpreting chemical changes, and the revision of ideas that results from new observations or new interpretations of previous observations. They will also realize that although the physical world remains essentially unchanged, our understanding of it changes as we describe it in different terms. They will learn, too, that a scientist's description of the world is influenced by the concepts he holds and by his background. Finally, your students will be able to recognize some of the interactions between science, technology, and society, and see the variety of personal characteristics that different scientists possess.

Although students studying *The Discovery of the Halogen Elements* will find that it contains considerable science content, they should realize from the beginning that the case is not primarily a vehicle for learning science subject matter. While they should learn some chemistry from their study of this case (see Sections A and B under "Objectives of the Unit," page 7 of this guide), the main purpose of this and all other HOSC units—to teach *about* science and scientists—should always be in the foreground. (The particular ideas concerning science and scientists that are illustrated in *The Discovery of the Halogen Elements* are listed in Section C of the objectives.)

In the final analysis, the goal of the HOSC units is to develop in the students a sensitivity to the manner in which scientists work and think. If, through the study of one or more cases, students become more alert to certain ideas about science and scientists, they will then have acquired an understanding of science and of scientists that will become a functional part of their lives.

Materials and Teaching Procedures

Although there are various ways of presenting this case to your class, the suggestions offered in this guide have been found particularly effective in practice. Of course, the instructor is free to make whatever adaptations and extensions he believes will improve instruction in his class.

Basic to this case is the narrative that appears on the even-numbered pages of the student booklet. Implicit in this narrative, which tells the story of some early nineteenth century developments in chemistry, are important ideas about science and scientists. In studying the narrative, the students usually will be able to discover these important ideas through careful consideration of the comments and questions in the left-hand margin of these pages.

Some of the marginal comments lend themselves to individual and group assignments of supplementary reports based on suitable reference books. Marginal questions have been repeated in more detailed form on the page to the right of the narrative, and space has been provided there for students to write their answers. To assure consideration of the important points raised in these questions, it is good procedure to have students write out their answers as homework assignments. They should do so either directly in their case booklets or on separate sheets of paper. However, since the questions in the case booklet are not to be regarded as standard workbook questions, they should not be graded as workbook materials would be. Many of the questions do not have definite answers; and even when definite answers exist, they are seldom explicit in the text. Rather, the questions may be considered starting points and encouragement for student observation, for seeking additional ideas and information, and for thinking through problems.

Some teachers may wish to give grades for day-to-day assignments of questions. This, of course, can be done. But a check of a student's daily work might better assist the teacher in evaluating the student's progress and his need for help in thinking, researching, and observing in new areas.

The suggested experiments that appear on many right-hand pages of the case booklet are an essential part of this HOSC unit. As many of these as possible, as well as other pertinent experiments that the teacher may know of, should be carried out at appropriate points in the study of the case. The additional activities suggested on pages 26–31 are extensions of certain ideas covered in the unit.

Together, the suggested experiments and additional activities are designed to provide students with an opportunity to develop a variety of abilities and skills. However, the instructor will need to determine which experiments and activities are best done as special projects by some students only and which ones should be done by all members of the class.

With due recognition of the controversy regarding the superiority of experiments over demonstrations, or vice versa, it does seem that for maximum success in achieving the objectives of this unit it is most important for students to get a feeling for the kinds of problems the scientists in the case were wrestling with. This can be accomplished most effectively by having students perform experiments similar to the ones actually done by participants in the case. Ideally, every student should have a chance to carry out and observe for himself at least a few of the experiments.

The Teacher and the Teacher's Guide

Perhaps the most important factor in the study of this HOSC unit is not included in the student booklet: namely, class discussion. The opportunity to supply this factor, which is essential to success, has been reserved for the teacher. The objectives of the HOSC units can be effectively achieved only through the kinds of exposition and synthesis that come about in well-led, intensive, daily classroom discussions. In these discussions an important function of the instructor is to set the stage for the period of history in which the case takes place and to supply some of the background facts and ideas that the students may lack. This is because it is important that some of the students' thinking be done within the intellectual framework that was available to nineteenth century scientists.

In developing effective class discussions, the instructor will find much help in the "Commentary and Teaching Suggestions" section of this guide. Presented therein are general commentary related to the unit, answers and specific commentary related to questions in the student booklet, notes on student activities and experiments, and references to sources of further background information.

Although this guide can supply materials and ideas not otherwise readily accessible and offer suggestions for using them, in the long run the teacher must make the major decisions as to how these materials can be most effectively used in his classroom to attain the goals of the HOSC units.

OBJECTIVES OF THE UNIT

Listed below are the objectives of *The Discovery of the Halogen Elements*. Although some overlapping occurs, the objectives may be divided broadly into three categories: factual knowledge (the "A" objectives), subject-matter concepts (the "B" objectives), and concepts of the nature of science and the work of scientists (the "C" objectives).

A. After studying this unit, students should have acquired information about the following:

1. Discovery of chlorine by Scheele.

2. Establishment of chlorine as an element by Davy.

3. Discovery of iodine by Courtois.

4. Establishment of iodine as an element by Davy and Gay-Lussac.

5. Laboratory preparation and properties of iodine and HI.

6. Discovery of bromine by Löwig.

7. Discovery of bromine by Balard.

8. Physical and chemical properties of bromine, based on the experiments of Balard.

9. Laboratory preparation and properties of chlorine and some of its compounds.

10. Preparation of hydrogen bromide by several alternative procedures. Contrast of preparation of HBr with preparation of HCl and HI, and reasons for the differences and similarities. Great solubility of HBr, as shown by the fountain experiment.

11. Comparison of properties of bromine with those of chlorine and iodine.

12. Test for free bromine and bromides; comparison with test for free iodine and iodides.

13. Döbereiner's law of triads, based on similarities of properties of elements and on the numerical relation between their atomic weights.

B. After studying this unit, students should understand (see note) the following concepts and principles:

1. Concept of "element" as it has changed through history and as it applies to chemistry.

2. Principle of chemical replacement based on relative activity. (Illustrated by the replacement "train" in which chlorine replaces bromine in its compounds and the released bromine in turn replaces iodine in iodine compounds.)

3. Similarities and differences within a family group. (Illustrated by the gradation of physical and chemical properties of the halogens.)

C. After studying this unit, students should understand (see note) the following ideas concerning science and scientists:

1. There is a continual interaction of ideas and experiments in scientific work. Scientists with imagination are needed to make hypotheses and to plan experiments for testing them.
2. Chance observations may be fruitful of new experiments and new ideas, but they must meet with a "prepared mind" and they must be followed up.
3. Many problems, both conceptual and manipulative, are involved in scientific definition, and in the positive identification of a substance.
4. Discovery in science generally involves a series of experiments and interpretations rather than a single, clearly identifiable event. Frequently, different scientists participate in the evolution of a scientific discovery over a period of time. Two or more scientists working independently sometimes make the same contribution to scientific discovery at about the same time.
5. The major aspects of a discovery in science, each of which may be achieved by the same person or by different persons, include an initial observation of a new phenomenon, a thorough exploration of the new phenomenon, a report of the results to other scientists, and the incorporation of the new phenomenon into a larger framework.
6. Free communication between scientists is the lifeblood of science. Scientists communicate with one another through meetings, journals, books, and personal correspondence.
7. Scientific societies and associations are the professional organizations of scientists. Through their activities, they further the progress of scientific work and provide a professional home for scientists.
8. Science is an international activity.
9. Scientists are human beings with certain well-developed abilities and some special training. They vary widely in personal characteristics.
10. Scientists have varied abilities and make varied contributions to experimental and theoretical advances in science.
11. A hypothesis in science is a statement of a scientist's ideas about a certain phenomenon.
12. A scientific law is a generalized statement of observed empirical relationships.
13. A scientific theory is a broad generalized statement, or group of statements, that expresses a scientist's views on some portion of the natural universe. A theory serves to correlate many phenomena within its scope and tends to stimulate new scientific research.

NOTE: By "understand" we mean that the students should be able to do more than simply parrot a statement of a principle, concept, or idea. They should be able to apply the principle, or seek out an example of the idea, in a new and different situation such as they might face on a question in the unit test for this case.

COMMENTARY AND TEACHING SUGGESTIONS

In this section of the Teacher's Guide you will find the following instructional aids:

1. General commentary and suggestions related to the introduction and presentation to the class of the total unit and major sections of the unit.
2. All questions from the student booklet, answers to the questions, and commentary and teaching suggestions related to specific questions.
3. Notes on experiments and additional activities.
4. References to additional, related reading matter. (In the text these are referred to only by the author's last name. Titles and publishers are included in the inside front cover of this guide.
5. Sample questions for a mid-unit quiz and for a review lesson.

To simplify reading, all numbered questions, questions within experiments and activities, and questions from quizzes have been printed in bold typeface; for example:

What is a chemical element by modern definition?

Paragraphs containing definite, factual answers to numbered questions from the student book are preceded by a check:

✔ Our new knowledge of atoms and molecules has not influenced the natural laws that matter obeys.

When to Use the Unit

There is considerable latitude as to when this case may profitably be studied, since only a limited prior knowledge of chemistry is required of the students. Before starting the case, the students should be well enough along in their chemistry course to have been exposed to some of the elementary definitions, to chemical equations, and to a smattering of descriptive chemistry, including that of oxygen, hydrogen, and water. In order to give students the proper historical perspective, it would be well to defer consideration of the great generalization of the periodic law, the early inklings of which are included in this case, until after the study of *The Discovery of the Halogen Elements*.

The primary concern of this case is not the subject matter of chemistry, but the methods of science and the work of scientists. Introductory chemistry texts are usually highly descriptive of what chemists have discovered; they present the results of scientific investigations, but rarely give any consideration to *how* a theory arose, *who* the investigators were, or *what* obstacles had to be overcome. The discovery of the halogen elements is usually treated very briefly in texts, with only a paragraph or two about the work of Scheele, Gay-Lussac, Davy, Löwig, and Balard. *The Discovery of the Halogen Elements* is intended to fill this gap.

An attractive instructional possibility is to use the case as a focus for the study of the principal halogen elements and their compounds, supplemented, of course, by the pertinent material in the regular chemistry textbook. In this way, not only is the chemistry of the halogens taken up in the logical context of the course, but the important ideas concerning science and scientists, which the case seeks to convey, will also be considered by the students.

The story of *The Discovery of the Halogen Elements* is divided into the following five sections:

Section One	The Meaning of "Element"
Section Two	The Discovery of Chlorine and Iodine
Section Three	The Discovery of Bromine
Section Four	The Spread of Knowledge About Bromine and Its Compounds
Section Five	Döbereiner's Triads

The division of the case into five sections is reflected in the suggested schedule (pages 7–8) and in the commentary that follows. This should prove helpful to you in organizing your presentation of the unit.

For the historical background of chemistry in the period covered by this case, you may wish to consult pages 167–214 of Partington. The chapter on the halogens in Weeks provides additional details about the men and events. The chronology of the elements given on page 192 of Davis is also of interest. You may wish to refer to the extracts from the discovery papers of the halogens on pages 136–141 of Davis. The current state of knowledge of the halogens is succinctly presented in a recent review article by R. T. Sanderson, "Principles of Halogen Chemistry," *Journal of Chemical Education, 41:* 361–366 (July 1964).

SECTION ONE
The Meaning of "Element"
Text: page 4

The case opens by directing the students to consider the term *element*—what this term has meant in the past, what it means to chemists today, and what connotations it carries. Examining this term not only is worthwhile in itself, but also leads to what is probably the principal problem encountered by the scientists in the case. Although by the early years of the nineteenth century, when our story takes place, chemists generally agreed on what they considered a chemical element, it was quite another matter to demonstrate experimentally that a given substance was, indeed, an element.

In connection with the definition of a chemical element, Partington says (page 13): "The conceptions underlying the definition of elements and compounds, although now almost obvious, were reached only after centuries of effort."

Through the series of questions in this section, the students should become aware of some of the difficulties and subtleties of the apparently simple idea of "element." The historical aspects of the growth of the idea of chemical elements are well treated on pages 13–14, 43–44, 51–52, 70–71, and 134–135 of Partington. The leading questions in the text (page 5) and the notes here are intended only as springboards for discussion. You may wish to direct this discussion into any one of several possible channels.

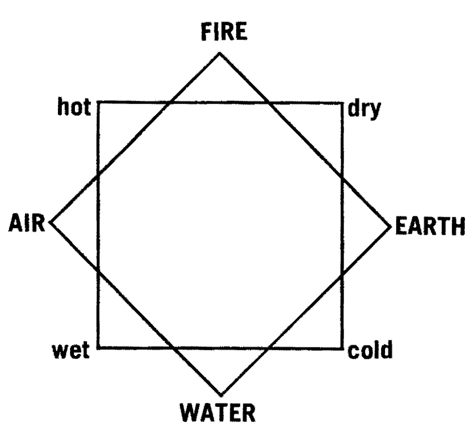
1. What is an element? This question is too broad to be handled at one time, so begin by answering part of it: What did "the elements" mean to the ancient Greek philosophers? How did they use the idea of elements?

✔ The first clear expression of the idea of an element was probably given by Thales of Miletus (640–550 B.C.). He observed water in its many forms as mist, dew, rain, snow, and ice. This led him to conclude that all substances are composed of water. Anaximenes and Leucippus, who followed Thales, looked upon air and earth as the fundamental elements. Heraclitus (535–470 B.C.) thought fire to be the fundamental principle. Empedocles (470–360 B.C.) effected a synthesis of these ideas and introduced the theory of the four "roots" of things—earth, air, fire, and water—together with two forces, attraction and repulsion, which presumably joined and separated the elements.

✔ Democritus of Abdera (460–370 B.C.) was the first to give definite form to the belief that all matter is composed of atoms, or particles separated by empty space and differing from one another in form, position, and arrangement. He believed that "bodies" come into being and vanish only through combinations and separations of these atoms. This belief, although astonishingly similar to our modern concept, was based on speculation and logic, not on experimental evidence.

✔ Aristotle (384–322 B.C.), also from logical considerations, rejected atomism and conceived of matter as being infinitely divisible. He accepted the four "elements" but added a "quintessence," a "higher essence" permeating all nature, which he believed accounted for the varied properties of the many forms of matter perceived by the senses. Because of Aristotle's vast prestige, the belief in this mysterious substance persisted for many hundreds of years and became the object of extensive search and experimentation by the alchemists.

