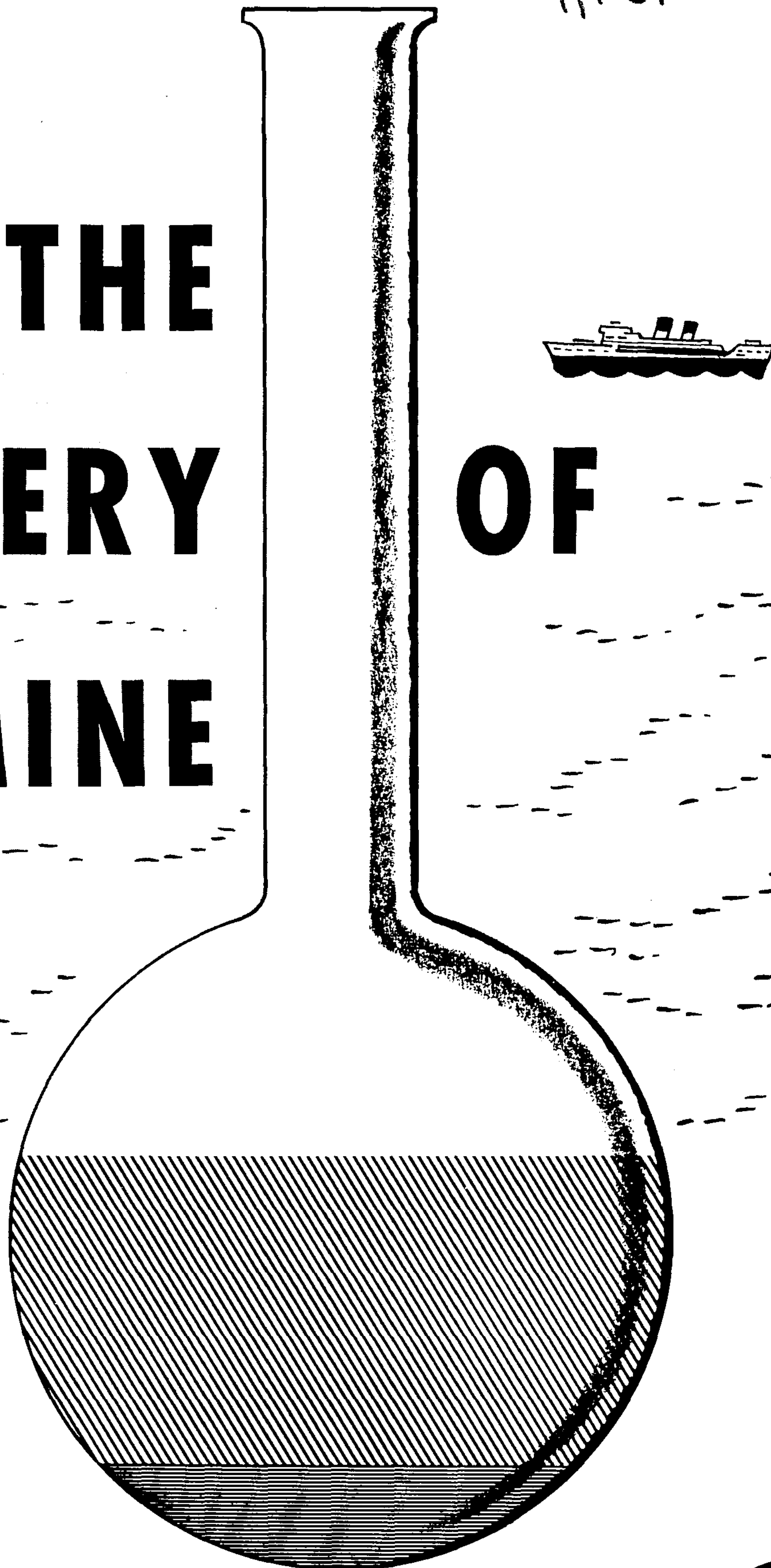
HISTORY OF SCIENCE CASES
FOR HIGH SCHOOLS