✔ Aristotle defined an element as "that into which other bodies may be analyzed." He also described the qualities (or properties) by which we can recognize whether or not a particular element is present in a material. His scheme is roughly summarized in the following diagram and rules:



(1) All that from which something hot and dry comes contains FIRE.
(2) All that from which something hot and wet comes contains AIR.
(3) All that from which something cold and dry comes contains EARTH.
(4) All that from which something cold and wet comes contains WATER.

As an example of how this scheme works, let us consider the qualities of a piece of wood. Wood is cold and dry, so it must contain the element earth. If we analyze wood further by heating it, we find that it gives off something hot and dry, showing the presence of the element fire, and something hot and wet, showing the presence of the element air. Further analysis reveals that something cold and wet remains after the heating is stopped, indicating the presence of the element water; and there is also a cold and dry residue, again indicating the element earth. Thus, by carefully noting the qualities of wood, we can discover which of the Greek elements it is composed of. (Students may enjoy thinking through similar analyses of bread, milk, sugar, alcohol, soap, salt, spinach, coal, aspirin, and so on.)

2. Is there a wish for simplicity evidenced by the persistence of this idea of elementary substances?

✔ Yes, there does seem to be a human wish for simplicity involved here, a desire on the part of scientists to view the phenomena of nature in the simplest and most concise forms. Yet this desire is clearly being grafted onto nature by man—more precisely, by the men who make science. We really don't know whether nature is simple or not, but we rather hope that it is, because then we have a better chance of understanding it with our limited minds. The recurrence throughout history of the idea of elements seems to illustrate this human desire for simplicity. Certainly four elements—or even three dozen fundamental particles—are easier to deal with, to see patterns in, than the myriad of material substances that nature presents to us.

3. How do scientists now define "element"? How is an element different from an elementary particle?

✔ Our present view of the chemical elements is a far cry from the four elements of the ancient Greeks. Our view is derived from the ideas of Boyle and Lavoisier. In 1661 Robert Boyle rejected Aristotle's four elements, as some of the later alchemists and iatrochemists had also done. Boyle defined an element as a "simple body." He used the term *unmixed,* by which he meant not compounded. However, while Boyle rejected the ancient doctrine, he failed to supplement his definition by providing a list of elements. Lavoisier, in 1789, did better. He not only refined Boyle's definition; he also published a list of elements that fit his definition. Lavoisier defined an element as "the last point which analysis is capable of reaching," that is, a substance that cannot be further decomposed. Lavoisier's list of elements (reproduced in Partington, page 135) is rather interesting. It lists principally substances which we consider elements today, but also includes three radicals as well as "lumière" (light) and "calorique" (heat). To Lavoisier, light and heat were elementary substances.

✔ During most of the nineteenth century the chemical elements were considered "simple bodies," since by definition they could not be further decomposed. This idea was greatly strengthened by the gradual acceptance of the atomic theory, first proposed by Dalton. The concept of atoms of elements was found to be quite adequate to explain chemical reactions. In the 1890s and early 1900s, however, new experiments and observations made it evident that atoms are not simple bodies at all. Indeed, ingenious scientists predicted, and later confirmed experimentally, the existence of subatomic particles. These particles were called electrons and protons. Later, neutrons were predicted and discovered. In our own day more than thirty other particles have been identified within the atom by the use of powerful particle accelerators and other devices, and the roster continues to grow. Thus the atoms of elements can no longer be considered simple bodies, as they were thought to be in the last century.

✔ Nevertheless, our modern definition of a chemical element is not very different from that of Lavoiser. At present we define an element as a substance that cannot be decomposed *by ordinary chemical means.*

4. How could we decide whether a substance is or is not a chemical element?

There are two dimensions to this problem. First we must ascertain whether the substance is elemental or can be further decomposed by ordinary chemical means. Once we have determined its elementality, we must identify the substance as a known element or a new one.

✔ The usual methods of decomposing a substance are heating it or passing an electric current through it. We may also test the substance in chemical reactions, to see whether it will replace an ion in a known chemical compound or be replaced by an ion of known electronegativity.

✔ Once we have established that the substance is not susceptible to further chemical composition, we have recourse to many tests for purposes of identifying it. We can determine its boiling point, freezing point, specific gravity, thermal and electrical conductivity, odor, color, solubility in various solvents, X-ray diffraction pattern, and emission spectrum. (See *Fraunhofer Lines* for a treatment of Robert Bunsen's work in identifying elements by their characteristic spectra.) If these properties of the substance in question prove to be consistently identical with those of a known element, we can be reasonably sure that the two substances are the same.

5. What are some important halogen salts? List about a dozen of them and their uses. Which of them can be obtained from seawater?

The purpose of this question is not to have students compile an exhaustive listing of the halogen salts and their uses, but rather to make clear the ubiquity and importance of the substances containing the halogen elements. Students can easily compile lists of the principal halogen salts and their uses from their regular chemistry textbook.

✔ Among the halogen salts that can be obtained from seawater in usable amounts are sodium chloride, sodium bromide, potassium chloride, potassium bromide, magnesium chloride, and magnesium bromide.

SECTION TWO
The Discovery of Chlorine and Iodine

Text: pages 4–12
Experiment 1
Activities 1 and 2

In this section of the case (and in the section that follows) major emphasis should be placed on laboratory work and on the interpretation of observations that are made. Both Experiment 1 and Activity 1 are designed to make this possible. You may wish to supplement or replace the laboratory experiments and exercises suggested in the case with others that you feel are appropriate. Activity 2, Iodine from Seaweed, is probably best done as a project by interested students (if an adequate supply of seaweed is available in your locality).

Another point worthy of emphasis in Section 2 is the contrast between the personalities and experimental methods of Davy and Gay-Lussac. This may be expanded to a discussion of the personalities of scientists in general. Two pertinent articles on this matter are Anne Roe's "The Psychology of the Scientist," *Science, 134:* 456–459 (18 August 1961), and Lewis M. Terman's "Are Scientists Different?" *Scientific American,* January 1955 (available as *Scientific American Reprint* No. 437 from W. H. Freeman Co., San Francisco). C. P. Snow's early novel *The Search* (New York: New American Library, 1958; paperbound, Signet No. T1864, 75¢) is also pertinent.

While your class is working in this section, it might be well to assign the biographical reports of Activity 5, Scientists and Nations, to individual students or to student teams for each country, so that they will be prepared to report later on in the unit.

6. Scheele was not seeking to isolate chlorine; he was investigating the behavior of an ore. Do unexpected outcomes or "accidental discoveries" such as this often occur in science?

✓ Popularizations of science sometimes mistakenly create the impression that an accidental discovery is a lucky incident that might happen to almost anyone. Although the element of chance often plays an important role in scientific progress, it should not be confused with blind luck. The so-called accidental discoveries usually occur in the course of an investigation planned for some other purpose. If the scientist is prepared to seize upon the new or unexpected phenomenon that he has come upon by chance, he may well be led to a new discovery and even into an entirely new area of research. The statement attributed to Pasteur is surely applicable: "Chance favors the prepared mind." But chance observation is only the beginning. Invariably it must be followed up by carefully planned experiments, to establish the full meaning of the "accidental" discovery.

✓ Examples of chance observations leading to important discoveries include Fleming's accidental observation of the antibiotic action of penicillin; Galvani's accidental observation of contraction in the leg muscles of a freshly dissected frog when an electrostatic machine was discharged; and Becquerel's accidental observation of the fogging of photographic plates by pitchblende, or radium ore. Galvani's observation led to his (incorrect) theory of animal electricity and to later (correct) theories of the electrochemical nerve impulse; Becquerel's observation led to the eventual discovery of spontaneous nuclear disintegration, or radioactivity.

Although some scientific discoveries are made in this way, the vast majority of important scientific discoveries are the result of long and painstaking experimentation and analysis. For further discussion and additional examples, see pages 47–51 of Goldstein, pages 108–122 of Conant, and pages 63 and 91–95 of Calder. More material related to the role of chance in scientific discovery can be found on pages 27–40 and 156–162 of Beveridge; in the article by Walter B. Cannon, "The Role of Chance in Discovery," *Scientific Monthly, 62:* 204–209 (March 1940); and especially in the book by R. Taton, *Reason and Chance in Scientific Discovery* (New York: Philosophical Library, 1957, or paperbound, New York: Science Editions, 1962).

7. What is acid of salt?

The purpose of this question (and the two following questions) is not simply to elicit factual answers such as "hydrochloric acid." Students should consider why this name was used.

✓ Whereas the modern name for the acid refers to the two elements from which it is compounded, Scheele's name for it refers to the compound (common salt) from which the acid is prepared. In other words, it is an acid made out of common salt.

8. Why should this gas smell like aqua regia?

✓ The same substance is stimulating the olfactory nerves. That is, aqua regia, in concentrations greater than one molar, releases a small quantity of chlorine, and chlorine gas smells like chlorine gas. Chemists of the eighteenth century, however, were not aware of the composition of aqua regia or of hydrochloric acid.

The question is intended to direct students' attention to the limited conceptual framework into which these chemists had sought to fit their observations. This limitation, of course, strongly influenced the interpretations they were able to make from their observations.

9. What is muriatic acid? How does it differ from acid of salt?

✓ These acids differ in name only. The importance of this difference should be stressed, however. The fact that Davy and Gay-Lussac used two names for the same substance led to confusion—just as it may have confused students on first reading the case. As the case points out (see Questions 22 and 24), scientists rely on the findings of other scientists in order to avoid unnecessary duplication of research work. Clear communication in science is vital; it is the *raison d'être* of the conferences that are held to standardize terminology and units of measurement.

10. Where have you heard the name of Gay-Lussac before? Was he a respected scientist at this time? In what ways does he seem to be different from Davy?

This is the first of several questions related to the personal characteristics of scientists; others are Questions 16, 19, 22, 33, and 43. Through a discussion of these questions your students should come to realize that scientists differ widely in temperament and personality, and that (fortunately) no valid stereotype of "the scientific personality" can be formed.

✓ Gay-Lussac (1778–1850) was one of the outstanding chemists of the first half of the nineteenth century. Among other accomplishments, he formulated the law of expansion of gases with changes in temperature (1802) and the law of gaseous volumes in chemical changes (1808). (The latter is generally known as Gay-Lussac's law. Your students are probably already familiar with it.) Gay-Lussac's reputation as a scientist is shown by his position of prestige in the French Academy of Sciences and by the esteem in which he was held by Davy, his direct rival in researches on chlorine, iodine, and the alkali metals.

✓ Gay-Lussac has been described as "patient, persevering, accurate to punctiliousness, perhaps a little cold and reserved, and not unaware of his great ability." In his study of iodine and its compounds, Gay-Lussac worked for at least six months before presenting his detailed report. He was therefore able to marshal a great deal of evidence to support his belief that a new element had been discovered. By contrast, the more dashing Davy worked for only ten days or so before announcing his conclusion that iodine must be an "undecompounded body." In turning in this virtuoso performance, however, Davy carried out some quite remarkable experiments with the limited facilities available to him. Davy might be described as the "romantic" scientist who intuitively grasps the essence of a problem and moves quickly to a solution; whereas Gay-Lussac represents the cautious, sedulous experimentalist who achieves his results more by perspiration than by inspiration.

11. Why should this experiment have led Davy to suspect there was no oxygen in muriatic and oxymuriatic gases?

✓ Davy had access to Lavoisier's definition of an element, just as we do. If chlorine were a compound of oxygen and a radical, we would expect strongly heated carbon to reduce the chlorine at least partially. The point to be made here, however, is that Gay-Lussac made the same observations as Davy but Gay-Lussac's interpretations were prejudiced by his belief that all acids contain oxygen.

12. What were the doctors interested in? How does technology differ from science?

✓ The principal aim of science is an understanding of the phenomena of the natural universe. By contrast, technology is concerned with the practical application of scientific discoveries. Technologists are interested in building and doing useful things. In this instance, the doctors sought to cure a disease. Scientists, on the other hand, consider scientific knowledge an end in itself. They sometimes display a casual disregard for the ultimate uses to which this knowledge will be put. In common usage the term *science* covers a great many activities—often, nearly any activity that requires a sophisticated knowledge of *scientific findings*. People whose main concern is the practical application of scientific knowledge are more accurately called *applied scientists* or *technologists*. This group includes, among many others, engineers, practicing physicians, nutritionists, dentists, and opticians.

The distinction between science and technology is discussed further on pages 53–62 of Conant. Also see pages 64–66 of Calder for his interesting description of "The Makers Possible and the Makers to Happen."

13. Isn't it unusual for a scientist to travel in an enemy country during a war? What changes have occurred in science and in society that would prevent such a journey from taking place today?

This question follows through on the previous question on the distinction between science and technology; it should provide you and your students with a springboard for an interesting discussion of the vast changes that have occurred over the past hundred and fifty years in the relationship between science and technology on the one hand, and between science and society on the other. A fascinating book that documents the continual interchange between British and French scientists during the war-torn period from 1689 to 1815, including Davy's visit to France in 1813, is Gavin De Beer's *The Sciences Were Never at War* (London: Thomas Nelson & Sons, 1960).

✓ Davy's wartime visit to France was an unusual occurrence, but not nearly so unusual as a similar visit of a distinguished scientist to an enemy country would be today. Such a visit would be extremely unlikely now, principally because of two major changes in society that have taken place since 1813. First, warfare has changed from a more or less gentlemanly affair between men under arms to a condition of total war that directly affects the whole civilian population of every country involved. Second, the role that scientists play in industrial nations has changed from that of people primarily engaged in innocent "philosophical" inquiries into nature having little bearing on practical matters, to that of people whose researches produce new knowledge that can often be readily applied to the solution of problems having an important bearing on the conduct of war.

When Davy applied to Napoleon for permission to make a scientific expedition to France and to meet with his French colleagues, the request was promptly granted; nor did the British government interfere with his plans. On 19 October 1813, at a time when Napoleon's battered army had been pushed back to its own borders and the battle for France was about to begin, Davy and his party landed at Morlaix. The party included Lady Davy, her maid, and young Michael Faraday, who acted as Davy's assistant and valet. They made their way to Paris in grand style, riding in Davy's own coach, which had been brought over from England. Davy and his party remained in the French capital for two months, during which time Davy conferred with and was honored by his scientific friends, attended numerous social functions and cultural events, and carried out his lightning-like researches on iodine. Davy was elected a corresponding member of the Institute of France on 13 December 1813. After leaving Paris, Davy and his party headed south and after stopping, among other places, in Auvergne and at Montpellier and Nice, left France for Genoa in February 1814.