Case 3

THE DISCOVERY OF BROMINE



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INTRODUCTION

In this HISTORY OF SCIENCE CASE, we shall make a critical study of a part of the development of a major scientific idea. Although we want to learn something about this idea, our chief interest in this CASE will be to find out as much as we can about:

- the methods used by scientists
- the means by which science advances and the conditions under which it flourishes
- the role of scientists as people and the personal characteristics of scientists
- the interplay of social, economic, technological, and psychological factors with the progress of science
- the importance of accurate and accessible records, constantly-improved instruments, and free communication

Proper study of this CASE consists of more than simply reading this little booklet. In the narrative outline, which follows this introduction, you will find numerous comments and questions in the margins. These marginal notes are intended to stimulate your thinking and to guide discussion on the points illustrated by the CASE. Space is provided on the left-hand pages for you to write answers to the questions which appear in the marginal notes . . . A most important part of the study of this CASE are the experiments and exercises which are suggested in this booklet, following the narrative outline. You should try to complete as many of these exercises as possible, so that you may get a real "feel" for the situations faced by scientists in creating science. Your teacher may suggest additional exercises and experiments that you can work on in connection with this CASE. On the last page of this booklet, you will find some reading suggestions of books and articles relating to the story of this particular CASE.

Some students will think that this CASE is out of date, because the story is set in the scientific past. Nothing could be further from the truth. The points about science and scientists which are featured in this CASE hold just as cogently in the present as they did in the past. The methods of scientific investigation are much the same today as they have been for several hundred years; similar non-scientific factors now interact with the progress of science as they did then; the character and personalities of scientists are always paramount factors when we think about science; adequate recording, free communication, and improved instrumentation continue as vital needs. These aspects of science held true yesterday, hold true today, and will hold true tomorrow.

As you study this CASE and work through the exercises, you will learn a great deal about scientists and about what goes on in science.

L.E.K.

The principal people you will meet in this Case are:

Joseph Louis Gay-Lussac	French chemist and physicist. Born 6 December 1778 at St. Léonard, Haute-Vienne. Died 9 May 1850 at Paris.
Johann Wolfgang Döbereiner	German chemist. Born 15 December 1780 at Hof, Bayreuth. Died 24 March 1849 at Jena.
Antoine Jérôme Balard	French chemist. Born 30 September 1802 at Montpellier, Hérault. Died 30 August 1876 at Paris.
Carl Löwig	German chemist. Born 17 March 1803 at Kreuznach, Prussia. Died 27 March 1890 at Breslau.
Justus von Liebig	German chemist. Born 12 May 1803 at Darmstadt, Hesse. Died 18 April 1873 at Munich.

[[Use these left-hand pages to take notes and to write out your answers to the questions suggested in the margins of the narrative outline.]]

What is an "element"?

Why are the halogens an important group of chemical elements?

THE DISCOVERY OF BROMINE

Scientists today believe that there are about one hundred different chemical elements that make up all the materials of the earth. Some of these elements were known in ancient times and the alchemists of the Middle Ages discovered a few more. All but about a dozen of the chemical elements were discovered after 1700. Someone had to make each discovery, and many scientists have taken part in this search. (Incidentally, we should probably first decide what we mean by the word "element." See Exercise 1, page 18.)

One of the most important groups of chemical elements is a family that we now call "the halogens," which means "salt-formers." A large number of very useful chemical salts, including our common table salt, sodium chloride, are composed of elements which are members of the halogen family. Many halogen salts may be obtained from the waters of the sea. The first halogen element to be discovered was chlorine, a greenish-yellow gas, which was first prepared by the Swedish chemist, Carl Wilhelm Scheele, in 1774. A second member of the halogen family, the beautiful violet-gray solid element, iodine, was discovered in 1811 by Bernard Courtois, a chemical manufacturer at Dijon, France. Courtois found iodine in washings of the ashes from certain seaweeds (brown algae), which were used at that time as raw materials for making several chemical salts.