Such an ambitious itinerary through enemy territory would hardly be undertaken by a scientist today. It is far more likely that a nation at war would keep its scientific talent at home working on projects connected with the war effort. Since World War I, and especially during World War II, scientists have been sought out by their governments in both camps and organized, more or less efficiently, to carry on "war work." By and large, this is a reflection of the increasingly successful applications in technology that have been developed from scientific findings during the past century and a half. Far from being looked upon as innocent "natural philosophers," scientists today are valued because their research findings may lead rapidly to useful and profitable applications. Scientists have become a national asset, and their work has been invaluable in wartime. It would be as unthinkable today to let a scientist wander through an enemy country in time of war as to turn over a division of troops to be used by an opposing army.

14. What is the Royal Society of London? What functions does it perform?

The year 1960 marked the tercentenary of the Royal Society, which dates from its founding meeting on 28 November 1660 at Gresham College in the City of London. Among the twelve founders were Christopher Wren, the architect, Robert Boyle, the chemist, two astronomers, and several men of public affairs. Henry Oldenburg served as secretary, stimulator of communication, and mediator of scientific and personal quarrels. Robert Hooke became curator, with the responsibility for producing experiments for the weekly meetings. Prior to this, there had been a group meeting weekly in London since 1645 for "philosophical inquiries," which moved to Oxford after the outbreak of the civil war. The Royal Society itself was formed in the year of the restoration of Charles II (1660). It received his endorsement at once and a royal charter in 1662.

Election as a fellow of the Royal Society, giving the privilege of using the initials F.R.S. after one's name, has always been the greatest scientific honor in Great Britain. Today, twenty-five new fellows are elected each year. Only four foreign members are elected annually, and of the total of sixty-six foreign members, nearly half are Nobel laureates. The total membership is about six hundred.

During its first century, and especially under the presidency of Sir Isaac Newton, the Royal Society was the source of most of the scientific research in England. In the first half of the nineteenth century, however, it lost some of its vigor, and the Lunar Society of Birmingham and the British Association assumed portions of the Royal Society's former role and prestige. But during the past century the Royal Society has recovered its primacy, although its role is now much different. Fellows enter after having performed substantial research in universities or in industry. Its major role is therefore no longer research as such, but the encouragement of national research into new and vital scientific questions through the facilities of universities and industry. Although it is not a governmental body, the Royal Society is in a position to allocate substantial government funds for research and hence is responsible for drawing up research priorities and standards for fund recipients. The governing council of the Royal Society is advised by more than fifty committees, subcommittees, and panels, and in turn acts as primary adviser to the government on matters of international science.

The Royal Society played a leading role in guiding the British participation in the International Geophysical Year and in follow-up programs. Throughout its three hundred years it has provided stimulus and support for the greatest British scientists: Boyle, Hooke, Newton, Wallis, Dalton, Faraday, Darwin, J. J. Thomson, and Rutherford.

In many of its functions, the modern Royal Society is similar to our own National Academy of Sciences. This is an excellent opportunity to introduce the role of the National Academy in the scientific community. The following statement of the purposes and functions of the National Academy and its principal operating agency, the National Research Council, is taken from a publication of the NAS-NRC committee on oceanography (Washington, 1959).

National Academy of Sciences National Research Council

The National Academy of Sciences National Research Council is a private, nonprofit organization of scientists, dedicated to the furtherance of science and to its use for the general welfare.

The Academy itself was established in 1863 under a Congressional charter signed by President Lincoln. Empowered to provide for all activities appropriate to academies of science, it was also required by its charter to act as an adviser to the Federal Government in scientific matters. This provision accounts for the close ties that have always existed between the Academy and the Government, although the Academy is not a governmental agency.

The National Research Council was established by the Academy in 1916, at the request of President Wilson, to enable scientists generally to associate their efforts with those of the limited membership of the Academy in service to the nation, to society, and to science at home and abroad. Members of the National Research Council receive their appointments from the President of the Academy. They include representatives of the Federal Government, and a number of members-at-large. In addition, several thousand scientists and engineers take part in the activities of the Research Council through membership on its various boards and committees.

Receiving funds from both public and private sources, by contributions, grant, or contract, the Academy and its Research Council thus work to stimulate research and its applications, to survey the broad possibilities of science, to promote effective utilization of the scientific and technical resources of the country, to serve the Government, and to further the general interests of science.

You may wish to use this question to point out the special functions of scientific societies, as a group, in advancing the progress of science. Scientific societies sponsor meetings and congresses, making possible formal and informal contacts between scientists; publish journals and books; stimulate and sometimes finance research; establish standards in terminology and physical measurement; help to publicize science and the work of scientists; and provide a focal point (a "home") for scientists. For further discussion of the stimulating role played by scientific societies, see pages 17–20 of Conant and pages 7–16 of Calder.

15. What is a hypothesis in science? What role does it play in science?

✔ A hypothesis is merely a statement of a scientist's ideas about a certain phenomenon. Usually a scientist tests hypotheses by using them to predict the outcomes of experiments, then performing the experiments and comparing the results with the predictions. ("Experiments" are here understood broadly to include controlled observations in sciences such as astronomy, where manipulative experiments are not always possible.)

✔ A hypothesis may be concerned with a very restricted idea, such as the countless conjectures made every day in a science laboratory. Gay-Lussac's two hypotheses probably fall in this category.) On the other hand, hypotheses may be on the grand scale, as Conant says, and may lead to a large number of predictions that can be tested by experiments. Some ready examples of this latter type of hypothesis include Copernicus' idea of the structure of the solar system, Lavoisier's ideas on the nature of combustion, Bohr's idea of the structure of the atom, Torricelli's idea of the "sea of air," and Schleiden's and Schwann's ideas on the cellular nature of all living things. These are examples of grand hypotheses that were later generally accepted, but this is not the fate of most hypotheses. For example, William Stokes, in *Science, 122:* 815 (1955), recounts twenty-nine different hypotheses proposed at various times to explain the origin of continental glaciers. All these hypotheses were eventually rejected.

The role of the hypothesis in scientific work is further discussed on pages 30–35 of Calder, pages 11–24 of Goldstein, and pages 47–53, 69–71, 265, and 286 of Conant. This subject will be considered further in connection with Balard's work in establishing that bromine is a chemical element (page 16 of this case).

16. Did Davy behave properly when he rushed in to work on a substance that Gay-Lussac was already investigating? Is it alright for a scientist to do such a thing, or was Davy a rather rude guest?

✔ Whether or not Davy behaved properly in this situation is difficult to judge, since the ethical guidelines regarding encroachment on another scientist's work were somewhat ill-defined, as they still are today. However, knowing the kind of colorful, lively, and sometimes impetuous man that Davy was (Anne

Treneer has titled her recent biography of him *The Mercurial Chemist: A Life of Humphry Davy*—London: Methuen, 1963), it does not surprise us to learn that when a sample of an interesting and doubtfully identified substance was presented to him, he hastened to investigate it. In all probability, Davy thought to take along on his journey his portable chemical laboratory (carried in two small boxes, one measuring 20 by 7 by 4 inches, the other 12 by 7½ by 6 inches) for just such an emergency.

✔ From the point of view of personal diplomacy, Davy's action probably did not contribute to his popularity with his hosts. Already at odds with some of the French chemists because of his stand on the chemical nature of oxymuriatic acid, Davy was certainly not very subtle about putting on a show of strength as a skilled investigator with his rapid and effortless experiments with iodine. Several French scientists were miffed by his performance; Gay-Lussac afterwards remonstrated with Ampère for giving Davy a sample of iodine to work on. Perhaps even Davy was a bit uncomfortable about what he had done, for the paper he sent to the Royal Society was almost apologetic about undertaking the investigation. In the sentence immediately following the excerpt from the paper quoted on page 10 of the case, after "may be anticipated," he added (italics are ours):

> "But as the mode of procuring the substance is now known to the chemical world in general, and as the combinations and agencies of it offer an extensive field for inquiry, and will probably occupy the attention of many persons, and *as the investigation of it is not pursued by the discoverer himself, nor particularly by the gentlemen to whom it was first communicated* [Davy refers here only to Courtois and to Désormes and Clément, not to Gay-Lussac], I shall not hesitate to lay before the Royal Society an account of the investigations I have made upon it; and I do this with the less scruple, as my particular manner of viewing the phenomena has led me to some new results, which probably will not be considered by the Society as without interest in their relation to the general theory of chemistry, and in their possible application to some of the useful arts."

✔ As to the general question of the propriety of rushing in to work on a subject on which someone else is already engaged, this is largely a matter of the particular circumstances and personalities involved. As members of a professional group, scientists are committed to sharing their findings promptly with their colleagues, so that the work of science as a whole can proceed as quickly and efficiently as possible. However, the point in an investigation at which a scientist feels ready to publish results, and the degree to which he is willing to discuss uncompleted research with others—as opposed to holding back so that all the credit would accrue to him—are matters for individual decision. The personality of the individual—whether, at one extreme, he is completely self-effacing or, at the other extreme, thoroughly self-aggrandizing, or somewhere in between—would clearly be a significant factor in making such a decision. Other factors usually involved are the practical demands that are generally placed on the scientist, such as the necessity of producing results in order to keep his job, the pressure to publish in professional journals, and the maintenance of the prestige of the institution with which he is associated. Faced with such demands, a given scientist might succumb to the temptation to take up an investigation that has already been started by another scientist and in which he feels he can achieve rapid success.

✔ In science, as in other fields, outright plagiarism is not condoned, and an elaborate system of footnoting and referencing in scientific publications ensures that due credit is always acknowledged. However, many of the problems investigated by scientists are so complex that they require more skills and insight than any one person can possibly possess. Thus, especially today, the taking up of an investigation begun by other scientists is very common, and it is also very necessary. Scientific work is characterized more by cooperation between scientists than by proprietary rights to certain subjects of investigation.

EXPERIMENT 1
Properties of Iodine

To enable your students to make a comparison with the preparation of bromine, you may wish to have them prepare their own iodine crystals for the tests in this experiment. This preparation also affords the classic example in introductory chemistry of a substance that sublimes. The most dramatic and rewarding way to obtain the iodine for these tests is to extract it from seaweed (Activity 2), but the yield may not be very large, either because of low concentration of iodides in the seaweed or because of inadequate student technique. To save time, you may decide to use iodine crystals from a stock bottle.

Solubility of Iodine. These tests are straightforward. Iodine is only slightly soluble in water, moderately soluble in ethyl alcohol, and soluble in potassium iodide and carbon tetrachloride. The solubility of iodine in carbon disulfide could also be demonstrated, but we have avoided using this solvent here because an open flame is used in the third part (iodine and mercury) of the experiment.

Iodine and Iron. Students will recognize the pale yellow solution from the first part of the experiment, where they found that iodine is only slightly soluble in water. As the iron powder is added, iron (II) iodide forms, which is highly soluble in cold water. All of the iodine now goes into solution; the red-brown color indicates a partial decomposition of the iron (II) iodide. With an excess of iron, the solution soon becomes pale green. A portion of this liquid can be removed and tested with sodium hydroxide to show the presence of divalent iron.

Iodine and Mercury. Be sure to caution the students about the danger of ingesting mercury. Use of a fume hood is advisable. Students may be tempted to use too much mercury here, so emphasis should be placed on a *small* globule. If there is no loss of mercury vapor, 4 g of iodine will react completely with .25 ml of mercury. The reaction is quite vigorous and both forms of mercury (II) iodide are produced in the synthesis, but the yellow form predominates under the conditions of this experiment. After standing for a day or two, the yellow form of mercury (II) iodide changes to the red form.

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17. Why is a chemist interested in solubility?

✔ When placed in a solvent, molecules of a compound dissociate into ions, thus increasing the surface area on which chemical reactions can occur. This increase in surface area tends to speed up the rate at which the reactions take place. Thus there is the practical consideration of time in the chemist's interest in solubility. By means of solutions, the chemist can also standardize concentrations as well as test reactions using only small quantities of chemicals.

✔ Beyond these conveniences, the chemist has other interests in solubility. Extraction and separation techniques often depend on the difference in solubility of various compounds. Electroplating requires solutions that will conduct a current. The formation of certain compounds (silver chloride, for example) is accomplished in some cases by replacement in a solution. And identification of substances often depends on their solubility in some solvent. For instance, the relative solubility of bromine and iodine in ether helps to identify these elements.

18. What is meant by "specific gravity"? Why is it important? What is the specific gravity of water?

✔ The specific gravity of a substance is the ratio of the density of that substance to the density of water (usually at 4°C or 20°C). Since water is the standard of comparison, its specific gravity is set at 1.00. Specific gravity is important in the identification of unknown substances and in problems involving separations and buoyancy.

SECTION THREE
The Discovery of Bromine

Text: pages 12–18
Experiments 2, 3, and 4

The recognition of iodine as an element and the similarity of its chemical properties to those of chlorine, whose elementary nature was established at about the same time, suggested to chemists the idea of a group of salt-forming elements. The idea was greatly strengthened by the subsequent discovery of bromine, to which we turn our attention on page 12.

The discovery of bromine is treated in greatest detail because it provides us with the rare opportunity, in Balard's very thorough paper, of observing at close range the actual progress of a scientific investigation, with its continual interaction of ideas and experiments. It also provides us with another chance to look at the nature of scientific discovery.

Although Löwig first came upon and studied bromine, the discoverer of the new element was, in effect, Balard. Was it merely the accident of circumstances that gave the honor of discovery to Balard, or were there vital differences between the two men? If so, what were these differences? Your students might profitably explore alternative hypotheses here. (Weeks gives a good account of the discovery of bromine and tells some interesting personal facts about Löwig and Balard.) If it is available, you may wish to look at the brief centenary note by Edgar F. Smith, "Bromine and Its Discoverers, 1826–1926," *Journal of Chemical Education, 3:* 382–384 (1926).

The discovery of bromine cannot be unambiguously credited to a single scientist, and, as we have seen, the same holds true for chlorine and iodine, though the circumstances were somewhat different. The question of what constitutes "discovery" in science is a fascinating one; a good article on this subject is Thomas S. Kuhn's "The Historical Structure of Scientific Discovery," *Science, 136:* 760–764 (1 June 1962).

The long section on bromine as an element occupies pages 12–18 of this case and includes three experiments. If you are pressed for time, Experiment 2 (Löwig's Experiment) or Experiment 3 (Balard's Discovery) may be done as a demonstration, but students should, if at all possible, work directly with bromine in the laboratory by carrying out at least Experiment 4 themselves.

19. Curiosity about nature is a personal characteristic of many scientists. How does this help them in their work?

✔ Curiosity probably represents the greatest driving force in scientific discovery. The young person who seeks out explanations of natural phenomena may well be taking the first steps toward a career in science. One who is not curious about natural phenomena, in whose mind no questions are raised by the sense impressions of the world that come to him, does not share a characteristic of personality found in most scientists. Before a scientist can find explanations for the phenomena of nature, which is his major work, he must have the curiosity to ask questions. The pursuit of the answers to such questions, in the final analysis, may well be what keeps science going.

✔ In the present instance, it is likely that people had bathed in the spa at Kreuznach for hundreds of years, and that the springs were used as a source of salt long before the time of Löwig. Yet we have no record of an analysis of the salt waters until Löwig made the attempt. Had no one before Löwig had the curiosity to ask, "What's in it?" It is interesting that Löwig, who later became a respected chemist, not only asked this question, but also did something about it.

20. What is meant by the term "mother liquor"?

✔ Students will probably not be familiar with this term, which refers to a concentrated solution containing a mixture of the materials present in the water of salt springs. Since the concentration of salts in the original water is generally much too low to make direct extraction feasible, the water is first evaporated to obtain the "mother liquor." (The need for doing this is shown to students in Activity 4, which they should carry out themselves later on in the case.)

21. How does a scientist find out about the work of his predecessors? List at least five different ways.

This is the first of three questions concerned with the means by which scientists communicate information and ideas. We shall return to this topic in Questions 23 and 35.

✔ Some sources from which a scientist may learn about the work of his predecessors and his contemporary colleagues are (*a*) published books; (*b*) articles in journals; (*c*) courses, lectures, and seminars; (*d*) papers presented at meetings of scientific societies; (*e*) informal talks with people he sees at meetings; and (*f*) personal correspondence or conversations with other scientists. From the context of the case, we may suppose that Löwig used at least sources *a, b,* and *f* in seeking to identify his newly found red liquid.

EXPERIMENT 2
Löwig's Experiment

As was mentioned previously, this experiment may be done as a demonstration if time is short. A facsimile of the "mother liquors from the salt springs at Kreuznach" is easily made, and its contents and concentrations are not critical. Prepare a water solution of various salts, except iodides, and be sure to include a fair amount of potassium bromide or sodium bromide. Add a few drops of hydrochloric acid until the solution has a *p*H between 4 and 6. Place the stock solution in an exotic-looking bottle and label it "Kreuznachwasser."

If chlorine water is not available, one part Clorox to three parts water can be used. Be careful not to add too much chlorine water to the mother liquors, since an excess of chlorine will oxidize the bromine that has been released and the yellow color will disappear. Gradual addition of the chlorine water will prevent this.

When sufficient chlorine water has been added, two liquid layers will form. The upper layer is the low-density diethyl ether; and since it is a much better solvent for bromine than water is, most of the bromine will be retained in the upper layer. Bromine is also quite soluble in such other organic solvents as carbon tetrachloride, benzene, and chloroform. Ether, however, is more volatile than the others (b.p. 34.6°C), and can be driven off more easily by distillation to obtain pure bromine (b.p. 58.8°C). For this reason it is best to keep the distilling temperature at about 40°C.

If you have the equipment, the best method of separating the ether layer is to use a separatory funnel to draw off the water layer. The remaining liquid is then poured into a distilling flask.

The high volatility and combustibility of diethyl ether presents some danger of explosion. *An open flame should not be used in this experiment.* Because of this danger, two alternative procedures are suggested below. A hotplate will provide adequate heat for the distillation in either procedure.

1. Extract the bromine with benzene, remove water with a separatory funnel as above, and distill

off the bromine, maintaining a distilling temperature of 60°C (benzene b.p. 80.1°C). The danger of explosion is replaced by the less serious hazard of bromine fumes, which can be neutralized by aqua ammonia or tincture of ammonia.

2. Extract the bromine with carbon tetrachloride. (CAUTION: CCl_4 vapor is poisonous; a hood should be used.) Since the specific gravity of carbon tetrachloride is about 1.6, the colored layer will now be on the bottom and the colorless water layer on top. Remove the lower layer with the separatory funnel and distill off the bromine, maintaining a distilling temperature of 60°C (carbon tetrachloride b.p. 76°C). Successive distillations may be necessary.

If this experiment is performed as a demonstration, you may wish to stop after extracting the bromine with an organic solvent, since the distillation of pure (or almost pure) bromine is somewhat tedious.

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22. Are scientists also poets? Before you try to answer this question, be sure that you think about not only what a poet does, but also what he is.

There is certainly no clear-cut answer to this question, but students should enjoy thinking about it. The question attempts to point out a dimension of science that is quite removed from the chemicals, test tubes, and other hardware of the laboratory; namely, the very personal, emotional reactions that a scientist may have to the natural phenomena he observes and studies.

As creators of imaginative literature, poets have much in common with other creative artists—painters, composers, sculptors—and, to an extent, with scientists and mathematicians. Aside from whatever "meanings," implied value judgments, or commentary on life the poet or his audience may attach to it, a poem has a structure and form that are aesthetically pleasing. A poem has an intrinsic value independent of its semantic value. The orderly structure of knowledge that the scientist builds is surely a source of aesthetic pleasure to him apart from any sense of personal gratification or accomplishment. One of James Hilton's characters speaks of a mathematician who was unable to read through Newton's binomial theorem without tears forming. This reaction may be extreme, but its appearance in a modified form is by no means unusual. Eric M. Rogers, in *Physics for the Inquiring Mind*, states: "The physicist who does not enjoy watching a dime and a quarter drop together has no heart." Just as the writer is sensitive to and moved by the material with which he creates his books—human life—the scientist is fascinated by the natural phenomena that he observes and generalizes about.

For an excellent expression of a scientist's views on the philosophic and aesthetic nature of his work, see Jean Rostand, *The Substance of Man* (New York: Doubleday, 1959).

23. How did Balard learn about the chemistry of iodine?

This is another question on the means of communication between scientists. (See Question 21 above.) Your students may come up with some good conjectures other than those given here.

✔ There is no record of how Balard learned about the chemistry of iodine, but he apparently was quite familiar with the properties and reactions of the element discovered by his countryman Courtois. It is likely that he read the reports in the *Annales de chimie*. He may have learned about iodine in his studies at the École de Pharmacie; since he was employed there as a *préparateur,* he might also have gained valuable knowledge through association with the chemistry professor. It is unlikely that Balard obtained his information by attending meetings of the Académie des Sciences, since he was not a member and did not live near Paris.

24. What is the importance of careful observation in scientific work?

✔ The need for careful observation cannot be overemphasized. In a sense, the development of modern science reflects the ability of scientists to make observations that are more and more precise. This has been made possible largely through the introduction of instruments that extend man's senses. In chemistry the most obvious example is the improvement in methods of weighing matter—from crude scales, to apothecary's scales, to the analytical balances used in laboratories, to microbalances. Yet all these sophisticated machines are of no avail if the man using them fails to observe carefully and to record accurately. Accurate qualitative observations are no less important. For further discussion, see pages 21 –32 of Goldstein.

EXPERIMENT 3
Balard's Discovery

This experiment is straightforward and may be carried out by the students exactly as described in the case booklet (page 15). If the experiment is presented as a demonstration, the sizes of the equipment and the quantities of materials should of course be scaled up.

"Washings from *Fucus*" can be prepared by dissolving in water a small amount of potassium iodide (or sodium iodide) and about twice as much potassium bromide (or sodium bromide). The solution should be made slightly acidic with hydrochloric acid. (You may want to experiment beforehand with the relative concentrations of KI and KBr that will produce the most convincing effect.) As in Experiment 2, the chlorine water should be added gradually to avoid an excess of chlorine.

Unless they have read ahead, students will probably not know at this point what function the chlorine water serves in these reactions. Hence the purpose here should be to encourage them to give their own interpretation of the observations, instead of aiming to develop a single "correct" answer. A discussion of the alternative hypotheses proposed by Balard to account for the observations can be most fruitful and will help the students to appreciate the problem he faced.

One of the key ideas of the case is presented on pages 14 and 16. It should be studied carefully. We are trying here to get as close as possible to what happens in an actual research situation. The point is made that there is a dynamic interaction between hypotheses and experiments when scientific work is in progress. The neat, step-by-step "scientific method" we hear so much about is a lifeless analysis devised *after* the work is completed and the excitement has long since quieted down. Note that Balard deals with two hypotheses almost simultaneously, that he deduces certain consequences from each one, and that he plans experiments to test these conclusions. The results of these experiments then allow him to decide between the two hypotheses. (Notice that even here our analysis is a postmortem lacking the excitement of the work itself.) The role of hypotheses in scientific work was discussed in Question 15; now we shall see how hypotheses (of the restricted kind) function in an actual situation.

25. What hypotheses does Balard propose here? Write two word equations to represent them.

✔ (1) chlorine + X → X chloride (where X stands for "some substance"). Near the middle of page 12, Balard says that he believed X to be iodine, so that the equation would be

chlorine + iodine → iodine chloride

(2) chlorine + X compound → X + chlorine compound

26. How did Balard know that the coloring matter was volatile?

✔ Balard had noted that the color and odor of the solution disappeared after standing in the air for a day or two (page 14).

27. How does Balard test his first hypothesis?

✔ To test the first hypothesis, Balard took advantage of the high volatility of the unknown substance and obtained it in a pure state by distillation. He then subjected part of it to an electric current and part of it to high temperature. There was no evidence of decomposition in either case. The test for iodine with starch and chlorine water was negative. These results indicated that the unknown was not a compound of iodine and probably not a compound at all.

28. What sort of instrument is a voltaic pile? Why does Balard use this instead of a DC line?

✔ The voltaic pile corresponds to what we would today call an electric battery. One type of pile consisted of many alternate layers of copper and zinc (two dissimilar metals) separated by paper or cardboard moistened with salt. (See diagram on page 114 of Conant.) The first voltaic pile was devised by the Italian physicist Alessandro Volta in 1800. It was a very significant invention, for it made available a source of continuous electric current for the first time, thereby opening vast new areas of investigation in physics, chemistry, and physiology, as well as leading to a myriad of practical devices. In chemistry, two direct results of the invention of the voltaic pile were the isolation of the alkali metals by Davy and the development of the dualistic theory of matter by Berzelius. (The developments that led to Volta's construction of the pile are the subject of another case in the HOSC series, *Frogs and Batteries.*)

✔ Plugging into a DC line would have been impossible in 1825, because there were no DC lines. Transmission systems and wall plugs had yet to be developed, and the convenient batteries that we possess today were still far in the future.

Perhaps it will be appropriate here for you to remark on the advantages that developments in technology and culture in general (such as electric wiring in homes and laboratories) can bring to scientific work. Often these developments have resulted from prior scientific achievements. Excellent background reading on this point can be found on pages 57–61 of Calder.

29. How can Balard test his second hypothesis?

✔ The testing of Balard's second hypothesis is twofold. In the first place, he had to show that the volatile substance was not chemically altered by anything at his disposal—strong reagents, high temperature, electric current. Since substance X was not decomposed in any of these trials, Balard was convinced that he "had to do with an element." In the second place, Balard could add silver nitrate to the colorless solution remaining after substance X was distilled off. A curdy white precipitate insoluble in nitric acid would show that a chloride was present. This test was known to Balard. (Of course, we must assume that all extraneous sources of chloride ions have been eliminated.)

Page 16 and Experiment 4 on page 19 are concerned with the physical and chemical properties of bromine and with its preparation. Comparisons should certainly be made with the corresponding properties of chlorine and iodine. A startling aspect of Balard's work is the astonishing accuracy he achieved in specifying the properties of bromine with the minute amounts of material he had at his disposal. In connection with the properties of bromine, the descriptive account given in a regular textbook can be used with profit here.

EXPERIMENT 4
Balard's Preparation of Bromine

This is the standard laboratory exercise on the preparation and properties of bromine, and little needs to be added to Balard's instructions given on page 19 of the case.

Bromine can be prepared and examined as a class exercise with little risk, providing the students are sufficiently cautious. Any student with a history of respiratory disease or susceptibility (real or imagined) to noxious fumes should be excused from the experiment and excluded from the laboratory. Windows should be kept open to ensure good ventilation, and a fume hood should be used. Students should work in groups of three or four, so that enough hands will be available to manipulate the apparatus and to counteract any possible mishaps. One student should be assigned the task of waving an ammonia-soaked filter paper. As an additional precaution, you should have ready at hand an extra bottle of ammonium hydroxide and a supply of ammonia-soaked paper.

This experiment should be done as a demonstration if there is any doubt in your mind about your students' ability to conduct the experiment safely.

Concentrated sulfuric acid should *not* be used in the preparation. Balard suggests diluting the concentrated acid with half its weight of water. This works out to an acid-to-water ratio *by volume* of about 10:9. G. Fowles—in *Lecture Experiments in Chemistry*, 4th ed. (G. Bell & Sons, London, 1957), page 263—recommends a moderately dilute sulfuric acid consisting of 11 volumes of acid to 8 volumes of water. A dilution of 2 volumes of acid to 1 volume of water has also been used successfully.

You may wish to point out at this time the similarity in Balard's methods of preparing bromine, chlorine, and iodine. See the demonstration described on page 18 of this guide. It would also be instructive and interesting to consider the strikingly different means of collecting these three halogens during preparation because of their differences in physical state and solubility.

30. Who tasted the bromine? Whose skin did Balard use to discover its destructive effects? What do these two instances tell you about the nature of scientific experimentation?

✓ It is very likely that Balard made both tests on himself. These instances show that strong scientific curiosity sometimes brings voluntary risks to health and even to life. The history of science and medicine offers many examples of self-sacrifice.

✓ Gay-Lussac was one of the well-known chemists who sustained bodily injuries in the course of his scientific investigations. An explosion that occurred while he was working with potassium in June 1808 left him almost blind for nearly a year. Gay-Lussac later suffered a severe injury to his hand from a chemical explosion, and this injury, it is believed, resulted in the illness that ended his life. Another famous chemist, Robert Bunsen, lost the sight of his right eye in an explosion that occurred in one of his experiments on cacodyl cyanide, whose poisonous vapors nearly killed him. Afterward Bunsen calmly reported:

> "The smell of this body produces instantaneous tingling of the hands and feet, and even giddiness and insensibility. The cacodyl compounds appear to exert a specific action on the nervous system. It is remarkable that when one is exposed to the smell of these compounds the tongue becomes covered with a black coating, even when no further evil effects are noticeable."