Chemists soon learned that chlorine and iodine were similar in many of their chemical properties, but they did not realize that these two elements were a part of an important chemical family. Such similarities between two elements might easily happen by chance, and chemists had not yet learned to think of elements as being arranged in families . . . The discovery of bromine, which we shall learn about in this case, not only filled a large gap in our knowledge but also helped to bring chemists to a new view of the relations between chemical elements.

How does the personal characteristic "curiosity" help scientists in their work?

What do you suppose is meant by the term "mother liquor"? (No wise cracks, please.)

How does a scientist find out about the work of his predecessors? (Give at least five different ways.)

When Carl Löwig died on 27 March 1890, the German Chemical Society, although he was not a member of their group, paid noble respects to this able pioneer and teacher. Eighty-seven years before, on 17 March 1803, Löwig was born in Kreuznach, Germany, a town noted even today as a bathing spa with fine salt springs. In his youth, Löwig studied pharmacy but he was also interested in the salt springs in his native town. In one experiment which he did with the mother liquor of water taken from a salt spring, Löwig obtained a small amount of a peculiar red liquid. (For the details of Löwig's experiment, which you can easily perform, see Exercise 3 on pages 18 and 19 of this Case.) He could not identify this material and there was no record of it in the chemical literature.

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

> A scientist must know the work of those who have gone before. -- How does he find out about it?

In 1825, Löwig decided to take up seriously the study of chemistry. He journeyed to the University of Heidelberg to become a student in the laboratory of Professor Leopold Gmelin, one of the great chemistry teachers of the time. Löwig took with him to Heidelberg the strange red liquid he had prepared and consulted Professor Gmelin about it. The learned professor could not identify the peculiar material either, and Löwig did not have enough of it to carry out tests to find out what it might be. Gmelin urged Löwig to prepare more of his red liquid so that he could study its chemical properties, and the young chemistry student from Kreuznach immediately busied himself with this assignment.

> Free contacts between scientists are essential.

> To get answers in science, you must ask questions by making experimental tests.

At about the same time, another young chemist at the École de Pharmacie (School of Pharmacy) in Montpellier, France, was making interesting observations and doing experiments. Antoine-Jérôme Balard, born 30 September 1802 in Montpellier, a city near the Golfé du Líon of the Mediterranean Sea, was studying the plants in a salt marsh one day when he came upon a pan containing waste mother liquors from common salt. A deposit of crystals had formed in the pan, and Balard wondered

> Curiosity about nature.

What role does chance play in the progress of science? --- Do you know of any other instances where chance observations have led to important discoveries? Does this happen very frequently in science?

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.)

How do you suppose Balard learned about the chemistry of iodine?

What is the importance of careful observation in scientific work?

if any use could be found for these waste liquors. He set about trying to separate the various chemicals they contained. As it turned out, this work and related projects kept Balard busy for much of the remaining fifty years of his life and led him to many important discoveries. Balard was to become a famous chemist and a professor at the Sorbonne, but he always kept his love for the sea and the products it contains. Whenever he could, Balard would journey down from Paris to the sea to delight in its excitement and ponder its mysteries.

What role does chance play in the progress of science?

Are scientists also poets?

As we mentioned in the second paragraph of this Case on page 1, the element iodine had first been obtained from certain seaweeds in 1811. The chemistry of iodine was well known to Balard. Around Montpellier, iodine was found in seaweeds which belong to the botanical genus Fucus. When the ashes of Fucus are treated with a solution of starch and chlorine water, the starch becomes a dark blue color, indicating that free iodine is present. (This is the standard test for iodine, which you probably know.) But, when Balard carried out this test on Fucus, he noticed something else. He tells us:

How did Balard learn this?

Carry out a test to get answers.

What is the importance of careful observation in scientific work?

> I had repeatedly observed, upon treating the washings of the fucus which contain iodine, with an aqueous solution of chlorine, that after having added a solution of starch, there was not only a blue colour, caused by the iodine, but also a little above it, a yellowish colour of considerable intensity.