For further explorations of the personal risks often taken by scientists, see the fascinating essay by J. B. S. Haldane, "On Being One's Own Rabbit," in his *Possible Worlds* (reprinted in part in A. Norman Jeffares and M. Bryn Davies, *The Scientific Background: A Prose Anthology*—New York: Pitman, 1958). Also see the article by Samuel Soloveichik, "Toxicity: Killer of Chemists?" *Journal of Chemical Education, 41*: 282–284 (May 1964).

31. How could you tell the difference between bromine vapor and nitrogen dioxide?

✔ The intent of this question is not so much to point out the different chemical properties of bromine and nitrogen dioxide as to indicate the experimental approach to such a problem. If a chemist comes upon a flask containing a red-brown vapor and wishes to know what the vapor is, his experience suggests two alternative hypotheses (of the restricted variety): (1) "This vapor is bromine" and (2) "This vapor is nitrogen dioxide." The known properties of bromine and nitrogen dioxide then suggest certain experimental tests which should allow him to decide between the two hypotheses. Several distinguishing properties are given below. It may also be interesting to consider hypothesis 3: "This vapor is a mixture of bromine and nitrogen dioxide."

✔ Bromine reacts directly with hydrogen to produce a colorless gas that is highly soluble in water; nitrogen dioxide does not readily react with hydrogen. Bromine is only slightly soluble in water and yields an orange-brown solution; nitrogen dioxide is quite soluble in water and yields a colorless solution. Water solutions of bromine decolorize organic dyes; water solutions of nitrogen dioxide do not. Each has a characteristic odor. (This test is dangerous, however, since both gases are poisonous.)

32. What is the importance of the fact that electricity does not decompose bromine? Is a negative result of any value in science?

✔ Electricity was the most powerful means available to Balard in trying to decompose bromine. The negative result in this experiment greatly helped to establish that bromine is an element.

Here is an interesting question you may wish to raise for class discussion: Is failure to conduct electricity sufficient reason for concluding that a given liquid is an element? Liquid hydrogen chloride, for example, is nonconducting.

✔ Concerning the more general question, a negative result can eliminate an incorrect hypothesis and thereby narrow the field of possibilities. In Ehrlich's search for a drug to cure syphilis, 606 experiments were required. We can say that each of the 605 negative results brought Ehrlich closer to number 606. The present research on the chemotherapy of cancer is essentially a problem of eliminating incorrect hypotheses. Where there are only two possible hypotheses, the negative result with one points to the correct hypothesis. Balard's negative results in testing the red liquid for decomposition indicated that the unknown substance was very likely an element rather than a compound. (See pages 134–135 of Goldstein on the value of negative results in scientific experimentation.)

PAUSE FOR A QUIZ

At about this point in the study of the case, you may wish to give your students an informal fifteen- or twenty-minute written quiz. There might be two questions, one dealing with the chemistry subject matter of the case and the other with an idea about science and scientists that has been explored thus far. Following are two appropriate questions.

1. Give the physical properties of iodine and bromine and two chemical properties of each element.
2. Suppose a freshman science student said to you: "The scientific method has five steps, which are (1) define the problem, (2) make a hypothesis, (3) experiment and observe, (4) draw a conclusion, and (5) apply the conclusion. A scientist always follows these steps in order."

Keeping in mind what you have seen in *The Discovery of the Halogen Elements,* what would you say to this naive freshman?

SECTION FOUR

The Spread of Knowledge About Bromine and Its Compounds

Text: pages 18–22
Experiments 5 and 6
Activities 3 and 4

In this section of the case, attention is first directed to the chemistry of an important compound of bromine—hydrogen bromide. Experiment 5 (Preparation of Hydrogen Bromide) and Activity 3 (Hydrogen Bromide Fountain, page 30) are pertinent here. Following this, the case deals with the growing recognition of a family relationship between halogen elements as the chemistry of bromine and its compounds became better known. Related to this section are Experiment 6 (Replacement of Bromine and Iodine) and Activity 4 (Bromine from Seawater, page 30).

There may not be sufficient laboratory time for all students to carry out all the experiments indicated for this section. If so, portions of Experiment 5, Activity 3, and Experiment 6 may be carried out as demonstrations, either by yourself or by interested student volunteers. Experiment 6 (Replacement of Bromine and Iodine) should probably be done as a demonstration in any event. If there is time for only one class laboratory experience in connection with this section, Activity 4 (Bromine from Seawater) should be carried out. This activity is a more demanding and realistic experience than any of the other experiments in this group. Students should bring in their samples of seawater at least one day before beginning work on this activity.

For further information on Justus von Liebig, who appears near the end of this section, see Weeks and pages 228–230, and 237 of Partington.

EXPERIMENT 5
Preparation of Hydrogen Bromide

Hydrogen bromide is the only compound of bromine taken up in detail in the case. A number of procedures are available for its preparation. Details of the four methods suggested by Balard are presented here, with suggestions for a fifth method.

1. *The direct synthesis of hydrogen bromide can be accomplished by either of two alternative procedures:*

(a) Warm a flask to 40–50°C on a sand bath. Transfer the flask to a wood block and, with a pipette, add about .5 ml of liquid bromine. The bromine volatilizes. When the brown vapor reaches the top of the flask, close the flask with a glass jar cover. On top of the flask invert a hydrogen-filled jar comparable in size to the flask. Remove the covers and mix the gases by inverting several times. Cover each jar. Insert a lighted taper or red-hot wire into one jar. As in Balard's experiment, combination takes place with a slight flame. Test with moistened litmus paper. Also breathe into the flask through a tube (do not inhale). Point out the similarity with HCl in both tests. Ignite the second jar and insert into the fumes a rod moistened with strong ammonia. Compare with HCl.

Reference: Experiments 313 and 335, pages 264 and 275, in G. Fowles, *Lecture Experiments in Chemistry,* 4th ed. (London: G. Bell & Sons, 1957).

(b) Another method is illustrated in the following diagram:

2. *Replacement of iodine in hydrogen iodide by bromine*

As in the direct combination method 1(**a**) above, a jar of bromine is inverted mouth down over HI gas in a similar jar. The iodine vapors upon cooling will crystallize on the inside of the containers, leaving HBr vapors.

3. *Action of concentrated sulfuric acid on a bromide salt*

Unlike HCl, HBr is somewhat unstable. This is made evident in this reaction. As a result of the instability of HBr, free bromine and hydrogen are formed by adding concentrated H_2SO_4 to a bromide such as NaBr. The free hydrogen then reduces the sulfate radical to sulfur dioxide. Water is also one of the products.

Similar results are produced in the preparation of HI, which is even less stable than HBr. The reducing action is also greater and the sulfuric acid is reduced, with the evolution of some H_2S. This procedure is the least satisfactory if purity of the product is desired.

If this procedure is used, the HBr can be sent through (**a**) a bottle containing glass wool sprinkled with red phosphorus to absorb the bromine and (**b**) a drying tube charged with calcium chloride to remove water vapor.

Because of the extreme solubility and high density of HBr, the gas is collected by downward displacement of air. To avoid noxious gases, perform this experiment under a fume hood.

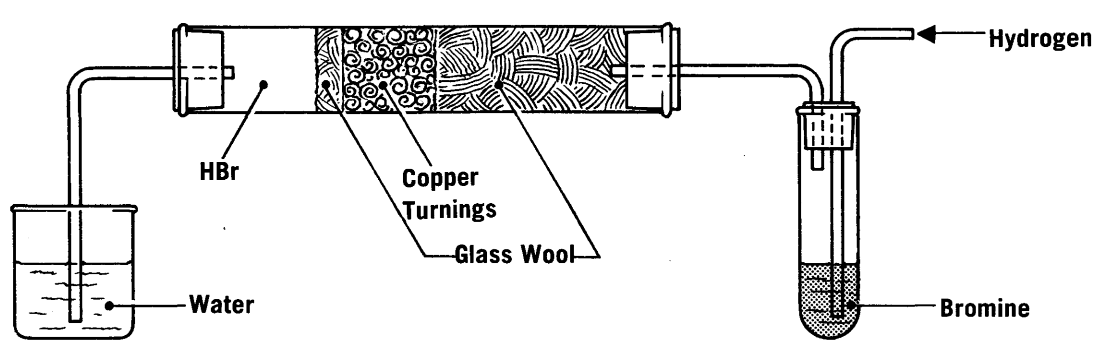
4. *Hydrolysis of phosphorus bromide*

In this experiment, bromine is added drop by drop to moistened red phosphorus. Phosphorus bromide is first formed and is hydrolyzed by water:

$2P + 3Br_2 \rightarrow 2PBr_3$

$PBr_3 + 3HOH \rightarrow 3HBr + H_3PO_3$

Place in the generator flask (clamped on a ring stand) 5 grams of red phosphorus mixed with 20 grams of sand and 5 ml of water. Cover the mixture with 10



Hydrogen is bubbled through the bromine after the air has been driven out of the apparatus. The mixture of the two gases is passed over heated glass wool, where combination takes place. Copper is used to remove any uncombined bromine. The gas is bubbled through water to form a solution of HBr.

grams of dry sand. Using a dropping funnel, run one or two drops of bromine into the flask. The reaction takes place with a flash of light. Run in another drop or two. There will be a second flash. The flashing is possibly due to the formation and oxidation of phosphine, for it stops as soon as the evolved HBr expels the air from the flask. The HBr is then sent through a bottle filled with glass wool sprinkled with red phosphorus to absorb excess bromine. The gas is then led into another bottle and collected by downward displacement. To avoid noxious fumes, allow the excess fumes to enter a bottle containing a small amount of NaOH solution for neutralization. This seems to be the most widely preferred procedure.

Reference: Fowles, *op. cit.,* Experiment 337, p. 276.

5. *Another procedure sometimes used is the interaction of phosphoric acid and a bromide salt:*

$$KBr + H_3PO_4 \rightarrow HBr + KH_2PO_4$$

In a flask fitted with a one-hole cork stopper and delivery tube, place 20 grams of KBr and just cover it with syrupy phosphoric acid. Heat the mixture until hydrogen bromide comes over. The evolution of the gas is very slow and stops when the flame is removed. The gas evolved is fairly dry.

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33. What are some desirable personal characteristics of a scientific experimenter? Do all scientists need these same personal characteristics?

This question continues the discussion that was begun in Question 10, and extended in Questions 16, 19, and 23.

✓ At present we have very little evidence regarding what personality types make good scientists, although psychologists are exploring this problem. Jobs in science are highly diverse and accommodate a wide range of personalities. It may be that scientists who are primarily experimentalists have quite different personal characteristics from scientists who are primarily theoreticians. At any rate it is unrealistic to envision a specific "scientific personality," since scientists, like members of any professional group, differ widely in personal characteristics. (Note that personal characteristics are quite distinct from the special abilities and skills that scientists develop.)

Since a major task in scientific work is the development of new ways of thinking about problems and attacking them, a definite creative effort is demanded of scientists. Scientists have studied their own traits and have made judgments about those which contribute most to creativity. The key traits include adaptive flexibility, idea fluency, sensitivity to problems, tolerance of ambiguity, and resistance to idea reduction.

There are many aspects to the creative process, and some traits that appear to have no direct link with creativity (humor, for example) seem to show up very frequently in the makeup of creative scientists. It should also be mentioned that scientists, like artists, are creative at some stages of their work and not at others.

34. Why do scientists repeat experiments?

✓ Most scientists are cautious workers and try to avoid drawing conclusions from too few observations. Moreover, even the most skillful scientist can make errors in judgment or technique. For these reasons an experiment might be repeated many times before the scientist is satisfied that the results obtained are consistent and reproducible. Furthermore, by such repetition, the influence of factors that might otherwise have been overlooked (atmospheric conditions, interference of measurement devices, time of day, and so on) can be detected.

There is another aspect of the repetition of experiments that you may wish to bring up here. Scientists are only human and occasionally may grow careless in their work or unconsciously distort the reports of their findings. The knowledge that his experiments can, and probably will, be repeated by someone else encourages the scientist to be particularly careful in performing his work and unbiased in reporting it. (This aspect of the question comes up again in Question 37.)

35. Why do scientists publish books and papers about their work? (This is a double-barreled question; in relation to the advancement of science the reasons are quite clear, but scientists also have personal reasons for publishing. Your answer should include both kinds of reasons.)

From their work on the preceding two questions on this theme (Questions 21 and 23), your students will have realized that communication is the lifeblood of science. (See pages 86–88 of Goldstein.) Further comment on this subject is probably unnecessary. Students will probably find, however, that the scientist's personal reasons for publishing are an interesting topic of discussion. The following are some of these reasons.

✓ **1.** The publication of a paper describing his research assures a scientist credit for his discoveries and thus helps to establish his professional reputation.

2. A scientist's ability to obtain grants to finance continued research is frequently dependent on the number and quality of papers he has published. Indeed, at many universities a scientist must publish in order to advance, or even to retain his position.

3. There is a great deal of personal satisfaction in seeing an account of one's own work in print in a good journal. Like anyone else, scientists value the respect of their colleagues.

4. Publications often help establish valuable professional contacts.

5. Publishing a book is sometimes financially profitable.

To introduce the part of this section that stresses the family relationships of the halogen elements, you may wish to carry out an additional demonstration that shows the striking similarity in the preparation of free halogens by the oxidation of their respective halogen acids. This can be done as follows:

Place three 1-liter flasks on hot plates under the fume hood. Each flask should contain 5 grams of manganese dioxide, 5 ml of water, and 10 ml of concentrated sulfuric acid. Warm the three flasks. Add 5 grams of sodium iodide to the first flask, 5 grams of sodium bromide to the second, and 5 grams of sodium chloride to the third. Swirl to mix. The free halogens are liberated in their respective flasks; iodine most readily, bromine less readily, and chlorine least readily. (CAUTION: Keep the apparatus under the hood during the entire experiment.)