Balard had seen this color before in his experiments with the waste mother liquors from salt-making. He goes on to say:

> This orange colour was also apparent when the mother water of our salt-works was treated in the same manner; and the tint was strong in proportion to the concentration of the liquid. [In other words, the more concentrated the salt water was, the darker was the color.] The production of this colour is accompanied with a peculiar penetrating smell.

(Phew!)

What causes this yellowish color and how does the coloring matter behave? Balard did some preliminary experiments to find out. First he

What is a scientific hypothesis? How is it used in scientific work?

How did Balard know that "the colouring matter was volatile"?

Write two word equations to represent Balard's two hypotheses.

1.

2.

How does Balard test his first hypothesis? Explain the test.

What sort of an instrument is a "voltaic pile"? --- Why does Balard use this device instead of simply plugging into the D.C. line?

How can Balard test his second hypothesis?

learned that when the mother liquor of the salt-works, after having been treated with chlorine and starch, is left standing in the air for a day or two the yellow color and peculiar odor disappear. The color and odor also disappear immediately from the treated mother liquors when an alkali is added. Likewise, if he added any reagents that produce hydrogen, such as zinc plus sulfuric acid, to the treated mother liquors, Balard found that the yellow color and odor promptly disappeared. In all these cases, once the color and odor had disappeared, adding chlorine water to the solution would not bring them back.

Observation.

Tests and observations.

Careful work calls for trying all possibilities.

> Two explanations naturally present themselves to account for these various phenomena. In the first place, it may be supposed that the yellow matter is a compound of chlorine with some substance contained in the mother water of the salt-works; in the second place, it may be imagined that the colouring matter had been released from some of its compounds by the chlorine and that the chlorine had taken its place.

Scientists try to find explanations for observations. Trial explanations are often called <u>hypotheses</u>.

> To determine which opinion to adopt, it was necessary to obtain the colouring matter in a separate state. Since the colouring matter was volatile, I had some hope that I could separate it from the liquid by distillation, and I had recourse to this process.

Hypotheses have to be tested!
How did Balard know that "the colouring matter was volatile"?

By very careful distillation and drying, Balard obtained a few drops of a deep red liquid, which displayed all the properties and reactions he had found in the original yellow coloring matter. Thus, he knew that he had separated the substance in a pure state. With the minute quantities of the red liquid that he was able to produce, Balard continued his experiments.

Experimental work often demands a lot of skill.

> I was at first induced to take this substance as a chloride of iodine, different from those compounds which are already known to chemists. It was in vain that all my trials were directed to this end. It gave no blue colour with solution of starch, ... it was evident that it contained no iodine.

Balard tests his first hypothesis.---
How?

> On the other hand, I had repeatedly subjected this substance to the influence of the voltaic pile, and also to a high temperature, but it did not in either case exhibit the slightest appearance of decomposition. Such resistance could not fail to suggest that I had to do with an element, . . . and this opinion has been strengthened by every trial to which I have

What sort of instrument is a "voltaic pile"?
What is Balard's second hypothesis?
How can he test it?

Who tasted the bromine? Whose skin did Balard use to find out that bromine destroys the skin? --- What do these two instances tell you about scientific experimentation?

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

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

> subjected it. I imagined it to be an element, strikingly similar in its chemical reactions to chlorine and iodine and forming similar compounds; but always presenting physical and chemical properties which furnish the strongest reasons for distinguishing it from them.
>
> M. Anglada advised me to call this substance <u>Brome</u>, deriving this name from the Greek word βρωμος (bromos), which means "bad smell."

Balard next made a thorough investigation of this new substance, bromine (which is the English name we now use for his <u>brome</u>), and some of its compounds. He found a more fruitful method for preparing bromine. This is the method which we still use in our laboratory preparation of bromine today. (For details of this preparation, see Exercise 6 on page 20.) About the physical and chemical properties of bromine, Balard discovered the following:

> When we observe a large quantity of brome by reflected light, it is of a blackish-red fluid; but when a thin layer is placed between the light and the eye, it is of a hyacinthine red colour.
>
> Its disagreeable smell reminds one of that of the oxides of chlorine, but is much less intense.
>
> Its taste is extremely strong.