EXPERIMENT 6
Replacement of Bromine and Iodine

In this demonstration the students have an opportunity to see the electrochemical series of these nonmetals. If a hood is not available, the exit tube on the iodine end of the cylinder can be run into a beaker of dilute sodium hydroxide. Generate the chlorine slowly by adding concentrated hydrochloric acid through a dropping funnel, drop by drop, into a solution of potassium permanganate (or use a *slow* stream from a cylinder of chlorine).

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36. Was Liebig using good scientific procedure here? Give your reasons why or why not.

✔ Liebig did not experimentally verify the assumption that the colored liquid was iodine chloride. Later, Liebig himself admitted that his hypothesis had been wrong and decried his failure to apply the necessary tests. He placed a bottle of bromine in a special showcase which he called his "museum of blunders." Liebig's error here is one that was generally committed by the ancient Greek scientists. Hypotheses were elevated to the level of theories and natural laws without adequate experimental investigation. Aristotle stated that women have two fewer teeth than men. Bertrand Russell points out that Aristotle could have avoided this error "simply by asking Mrs. Aristotle to keep her mouth open while he counted." The Greeks depended too much on large leaps of thought and not enough on simple observation.

There is no implication in this question that Liebig was a poor scientist simply because he failed to follow through effectively in this instance. It frequently happens that a scientist who is preoccupied with an investigation that is very important to him feels he cannot take time to experiment thoroughly on some other problem that is brought to his attention.

37. How does the fact that reports can be checked by others influence the work of scientists?

✔ The observations and experiments that a scientist makes on the natural world can usually be checked by someone else who has the interest and the proper equipment. Thus the scientist whose reports are inaccurate, or whose conclusions are overextended, is readily exposed. Such a person quickly loses the respect of his fellow scientists and may find himself unwanted in scientific circles. To avoid this, the scientist tries to do his work accurately, to make conclusions cautiously, and to report his results honestly. Then if some other scientist checks his reports, they will not be found wanting.

See also the comments under Question 34.

38. Among scientists, are authorities—persons with established reputations—considered more important than newcomers?

✔ As in other professional groups, scientists are judged by their achievements. Newcomers can gain prestige and importance among scientists only by demonstrating their competence. It is not unnatural for scientists to view the claims of untried newcomers with some reservation. Most people tend to look on the novice with indulgence, feeling that an inexperienced person doesn't really "know the score." This feeling is frequently justified. Unfortunately, it sometimes happens that significant scientific discoveries or ideas of newcomers are not given adequate consideration by established authorities because of the discoverer's lack of prestige. Nevertheless, authorities perform the important functions of maintaining standards and preventing the course of progress in an area of science from being diverted by wild speculations.

Several striking examples of established authorities being in error are given on pages 25–27 of Goldstein. See also pages 77–78 of Conant.

SECTION FIVE
Döbereiner's Triads

Text: pages 22–24
Activity 5

The concluding section of the case, beginning at the middle of page 22, deals with a further development that was greatly influenced by the discovery of bromine, namely, Döbereiner's law of triads. There are no laboratory activities for this section, since Döbereiner's achievement was essentially a paper-and-pencil activity.

In this section we return to an issue raised earlier in the case: What is the nature of discovery in science? New ideas introduced in this section (Question 40) concern the nature and function of theories in science. Question 43 returns to the theme of the variety of personality traits among scientists. This theme may be treated further by scheduling the students' biographical reports (Activity 5, Scientists and Nations) during this section.

For a brief account of the later development of the periodic law, a development which Döbereiner's law of triads may be said to have initiated, see pages 343–352 of Partington. Also see the article by Jan W. Van Spronson, "The Prehistory of the Periodic System of the Elements," *Journal of Chemical Education, 36:* 565–567 (November 1959). An extract from Mendeleev's paper is given on pages 9–12 of Davis.

39. What is meant by "atomic weight"? How are atomic weights determined?

✔ The atomic weight (more properly called atomic mass) of an element is a number representing the mass of an atom of that element compared with the mass of an atom of an arbitrarily chosen standard. At the present time the standard used by chemists and physicists is the mass of an atom of a stable isotope of carbon taken as 12.0000 atomic mass units. The standard has not always been the same. (Until quite recently, chemists used an atomic mass of 16.0000 for naturally occurring oxygen as the standard.) For the atomic weight values given in Döbereiner's paper, the standard of hydrogen as 1.0000 was used.

✔ The atomic masses of the elements are determined through an interlocking series of quantitative analyses of mass ratios. The analyses must measure the mass ratios of elements that react to form compounds. The volumes of reacting gases must also be measured. The actual procedures used are often very elaborate and must be carried out with great precision. Another difficulty is that some independent criterion must be available for determining the chemical formula of each compound, that is, the number of atoms of each element that make up a molecule of the compound. The chemist is here dealing with three ratios: the mass ratio of the elements in the compound, the ratio of the number of atoms of each element per molecule of the compound, and the ratio of the atomic masses of the elements concerned. Only the first of these ratios can be directly determined by experiment. The lack of reliable criteria for setting the chemical formulas of compounds was largely responsible for the failure to establish a single set of relative atomic masses of the elements during the first half of the nineteenth century.

You may wish to emphasize here that the concept of atomic mass, which is now so useful to us, is a part of a broad conceptual scheme—the atomic theory—which was developed over a period of many years by a large number of scientists. When the atomic theory was finally established about 1860, it was used to explain satisfactorily a large body of previously confusing numerical data. Pages 196–204 of Conant discuss the growth of the atomic theory, cite some of the scientists who contributed to it, and comment on the resistance with which the theory was met. (Also see *The Rejection of the Atomic Theory* in the HOSC series.) Berzelius' work on the determination of atomic weights, to which Döbereiner refers at the beginning of his paper, is discussed on pages 205–207 of Partington.

40. Might Döbereiner's idea be considered a theory? What is a theory in science? Of what use are scientific theories?

In the wording of this question a trap is intentionally laid for the unwary student who somehow feels that most questions in textbooks call for a yes answer. Of course, Döbereiner's idea of triads cannot properly be called a theory; it is a generalization based on observed relationships—in other words, a scientific law. Quite a few students will probably fall into this trap. In pulling them out, however, you will have a good opportunity to discuss the differences between a scientific theory and a scientific law.

Note that the brief mention of the term *theory* on pages 31–33 of Calder is both inadequate and misleading. Conant prefers not to use the word at all because of the confusion connected with it. Instead he uses the term *conceptual scheme* throughout his book for what we are here calling a scientific theory. See pages 23–27 of Conant.

✔ No, Döbereiner's idea would not be considered a theory, as it is understood in science. A look at the second part of the question will help explain why.

✔ A theory in science is a concise statement of a scientist's view of some part of the universe. It consists of a small number of postulates or assumptions, which can usually be expressed in mathematical form. A scientific theory evolves from repeated cycles of observations of nature (experiments), analyses of the observations, and evaluations of the analyses. Through the construction of theories with ever widening scope, the theoretical scientist attempts to approach the ultimate aim of science, the description of the universe in terms of a few basic factors.

✔ More important than the definition of a scientific theory, however, are its functions, since the acceptability of a theory is determined by how useful it is. One criterion for the acceptability of a theory is whether it is fruitful of new hypotheses and new experiments. Testable hypotheses may be deduced from the postulates of a theory, in much the same way that theorems are deduced from postulates in geometry. An acceptable theory should lead to numerous problems for research investigation. Another criterion for acceptability is whether the theory ties together in a consistent and rational manner the various observations and laws in the area that it covers. (The breadth of its area—in other words, its generality—is considered here.) A third criterion for acceptability is whether the theory explains in abstract terms the phenomena and laws in its area. (The three criteria just mentioned have been called the heuristic, correlative, and explanatory functions of a scientific theory.)

✔ Might Döbereiner's idea be considered a theory? Döbereiner noticed some interesting relationships in certain groups of chemical elements. Not only was the middle element of each group intermediate in chemical and physical properties between the two extremes, but its atomic mass was also very close to the average (within experimental error, Döbereiner said) of the atomic masses of the other two. For example, using modern values, the atomic mass of bromine, 79.9, is very close to the average of the atomic masses of chlorine, 35.5, and iodine, 126.9. (The average is 81.2.) Döbereiner cited other such triads (Li-Na-K, Ca-Sr-Ba, S-Se-Te) in which the middle element is close to the average of the outer elements in properties and atomic mass. He further suggested that this triad grouping was generally applicable to the chemical elements. In generalizing these observed relationships to include all (or most) of the elements, Döbereiner was formulating a scientific law.

✔ Döbereiner's formulation was, as the title of his paper indicates, "an attempt to group"; it did not involve any postulates from which the groupings could be deduced. It did not attempt to explain the reasons for the groups. Although Döbereiner's idea initiated a futile search for numerical relations of all kinds between the atomic masses of the elements (a sort of scientific numbers game), it stimulated no new experiments, except perhaps additional atomic mass determinations. Thus the functions of a theory cannot be attributed to Döbereiner's idea. It should be considered an example of a scientific law.

41. Fluorine was not isolated until 1886. How could scientists know about an element that had not yet been isolated? Who discovered fluorine?

This question continues the discussion of how we can decide when an element is actually discovered. Does discovery take place when the substance is first seen, when it is first named, when some of its reactions are described, or when, on the basis of laboratory tests, it is decided that the substance is of an elementary nature? You might ask your class to discuss who in this case can be called the "discoverer" of chlorine, bromine, iodine, and, as Question 41 asks, of fluorine. A more precise nomenclature may be useful in assigning the various scientists involved to the roles of isolator, namer, nominal discoverer, classifier, and so on, of each element in question.

✔ In the case of fluorine, Döbereiner and his contemporaries knew of numerous compounds—acids and salts—which had properties similar to those of the compounds of chlorine, bromine, and iodine, and which were produced in much the same way as these compounds. They reasoned that some substance analogous to the halogens must exist, and they referred to this substance as fluorine. Yet the conjectured element itself was not isolated at that time because no material was known that could be used as a container for the element without reacting with it.

Fluorine was first isolated by the French chemist Henri Moissan, by the electrolysis of a solution of potassium fluoride in liquid hydrogen fluoride. Moissan used platinum electrodes and vessels to achieve this isolation.

42. In the light of what we now know, are there any errors in what Döbereiner states as facts? If so, list any corrections that should be made.

The intent of this question, of course, is to point out the self-correcting nature of the scientific enterprise, not to indict Döbereiner for any misstatements he might have made owing to limitations of the data available to him. It is inevitable that some inaccuracies, mistaken notions, and outright errors should accompany scientific work. Likewise it seems inevitable that such errors will sooner or later be corrected as a result of further work and the subsequent communication of information and ideas between scientists.

✔ Döbereiner's statements about physical facts are actually quite accurate. The discrepancies that can be pointed out between the facts stated in the excerpts from Döbereiner's paper and present-day information amount to relatively minor quibbles.

✔ In his discussion of the seven metals Fe, Mn, Ni, Co, Zn, Cu, and Mg, Döbereiner says that they are the best conductors of electricity. This is correct in that all seven metals are excellent conductors of electricity; but Döbereiner did neglect to mention two of the best conductors, silver and gold, whose conductivity is comparable with copper's and which were well known as elements in Döbereiner's time. Several excellent conductors that were not readily available in elementary form at that time—for example chromium, aluminum, tungsten, and platinum—are also not mentioned. Incidentally, Döbereiner calls the seven metals listed above magnetic metals, and this is correct; some students may know of only the ferromagnetic metals (Fe, Ni, Co) and might not realize that the remaining four belong to the less widely known group of diamagnetic metals.

✔ For the triad Ag-Pb-Hg, Döbereiner claims that the specific gravity of lead is near the arithmetical mean of the specific gravities of silver and mercury. Actually the discrepancy (using modern values) is about 6 percent.

Specific gravity of silver	= 10.50
Specific gravity of mercury	= 13.54
Mean	= 12.02
Specific gravity of lead	= 11.35

✔ In his statements based, at least in part, on theoretical considerations, Döbereiner is less accurate when viewed in the light of present-day information. Thus, for example, several of Berzelius' values for atomic masses used by Döbereiner are very different from the presently accepted values. An interesting case is the Ag-Pb-Hg triad, which works out fairly well for the values Döbereiner used (see page 207 of Partington), but is wide of the mark when modern values are used.

	Berzelius	Modern
Atomic mass of silver	216.6	107.88
Atomic mass of mercury	202.86	200.61
Mean	209.73	154.25
Atomic mass of lead	207.46	207.21

43. Döbereiner's idea of triads was an important contribution, and he probably knew that it was. Yet his remarks near the end of his paper seem quite timid. Why? Are scientists usually this cautious?

✔ Döbereiner's triad idea was not well established; it depended on further empirical data for corroboration. In not claiming much for his notion, he might appear diffident toward the end of his paper.

✔ Yet we cannot draw conclusions on the general timidity of scientists from this one example. As we have seen in Questions 10, 16, 19, 22, and 33, scientists vary widely in personality traits and, as a result, often behave differently when faced with similar problems. Thus some scientists have great confidence in their ideas and claim with certainty that experimental verification is forthcoming; other scientists are more cautious and hesitant, preferring to wait for confirming evidence before boldly announcing their ideas to the world.

You may want to consider with your students to what extent Döbereiner's law of triads was applicable to various groups of three elements. Döbereiner himself noted about half a dozen triads, in which the atomic mass of the element with intermediate properties was rather close to the average of the atomic masses of the outer two elements. He based his generalization on these examples. Actually, for most groups of three elements that display a gradation of properties, the agreement with the law is not very good. For example, in the group N-P-As, the average of the atomic mass of nitrogen and arsenic (modern values) is 44.5, whereas the atomic mass of phosphorus is 30.9. Given enough time and not much else to do, we could probably find all sorts of arithmetical relations between the determined atomic masses of the chemical elements. However, there is no guarantee that the relations that we might turn up would have any physical significance.

NOTES FOR ADDITIONAL ACTIVITIES

ACTIVITY 1
The Discovery of Chlorine

The word *discovery* in the title of this activity is intended to imply the several meanings of this term in science, just as different senses of *discovery* are implied in the title of the entire case. The following are among the identifiable aspects of the discovery of chlorine suggested by this activity:

1. The initial observation of a new gas, isolated in the course of his researches, by Scheele.
2. The preparation of the new gas in a more or less pure state and the study of its principal properties, also by Scheele.
3. The incorporation of the new gas into the existing conceptual framework of chemistry by Scheele, followed by publication of his experimental findings and his ideas.
4. The further study of the new gas by other scientists, resulting in a more complete understanding of its physical and chemical properties. (These further studies during the period 1775–1810 are briefly indicated in the case, but numerous discoveries about chlorine continued to be made after that time.)
5. The establishment of the new gas as a chemical element by Davy (see page 6 of the case).
6. The recognition of the gaseous element as a member of a family of elements having similar chemical properties.
7. The discovery of chlorine by the students through their laboratory work, their study of this case, and their other readings.