Who tasted it?

> It corrodes the skin especially, giving it a deep yellow colour, which is less intense than that produced by iodine . . . . If bromine has remained in contact with the skin for some time, the yellow colour disappears only when the epidermis is destroyed.

Whose skin did Balard use to find this out?

> It acts upon organic substances, upon wood, cork, etc.
>
> It acts strongly upon animals. A single drop put into the bill of a bird killed it.
>
> Its specific gravity, as nearly as I could find out with the small quantities of the substance which I had, was 2.966, and it is a liquid at normal temperatures and even at 18° below 0° centigrade.

What is meant by "specific gravity"? Why is it important?

> It is readily volatilized, which is a great contrast to its specific gravity. When a drop of brome is put into any vessel, it is immediately filled with a deep orange red vapour, which, by its color, might be mistaken for nitrogen dioxide.

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

> It boils at 47° centigrade heat, which thus varies the physical state of brome but has no effect at all upon its chemical nature . . . .

Why is the fact that electricity does not decompose bromine important?

Why is a chemist interested in solubility?

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

In what ways do scientists communicate with one another?

> It is not a conductor of voltaic electricity; . . . neither does electricity appear capable of decomposing brome . . . .
>
> The vapour of brome does not support combustion. A lighted taper when immersed in brome is soon extinguished, but before it goes out, it burns for an instant with a flame which is green at the base and red in the upper part, just as it does in chlorine gas.
>
> Brome is soluble in water and alcohol, and especially in ether. It is but slightly soluble in sulfuric acid. Olive oil acts slowly with it; it does not redden litmus solution but decolorizes it rapidly, very much like chlorine. Solution of indigo in sulfuric acid is also decolorized by it.

Why is this fact very important?

(Try this; it's pretty!)

Why is a chemist interested in solubility?

With these many tests on bromine itself, Balard's researches had only begun, for he now turned to a study of bromine's compounds. In the same careful and thorough manner, he learned to prepare hydrogen bromide gas by four different methods and he investigated the properties of this new gas. (You can do the same; see Exercise 7 on page 21.) An important property of hydrogen bromide, which Balard discovered, is that it is very soluble in water. When hydrogen bromide dissolves in water, it forms hydrobromic acid, a new acid which Balard discovered and studied.

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

Balard carried out a large number of reactions with bromine, hydrogen bromide, and hydrobromic acid and prepared at least twenty new compounds of bromine. In all these reactions, he noted that the behavior of bromine was very similar to, and intermediate between, chlorine and iodine. Thus, these three elements, which have a common origin in the salty water of the sea, seem to form a kind of chemical family. In this family, Balard discovered, bromine has the power to take the place of iodine in its iodide compounds, while bromine is readily replaced from its bromide compounds by chlorine. (You can demonstrate this fact for yourself; see Exercise 9 on page 22.)

A scientist makes observations, but he must also put some thinking to his results. (Chemicals don't think.)

Balard collected and wrote about the results of his researches in a good-sized paper which he called "Memoire sur une particuliere

In what ways do scientists communicate with one another?

What role do scientific societies play in the progress of science? --- Incidentally what is a scientific society?

Why do scientists repeat experiments?

Have you heard of Gay-Lussac before? Where? Do you think he was a respected scientist at this time?

Why do scientists publish papers about their work? --- (This is a double-barrelled question: from the point of view of the advance of science, the reasons are quite clear, BUT scientists also have personal reasons for publishing papers. Your answer should include both kinds of reasons.)

contenue dans l'eau de la mer" ("Memoir on a peculiar substance contained in sea water"). On 3 July 1826, this paper was read by M. Auguste Berard to the French Academy of Science in Paris. So unusual and important were the contents of Balard's paper that the Academy appointed a special commission to review it and to repeat the experiments. Six weeks later, on 14 August 1826, the commission reported to the Academy and confirmed the accuracy of Balard's work. Said Gay-Lussac, the secretary of the commission, in his report:

What role do scientific societies play in the progress of science?

Scientists have a habit of repeating experiments. Why do they?

Have you heard of Gay-Lussac before? Where?

> The memoir of M. Balard is extremely well drawn up, and the numerous results which he relates would not fail to excite great interest, . . . The discovery of brome is a very important acquisition to chemistry, and gives M. Balard honourable rank in the career of the sciences. We are of the opinion that this young chemist is every way worthy of the encouragement of the Academy; and we have the honour to propose that his memoir should be printed in the Recueil des Savants Etrangers (Selections from the Works of Unknown Scholars).

Why do scientists publish papers about their work?

Following the commission's recommendation, Balard's memoir was published in the September 1826 issue of the Annales de Chemie et de Physique (Annals of Chemistry and Physics). The paper was translated into English and German and was reprinted in four different journals before the end of 1826. In this way, many chemists soon learned about Balard's researches. Among them was Carl Löwig in Heidelberg who was still working busily on trying to identify the peculiar substance which he found in the salt springs at Kreuznach. As soon as he read Balard's paper, Löwig knew that his unknown red liquid was the same as the bromine which Balard had prepared. Löwig had just missed the honor of being the discoverer of bromine.

Löwig, however, did not brood long over his disappointment. Using the information and procedures given by Balard, Löwig carried further the investigation of bromine and its compounds. He published several valuable papers on the subject and, in 1829, a book titled

Every scientist builds on the achievements of others.

How was it found out that bromine was present in the waters in Massachusetts, New York, and Virginia?

Is a negative result of any value in science?

What rule of scientific method did Liebig forget?

Is Liebig's report an example of an independent verification? [We'll give you the answer to this, so you can concentrate on the next one, which is more important.]

Yes, this is an independent verification. Liebig was not working together with Balard, although he used Balard's procedures. Liebig used materials from a different source, and he obtained similar results, thereby verifying Balard's work.

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

Among scientists, are authorities, that is, people who have established themselves, considered more important than newcomers?

Das Brom und seine chemische Verhältnisse (Bromine and Its Chemical Relations), which was a learned summary of all the knowledge of bromine up to that time.

By 1829, quite a store of knowledge about bromine had become available, because many chemists had taken an interest in this new element. They repeated and extended Balard's work, and looked for bromine in sea water from all parts of the world and in local salt springs. In America, for example, bromine was soon identified in the waters at Hingham, Massachusetts, at Salina and Saratoga Springs, New York, and in Kenahawa County, Virginia. No trace of bromine could be found in the sea water at New Haven, Connecticut.

Repetition of experiments.

How was this found out?

Is a negative result of any value in science?

One noted German chemist who took particular interest in bromine was Justus von Liebig, professor at the University of Giessen. Liebig, like Löwig, had missed discovering bromine. Some years earlier, he had been given a bottle containing bromine to examine and he had decided, without studying it thoroughly, that the bottle contained iodine chloride. Again, in 1825, Liebig had visited Kreuznach and had studied the mother liquors of the salt-works. After treating with chlorine water and starch, he noticed an intense yellow color. Again he decided, without experimenting, that the substance was iodine chloride. When Liebig read Balard's paper, he realized his mistake and immediately repeated the Frenchman's experiments. He wrote:

> The preparation of bromine, as Balard has given it, is really so simple that any improvements which could be given are unimportant. I prepared bromine . . . and was in a position to repeat a large part of Balard's researches. I did not come upon a single fact which could contradict his conclusions.

Thus, Liebig added his approval and the authority of his position to the work of the young Balard. Liebig also observed the striking similarities between chlorine, bromine, and iodine.

Scientists are human and make human mistakes.

What rule of scientific method did he forget?

Is this an example of an independent verification? How does the fact that reports can be checked influence the work of scientists?

Among scientists, are authorities consisered more important than newcomers?