The complexities of this matter of discovery in science are brought to the students' attention particularly in the last three paragraphs of this activity. The remarks there should serve as a suitable introduction to a discussion of this problem. The main point, as the case seeks to illustrate, is that discovery in science is seldom a single event, but rather a complex series of events taking place over a period of time and generally involving more than one scientist, and often many scientists. (Also see our comments in the introduction to Section Three, on page 17 of this guide, and the comments on Question 43, on page 28.

This activity also points out the changes in terminology that invariably accompany a major revision in chemical theory. Being familiar with a terminology based on presently accepted theory, we find it difficult to read chemical writings underlaid by a different theoretical formulation. However, as your students will readily discover, this difficulty is more apparent than real providing a dictionary that translates old terms into current ones is available. Though he uses names which are now unfamiliar to us, Scheele describes chemical reactions that we can readily reproduce in the laboratory. After all, the materials of the physical world have probably not changed very much in the past two centuries, even though the names we call them by and the concepts we hold about them may have been transformed. (For a further discussion of the functions of scientific theories, see the comments on Question 41, on page 27 of this guide.)

As to the actual amount of laboratory work to be done by the students for this activity, you are the best judge of your own school situation. Since working with chlorine gas is hazardous, many teachers prefer to exhibit its preparation and properties only through demonstrations. On the other hand, careful students can and do work safely with chlorine by taking the necessary precautions. Use of a fume hood is strongly recommended when experimenting with chlorine gas.

As mentioned previously, this case can be used most effectively in the study of the halogen elements, and the present activity provides a vehicle for the study of the chemistry of chlorine. You may wish to use the experiments suggested in the activity for this purpose, or you may wish to be suggestive rather than prescriptive. A fine resource for experiments on the reactions of chlorine is G. Fowles, *Lecture Experiments in Chemistry,* 4th ed. (London: G. Bell & Sons, 1957), pages 150–156. Some of the more interesting points relating to the suggested experiments in the activity are mentioned in the notes that follow.

The reactions of chlorine with iron and with mercury parallel the reactions of iodine with these metals, as given on page 9 of the student booklet (Experiment 1).

Breathing and Burning. It is not surprising that Scheele found that insects immediately died when placed in chlorine gas; it is surprising, however, that his sample of chlorine gas did not support combustion. In fact, a burning candle lowered into a jar of chlorine gas burns quite vigorously with a reddish flame. Hydrogen chloride and copious amounts of soot (carbon) are formed.

Chlorine and Turpentine. As an alternative procedure to the one given in the case, a piece of glass wool or filter paper can be dipped in turpentine and then inserted into a jar of chlorine gas. Glass wool is preferable to filter paper, for when filter paper is used it isn't clear that it is the turpentine which first catches fire.

The decomposition of water by chlorine can be demonstrated by placing a sample of chlorine water in strong sunlight for several hours. Fill a burette (or a similar tube closed at one end) with chlorine water, invert it, and clamp it into position over a dish containing a concentrated solution of sodium chloride. After a few hours in the bright sun, a colorless gas collects at the top of the tube. Test the gas with a glowing splint. It is thought that the free oxygen produced in a water solution of chlorine is responsible for the bleaching action of chlorine.

ACTIVITY 2
Iodine from Seaweed

This extraction really works, but only if the instructions are followed carefully. It is quite time-consuming, since a large amount of seaweed must be handled, most of which goes up in smoke. This in itself is a valuable lesson.

Dry drift kelp (genus *Laminaria*) contains about .5 percent iodine, compared with approximately .05 percent in the wracks. The factor of ten makes drift kelp the more practical source of iodine.

Equation for the action in the mixture of acidified HNO_2 and HI:

$$2HNO_2 + 2HI \rightarrow 2NO + 2H_2O + I_2$$

As for the oxidation-reduction aspect, the iodine is oxidized from -1 to zero oxidation number, while the nitrogen is reduced from $+3$ to $+2$ oxidation number.

For further details about this extraction, see Fowles, *op. cit.,* pages 265–267.

ACTIVITY 3
Hydrogen Bromide Fountain

This exercise demonstrates the high solubility of hydrogen bromide. HBr will dissolve in water, creating a lower gas pressure within the flask. Atmospheric pressure acting on the surface of the water in the jar pushes water up the long tube and into the flask in a fountain effect. Unfortunately, the HBr must be very dry for it to work satisfactorily. (The chance of failure is smaller if you demonstrate the high solubility of hydrogen chloride gas instead of hydrogen bromide.)

An excellent lab problem can be given to interested students: Why doesn't this sample of HBr (which is moist) function well in a HBr fountain?

ACTIVITY 4
Bromine from Seawater

This exercise enables students to become familiar with the problem of evaporating a naturally occurring very dilute solution to a concentrated solution that can be worked with. This is a time-consuming operation, and only the most ingenious setups will enable the students to evaporate a liter of water down to about 150 ml in less than forty minutes. Thus your students should be encouraged to plan their work beforehand. Evaporation may be hastened by using large, shallow dishes (pie plates perhaps) that provide a large surface.

Seawater is not necessary for the exercise; any natural water can be used. Even if it contains no bromine or iodine, there will usually be some residue of crystallized salts as the evaporation proceeds. Students should label the water they bring in with the source and the date collected.

You will note that in the suggested schedule, on pages 4–5 of this guide, we recommend that the students bring in their samples of water the day before it is to be used in the laboratory. This will give you an opportunity to ensure that at least one student "discovers" bromine in his sample. This is easily done by adding a teaspoonful of NaBr or KBr, or some of the Kreuznachwasser, to a selected sample. Students can be informed of the addition after the lab period is over. In almost all localities in the United States, the natural water contains no detectable bromine. Many students are disappointed when they get only a negative result after going through a lengthy procedure—another valuable lesson, however.

In procedure A, the darkening of the solution results from the liberation of iodine or bromine by chlorine replacement. The colorless chlorine solution is replaced by the yellow of bromine or the brown of iodine. An excess of chlorine, however, may convert free iodine into a colorless iodate.

When carbon tetrachloride is added, the upper (water) layer shows little or no color, while the lower (carbon tetrachloride) layer becomes more intense. Carbon tetrachloride is a much better solvent for iodine or bromine than water. The solute, as in the extraction of bromine in Experiment 2, tends to distribute itself in the two solvents in proportion to its solubility in each.

ACTIVITY 5
Scientists and Nations

This activity is intended to drive home several points. First, it is designed to combat the notion that advances in science result solely from the efforts of a relatively small number of great men. For every scientist whose name finds its way into elementary textbooks, there are hundreds of equally hardworking, dedicated men (and more recently, women) who have made their contributions. Consider the countless experiments, the multitude of papers and reports, the many proposals and counterproposals that are invested in the development of any major scientific idea. All this activity must be carried out by scores of people who bring their minds and skills to bear on some part of the problem.

Second, the activity is designed to emphasize that scientists are highly individual people. One can find a number of interesting contrasts by looking at the lives and activities of different scientists. Some scientists are gregarious, others are recluses; some scientists have many interests outside science, others appear to be concerned with little else; some scientists attain considerable distinction, others go almost unrecognized; some scientists are very generous, others are downright stingy; some scientists are mild and even-tempered, others are fiery and uncompromising; most scientists marry and have families, but a few remain bachelors.

In making their reports on the lives of the scientists listed under this activity in the student booklet, students can look into such matters. The best sources of information are biographies and biographical dictionaries. The next-best source is an encyclopedia. Since encyclopedias may be the only major reference works available in some school libraries, you will find below the names of those scientists mentioned in the case booklet for whom there is an article in the *Encyclopaedia Britannica* (1964).

France—Claude Louis Berthollet, Jean Baptiste André Dumas, Antoine Laurent Lavoisier, Louis Jacques Thénard, Louis Nicolas Vauquelin
Germany—Justus von Liebig, Friedrich Wöhler
Great Britain—William Henry
Sweden—Jöns Jakob Berzelius
USA—Benjamin Silliman

Regarding those scientists for whom there is no article in the *Britannica,* you may wish to emphasize again that science is made by both the famous and the not so famous.

The third idea to be emphasized by this activity is science's international scope. Since the phenomena of the natural world with which science deals are accessible to all, the people of all nations possess the potential for making contributions to science. This being true, if science is to progress at an optimum rate, free communication between the scientists of various countries is necessary. The scientific disciplines foster such communication through international conferences and by emphasizing knowledge of foreign languages in schools preparing scientists. Governments can foster or impede the flow of scientific information by the kinds of regulations they make in this regard.

Although science is international and people of all nations have the potential for contributing to science, the fact remains that at any one point in history some nations are more productive of scientific work than others. This points to the final area emphasized in this activity—the factors operating in a particular country at a given time that are likely to produce a large number of scientists.

The number of scientists a particular country will produce at a given time and the areas in which these scientists will work are largely reflections of the country's educational system, the national attitude toward science, the country's technological needs for research in a given area, and the availability of funds for the training of scientists and the support of scientific research.

The important role played by the educational system in producing scientists is quite clear. If the nation is to produce many scientists, it must provide a universally available, up-to-date educational system that will prepare potential scientists for their careers.

The national attitude toward science—that is, public opinion—plays a key role in determining the number and quality of scientists produced. Public opinion may either stimulate or retard the training of scientists and the progress of science. A country where public opinion toward science is favorable—where funds are provided for good education, where scientists and science have some prestige, where scientists can secure funds for research—will produce as many scientists as it needs. A country where the public is unwilling to provide an adequate education system, where the public regards scientists as unnecessary, mysterious, even sinister, and where the public does not provide funds for research, will find itself desperately short of scientists.

The technological demands of a culture affect the rate at which scientists are produced within the culture. Farsighted industrial leaders may make funds available for the training of scientists and for the support of "pure" scientific research in certain areas. (Such areas are usually those in which scientific research may lead, in the not-too-distant future, to the solution of practical problems.) Largely because of technological need, the governments of some countries (for example, the United States, England, France, and the U.S.S.R.) make funds available for the training of scientists and the support of scientific research.

In today's world, where every aspect of our lives is affected by science, it is important for citizens to be aware of the factors conducive to scientific advance.

QUESTIONS FOR REVIEW

The following questions are suggestive of the kinds that may be useful in reviewing the chemistry subject matter and the ideas about science and scientists developed in the case. For your own background prior to review, a rereading of the objectives for the units (pages 7–8 of this guide) and pertinent sections of the commentary would be appropriate.

1. Discuss the chemical and physical properties of the halogen elements, pointing out the similarities and differences.

2. What is an element?

3. How could Balard decide whether or not he had discovered a new element?

4. If you were given a gallon of muddy water from a pond, how would you go about determining whether or not it contained an iodine salt?

5. Consider a gas apparatus fitted with electrodes that can be connected to a high voltage source. The apparatus contains 2 volumes of hydrogen gas, 1 volume of chlorine gas, 1 volume of bromine vapor, and 1 volume of iodine vapor. An electric spark is passed through the mixture. Predict the approximate volume of each material remaining in the apparatus when the gases have cooled to room temperature after the explosion.

6. Write the chemical equations for

a) Balard's original preparation of bromine

b) Balard's laboratory preparation of bromine

c) two laboratory procedures for preparing HBr

d) the reaction of bromine with potassium iodide

7. Why do you think a man becomes a scientist?

8. Do you think scientists have to be handy? Of what value is this characteristic in helping scientists develop their ideas?

9. What is meant by "theory" in science? How are theories proved?

10. "Chance favors the prepared mind." Explain and discuss this quotation.

11. What do you think goes on at a scientific meeting? How is a convention of scientists similar to a convention of plumbers?

12. What effect do you think the invention of the printing press had on the progress of science? Explain.

13. In what ways would a computer be unable to replace a scientist?

NOTES FOR UNIT TEST

Permission to reproduce the test printed on pages 35–39 can be obtained by writing to

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Science Research Associates, Inc.
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Chicago, Illinois 60611

When the test is reproduced, adequate space should be provided for students to write their answers.

You will find information below about the different parts of this test and the ways in which these parts are related to the objectives of the unit that appear on pages 7–8 of this guide.

PART I

This part consists mostly of recall items. The primary emphasis is on testing for knowledge of factual information presented in the case or studied in connection with the case, such as the "A" objectives listed on page 7.

PART II

This is an attempt to test for some of the "A" and "B" objectives. Principles and concepts presented in the case appear in a new situation. Students must have some understanding of the principles and concepts, not merely the ability to recall them, in order to analyze and interpret the new situation, and must also have had extensive practice in scientific reasoning.

PART III

This part tests for understanding of ideas concerning scientists and scientific work (the "C" objectives). Some of the true-or-false items of Section A involve simple recall of statements of ideas discussed in connection with the case; others call for making rather careful discriminations. It is important that students rewrite false statements, because incorrect ideas should not be permitted to stand.

Section B attempts to measure the student's success in achieving one of the long-range aims of studying the HOSC units: a greater sensitivity to the nature of the scientific enterprise as evidenced by his ability to recognize fundamental ideas about science when reading unfamiliar materials (see page 8 of this guide). This kind of recognition is exemplified by the marginal comments and questions throughout the case. Nevertheless, the task of inducing general ideas from particular facts is not likely to be easy for many students. The general statements under A of this part of the test can be of great help in accomplishing the task successfully. These statements indicate the ideas to be sought in the selection. Students will find that the example at the beginning of Part III is also helpful.

PART IV (Optional)

Section A is an extension of the testing offered in Part III, Section B, but it is more open-ended, since the ideas to be sought are not specified. Actually, this is a better indicator of a student's sensitivity to the nature of the scientific enterprise than is Part III, Section B; however, the dual task of recognizing an example and formulating a statement of the general idea is more difficult. The grading of the performance is also more difficult, because it involves numerous separate judgments.

In Section B the student has an opportunity to demonstrate how well he comprehends the principle of similarities and differences within a family group of elements. Some recall is involved, since the question deals with halogen compounds that were presented in the case. (Use of an unfamiliar example would make this an extremely difficult question.) Grading may be a problem with this question, as it is whenever an essay answer is required.

POINTS SUMMARY:

PART	I –	8
	II –	14
	III –	24
		46
	IV –	variable (likely maximum – 16)

UNIT TEST

PART I

The principal participants in *The Discovery of the Halogen Elements* were Karl Scheele, Joseph Gay-Lussac, Humphry Davy, Bernard Courtois, Karl Löwig, Antoine Balard, and Johann Döbereiner. In front of each of the accomplishments listed below write the *last* name of the man who was responsible for it.

____________________ **1.** First suggested that chlorine and iodine were related.

____________________ **2.** Isolated a gas that bleached vegetable substances.

____________________ **3.** Brought crystals of iodine to the attention of French chemists.

____________________ **4.** Collected and studied samples of a liquid that he obtained in Kreuznach.

____________________ **5.** Considered, but then rejected, the hypothesis that chlorine is an element.

____________________ **6.** Felt there might be general significance to the position of bromine's atomic mass midway between that of chlorine and iodine.

____________________ **7.** First published a paper on the properties of bromine.

____________________ **8.** Studied the properties of iodine at the same time as Gay-Lussac.

PART II

Each question in this part is followed by four answers. Select the *one best* answer on the basis of the information given and your knowledge of chemistry and scientific reasoning.

1. Algernon and Kuno had decided to work together on an extra project for their chemistry class. Since they had access to salt spring water, they decided to experiment to see whether it contained bromine. They brought two gallons of this water to the laboratory and evaporated it to a concentrated salt solution, which they made acidic. To this concentrated salt solution they added two drops of chlorine water. The solution immediately turned yellow.

Algernon said, "Well, at least we know that we have a halogen present." Kuno agreed, "Yes, and the yellow is probably iodine if this water contains both iodine and bromine, as we hope it does." Why does Kuno think of iodine first?

- **a)** Iodine reacts faster with chlorine than bromine does.
- **b)** If iodine were present, it would be more easily replaced by chlorine than would bromine.
- **c)** Yellow is a characteristic color of dilute iodine solutions.
- **d)** Where both iodine and bromine occur together, the iodine salts are present in greater concentration.

2. "It will be easy enough to test whether this is iodine," Kuno said. "We'll just add some starch." Algernon added some starch to the yellow solution. The starch turned blue and the solution became colorless. "Well, that shows that we only have iodine," Algernon said in disappointment. But Kuno insisted that bromine might still be present. His thinking is correct because

a) the fact that the solution is colorless indicates that bromine may not have been replaced from its salts
b) chlorine doesn't replace bromine
c) the bromine, too, could have reacted with the starch
d) bromine cannot be replaced from its salts while free iodine is present

3. "Since we can't be sure whether bromine is present from the information we have so far, we will have to make some tests," Kuno said. He added more chlorine water to the solution. They observed that the solution turned orange and that a red-brown gas escaped. Algernon said, "The red-brown gas shows that bromine is present after all!" But Kuno disagreed that the color of the gas necessarily indicated this. Why did Kuno disagree?
a) Iodine may have reacted further with the chlorine to produce this gas.
b) The addition of more chlorine may have replaced a greater amount of iodine from the solution which was given off as a red-brown gas.
c) There are red-brown gases other than bromine vapor.
d) The red-brown color is a characteristic of all halogen gases.

4. "So little gas was produced that we can't do anything with it," Algernon remarked, "but the deep orange color that the solution now has may be significant." Kuno agreed with Algernon and correctly thought that the deep color might indicate that there was a greater concentration of
a) both iodine and bromine
b) chlorine
c) iodine only
d) bromine only

5. Kuno added fresh starch to the solution and noted that it turned blue. He filtered the starch from the solution and added fresh starch. This time it didn't turn blue. The solution was still colored, however. These results plus the previous escape of red-brown gas indicate that
a) all the iodine in the solution had been removed by the starch
b) more iodine had been displaced, and the orange-colored solution probably indicates the presence of bromine
c) the color of the solution and the gas was due to a compound of iodine and chlorine
d) more iodine had been displaced, but the orange color doesn't necessarily indicate the presence of bromine

6. Kuno wanted to test their results further. He suggested that they study some of the reactions into which bromine would enter if it were present in their solution. Algernon suggested adding some litmus to the solution because
a) only bromine is capable of decolorizing the litmus
b) no extra chlorine was present to discolor the litmus
c) even if there was some free iodine left in the solution, there couldn't be enough to discolor the litmus
d) only the bromine was left to discolor the litmus, since the addition of more starch showed that all the iodine had been replaced

7. "Now you must believe that what we have is bromine," Algernon insisted. Kuno agreed that the results of the experiments seemed to indicate this, but he thought they should check their interpretation by testing for another characteristic bromine reaction. Into part of the solution they stirred some ether. They observed that the ether became orange, while the water solution became colorless. Kuno concluded, correctly, that they had extracted bromine because bromine
a) is volatile
b) is more soluble in water than ether
c) is more soluble in ether than in water
d) reacted with the ether

PART III

A. Several statements about scientists and scientific work are given below. For each statement, decide whether it is *generally true* or *generally false,* and then print *T* or *F* in Column A to the right of the statement. Further, if a statement is false, write a true statement *about the same idea* in the space below the false statement. A sample has been worked out for you. (Do not write in Column B until you have read the directions for Section B.)

	Column A	Column B
Sample. The principal aim of science is to provide people with better things for better living.	F	
The principal aim of science is to attain understanding of the phenomena of the natural world.		par. 2
1. Though scientists today are seeking elementary substances different from those sought by chemists of the past, the nature of their pursuit is essentially the same.	____	____
2. A scientist isn't obligated to stop his investigations in a particular area if he learns that another scientist is also investigating it.	____	____
3. If an experiment has been conducted under carefully controlled conditions, it is not necessary to confirm the results by repeating the same experiment.	____	____
4. Communication through correspondence and journals often has a great deal to do with the advances a scientist makes in his own work.	____	____
5. The results of successful experiments are accepted and interpreted in the same way by nearly all scientists.	____	____
6. Obtaining a negative result, or no result at all, from an experiment represents a setback for science.	____	____
7. Even though several scientists may have arrived at the same ideas and hypotheses about a subject, the one who makes a thorough study of the subject and presents the material to his colleagues generally receives the credit for the discovery.	____	____
8. Because of the importance of science today, scientists have more freedom than in years past to travel in countries torn by war or political unrest.	____	____

B. The selection below contains illustrations of numerous ideas about scientists and scientific work like those discussed in *The Discovery of the Halogen Elements.* You may not fully understand some of the facts presented in the selection, but that is not important. What you should be able to recognize are illustrations of many of the true statements in Section A above—both true statements that were given and true statements that you wrote.

Read the selection through carefully. When you find an illustration for one of the ideas in Section A, underline it and write the number of the paragraph in which the illustration appears on the proper line in Column B above. For example, the idea expressed in the true restatement of the sample is illustrated by the underlined portion in paragraph 2 of the selection; hence, "par. 2" has been written in Column B.

Not all the true statements in Section A are illustrated in the selection, and some statements are illustrated more than once. For those ideas for which you find no illustration, mark an *X* on the proper line in Column B.

THE DISCOVERY OF FLUORINE

by Nancy and Uhlrich Klabunde

1 One of the problems most challenging to nineteenth century chemists was the isolation of another halogen, fluorine. The first known studies on a compound containing fluorine were performed around 1530 by a German chemist, George Bauer, who described the properties of the mineral fluorspar. Bauer, however, did not recognize the chemical composition of the compound. Many chemists worked on the problem of the reactions and chemical composition of fluorspar. But it was not until 1771 that a Swedish chemist, Karl Wilhelm Scheele, showed that fluorspar is a salt of calcium containing an ion of a "peculiar" acid which he obtained by heating fluorspar with sulfuric acid. This "peculiar" acid (now known as hydrofluoric acid) and many of its salts were studied by Gay-Lussac and Thénard, and many other chemists. All of them assumed that this acid contained oxygen, which was in accord with what was believed about all acids at the time.

2 Then it was shown by Gay-Lussac and Thénard that another halogen acid, hydrochloric acid, was composed of only hydrogen and chlorine. This work, added to work which they did on several other acids, showed that not all acids contain oxygen as chemists had previously believed. Even after their findings were published, many chemists still refused to believe that oxygen isn't a part of all acids.

3 Strangely, Gay-Lussac and Thénard didn't recognize any analogy between hydrochloric acid and the hydrofluoric acid that had been studied for so long. Another French chemist, André Ampère, who accepted the finding that not all acids contain oxygen, saw the analogy. In 1810 he wrote to Davy, who was studying the chemistry of hydrofluoric acid and its salts. He suggested to Davy that hydrofluoric acid, like hydrochloric acid, was oxygenless and that they could be considered analogous compounds. Ampère further suggested the name "fluorine" for this substance, which previously had been called fluor, and he proposed that it was really an element.

4 In 1813 and 1814, after extensive research, Davy published two papers, "Fluor Spar" and "Fluoric Compounds." In these papers he noted the resemblances between fluorine and chlorine in their compounds. He hypothesized that fluorine is an extremely reactive element. His papers carefully detailed all that was known about fluorine up to that time. Because of this work, he is credited with establishing the elementary nature of fluorine. However, none of his many experiments to obtain fluorine in its free state was successful.

5 Davy's hypothesis that fluorine is an element was finally found to be correct by a French chemist, Henri Moissan, in 1886. Moissan was a very versatile man—pharmacist, physicist, chemist, professor—with an impressive list of scientific achievements to his credit. Moissan studied the work that other men were doing. He saw that their various chemical methods and their attempts to electrolyze molten metallic fluorides had failed. His own attempts to produce fluorine by the electrolysis of nonmetallic fluorides failed also.

6 He next turned to the electrolysis of liquid hydrogen fluoride, although he knew from the work of Faraday that the acid itself was nonconducting. Surprisingly, his attempts at electrolysis were successful. He electrolyzed liquid hydrofluoric acid that he had distilled from potassium hydrogen fluoride. The result was a pale greenish-yellow gas, so reactive that it set a crystal of silicon afire. He reported these findings to the Académie des Sciences in Paris and stated that he had isolated fluorine. It was arranged that he would repeat his experiment before representatives of the academy. In order to be certain of good results again, Moissan redistilled the hydrofluoric acid in order to be sure of its purity. But when he repeated the experiment before the academy representatives, the solution failed to conduct electricity, just as Faraday had found.

7 Moissan thought that he had controlled the conditions of his experiment and demonstration. What he did not realize at first was that when he had distilled the hydrogen fluoride from the potassium hydrogen fluoride in the previous experiment, some of the potassium salt was carried over into the hydrogen fluoride. The potassium salt had made the liquid hydrofluoric acid conducting. When he purified the hydrogen fluoride before his demonstration, he removed the traces of potassium salt that had made the electrolysis successful. He soon deduced the role that the potassium salt plays in the isolation of fluorine.

8 Moissan's process for producing fluorine is still used today with only minor improvements in the type of apparatus he used. For the isolation of fluorine, he received the Lacaze Prize of the Académie des Sciences in 1887. For his outstanding work in chemistry, he received a Nobel prize in 1906.

PART IV (optional)

A. In the selection "The Discovery of Fluorine," there are a number of illustrations of ideas about scientists and scientific work that were not included in the true statements of Part III, Section A. Reread the selection to see whether you can spot them.

Write a concise statement of any new ideas (such as those discussed in *The Discovery of the Halogen Elements*) for which you find an illustration in the selection. Give the number of the paragraph in which the illustration appears.

B. **1.** A solution may contain salts of iodine and bromine. Explain how you could show whether or not iodine salts are present by performing only one test.

2. Suppose you have a sample of a solid that you know is the potassium salt of some halogen. Without doing a chemical analysis, how can you find out which halogen is in the salt? List as many experiments as you can.

KEY FOR UNIT TEST

Part I

(1 point for each correct answer)

1.	Davy	5.	Gay-Lussac
2.	Scheele	6.	Döbereiner
3.	Courtois	7.	Balard
4.	Löwig	8.	Davy

Part II

(2 points for each correct answer)

1.	*b*	5.	*b*
2.	*a*	6.	*d*
3.	*c*	7.	*c*
4.	*a*		

Part III

(1 point for each correct *T-F* identification; 1 point for each correct rewrite of a false statement; 1 point for each correct paragraph reference)

	Section A	Section B
1.	T	X
2.	T	par. 1 (sentences 4 and 6)
3.	F Since chance factors can enter into even carefully controlled experiments, the work should be repeated several times to make sure that such factors are ruled out.	par. 6 (sentence 8)
4.	T	Par. 3 (sentence 3) is the best illustration; also par. 2 (sentence 3), par. 5 (sentence 3), par. 6 (sentence 1), and by suggestion par. 1 (sentence 7).
5.	F Scientists might not accept positive results of some experiments as facts, and they might interpret the results in different ways even if they do accept them as facts.	par. 2 (sentence 3) and par. 3 (sentence 2)
6.	F A negative result can have positive effects in the sense that it narrows the scientist's possible field of investigation and may direct his work into more constructive channels.	par. 5 (sentence 3) by suggestion
7.	T	par. 4 (sentence 5)
8.	F Science has become an important factor in national defense. A scientist who is a national asset is therefore not permitted to travel in war-torn countries.	X

Part IV

A. (2 points for each correct idea ferreted out and referred to an appropriate paragraph)

Some of the ideas illustrated in the selection and not cited in Part III, A, are listed below. Students may find others which may be counted as correct if they are referred to an appropriate sentence or phrase in the selection.

- Scientists build constantly on the work of their predecessors to explain and refine their knowledge. (par. 4, sentence 4; par. 5, sentence 3)
- A hypothesis expresses a scientist's view of some phenomenon in the natural world. (par. 4, sentence 6)
- A scientist verifies hypotheses through experiment and observation (par. 5, sentence 1)
- Chance sometimes plays a significant role in scientific discoveries. (par. 7, sentence 4)
- Scientists must be prepared to devise new equipment to perform experiments. (par. 9, sentence 1)

B. (4 points for Question 1; 3 points for each correct answer to Question 2. Partial credit may be given for each question.)

1. Add bromine water to the solution. If iodine salts are present, the color of the solution will darken. If no iodine salts are present, there will be no color change.

2. **a)** Measure its solubility in water and compare with solubilities of the various potassium halides given in a handbook.
   b) Measure its specific gravity and compare.
   c) Measure its melting point and compare.
   d) Measure its solubility in organic solvents and compare.