Might Döbereiner's idea be considered a theory? --- What is a theory in science?
Did he have any proof?

How are scientific theories proved?

With the discovery of bromine, the idea of family relationships among certain chemical elements began to find favor among some chemists. The discovery and careful study of numerous other elements during the first quarter of the nineteenth century also helped to form this idea. The earliest important proposal of the family idea was made by Johann Wolfgang Döbereiner, just three years after the discovery of bromine, in a paper entitled "Versuch zu einer Gruppirung der elementaren Stoffe nach ihrer Analogie" ("An Attempt to Group the Elements by their Similarities"). Döbereiner formulated his famous triads, or groups of three elements, in which the middle element was intermediate in properties and atomic weight between the outer two. The first triad which Döbereiner gave as an example of these groupings consisted of chlorine, bromine, and iodine.

Many facts must be gathered before any generalizations can be confidently made.

Might Döbereiner's idea be considered a theory? Did he have any proof?

How are scientific theories proved?

Döbereiner's triads led eventually, after many years and many by-ways, to family groupings for all the chemical elements in the great generalization of the Periodic Table of the Elements. But, that is another story. The part which the scientists who discovered bromine played in that story has already been told.

Experiments and Exercises

1. The first question we must ask in studying this Case is: "What is an element?" We can easily find in a book what a chemist means by "element," but the question goes deeper than that. For instance, what did the ancient Greeks take to be "the elements"?

How do we look at the chemical elements in the 20th century A.D.? Are the chemical elements really "simple bodies," as scientists believed in the 19th century? Are the chemical elements the same as the elementary (that is, simplest, fundamental) particles of matter?

Do you think that there is a very human wish for simplicity --- for getting down to fundamentals --- involved here? What else is involved?

2. Suppose we can agree on what we mean by a chemical element. (Scientists must make such agreements in order to get on with the business of science.) How can we decide if a certain substance which we have under study <u>is</u> or <u>is not</u> a chemical element? What tests can we use?

How did Balard decide that bromine was an element?

How do we identify a new element today?

3. Löwig's Experiment. --- To repeat Löwig's experiment, first obtain some mother liquors from the salt springs at Kreuznach. [Since this may be rather hard to come by, a reasonable facsimile may be made as follows: Make up a solution of various salts (not iodides) and be sure to include a fair amount of potassium or sodium bromide. Make the solution acidic with a few drops of hydrochloric acid.]

YOUR Observations

To 100 ml of mother liquors, add about 50 ml of chlorine water ("Chlorox" will do) and shake thoroughly. The solution will become pale yellow. Now add 50 ml of diethyl ether, cork the flask loosely, and shake vigorously. [CAUTION! Don't inhale too much ether. KEEP AWAY FROM FLAME!!!] Let the liquid settle and note that two layers are formed. The lower water is colorless; the upper ether layer is yellow or orange. Why?

Pour off the ether layer into a distilling flask. Slowly distill the ether at a temperature of less than 40° C, using warm water to heat the flask. When the ether has been carefully distilled, a small amount of bromine will remain in the flask. (Depending upon the original concentration of bromide, either a few drops of red liquid bromine or some bromine vapor will be left.) [BE CAREFUL when working with bromine!!!]

4. Iodine from Seaweeds. --- Audrey H. Heap gives the following method of extracting iodine from seaweed on pages 140-141 of The Science Masters' Book, Series II, Part II, (London: John Murray, 1936). See also pages 138-139 of this book, and G. Fowles, Lecture Experiments in Chemistry. Fourth Edition (London: Blakiston, 1957) pages 265-267.

Collect about six pounds of moist seaweed, which has been washed up on shore after a rough sea. Not all seaweeds contain the same percentage of iodine. Best yields are generally obtained from drift kelp or "ribbon seaweed" (genus Laminaria); the wracks (genus Fucus) yield considerably less iodine, but may be used. [Indeed, Balard used Fucus.] Wash the seaweed lightly to remove sand and debris and then let it dry in the air.

Crush the dried seaweed into small pieces, and then char it in a frying pan. Grind the charred seaweed to a powder. Heat the powdered seaweed in large crucible (or a frying pan) to remove all, or almost all, the carbon. The ash which remains contains the iodine.

Leach the ash with water and filter. Collect the filtrate and reduce it to a manageable bulk by evaporating most of the water. Now, strongly acidify the liquid with concentrated hydrochloric acid; any iodate present will yield up its iodine, which precipitates.

YOUR Observations

Dissolve a teaspoonful of sodium nitrite in about 50 ml of water and add this in small quantities to the liquid, while shaking the flask and cooling if necessary. The nitrous acid will precipitate iodine from the iodides present. If it is needed, add more hydrochloric acid to keep the liquid strongly acidic. Continue adding sodium nitrite solution until no more iodine precipitates. Let the flask stand until all the iodine has settled, then pour off the liquid and throw it away.

Place the crude iodine in a retort and half fill the retort with water. Heat to boiling. The pure iodine will come over with the steam in a few minutes. The neck of the retort should be inserted into a flask or test-tube cooled by water or ice. Solid iodine will collect in the cold receiver and a violet vapor will fill the retort. (With poorer samples of seaweed, there may be no solid iodine obtained, but the violet vapor will be seen, and a straw-colored distillate should be collected. This distillate will give a good iodine test with starch solution.)

5. Bromine from Sea Water. --- A good part of our bromine supply is obtained from sea water, even today. Not all sea water, however, is a good source of bromine. What about the sea water in your vicinity? Does it contain any bromine? If there is no sea water nearby, does river water or lake water contain any bromine? (You may be surprised.)

Collect one-quart samples of sea, river, or lake water from several places. Filter each sample and evaporate most of the water until about 150 ml of solution is left. (This operation may take quite some time, and you will have to devise some techniques for carrying out the process, without losing any of your sample, rapidly.)

When you have evaporated your sample down to its "mother liquor," make it acidic by adding 5 ml of concentrated hydrochloric acid. Then add 15 ml of chlorine water. If bromine or iodine is present, the solution darkens. Why?

Add 25 ml of carbon tetrachloride and shake vigorously. Let stand and two layers will form. The upper water layer will be colorless, or nearly so. Why? --- If the lower layer is red-brown, bromine is present in the sea water; if the lower layer is violet or purple, iodine is present. What is in yours?

6. Balard's Preparation of Bromine. (Standard Lab Prep)
Follow the directions in a laboratory manual for the preparation of bromine from potassium bromide, manganese dioxide, and sulfuric acid. Or, you may wish to follow Balard's directions, given in 1826 in his Memoir. Balard first obtained crystals of potassium bromide by treating an ether solution of bromine with potash and then evaporating the liquid. He says:

YOUR Observations

It is these cubic crystals that I successfully employ for the preparation of brome. I mix these crystals, after pulverizing them, with purified manganese dioxide, and upon this mixture, put into a small distilling apparatus, I pour sulfuric acid diluted with half its weight of water. This acid, if it were mixed with the [potassium bromide] crystals alone, would extricate white vapours and very little brome, and the same effect is produced if the sulfuric acid in a more concentrated state be used with the mixture of salt and manganese dioxide, but employed as directed it produces orange vapours that condense into small drops of brome. These may be collected by immersing the end of the retort into the bottom of a small receiver filled with cold water; the vapours of brome dissolve in the water. The brome which condenses in the neck of the retort precipitates to the bottom of the vessel on account of its great specific gravity.

[As a precaution, when doing this experiment, keep a piece of filter paper soaked with ammonium hydroxide handy. Wave this about near the generator if any bromine escapes.]

On pages 9 and 11 of this Case, Balard gives the chemical and physical properties of bromine which he observed. How many of Balard's observations can you match? What did Balard miss? [CAREFUL; Bromine is POISONOUS!!!]

7. Preparation of Hydrogen Bromide. --- If your laboratory manual doesn't give any directions for preparing hydrogen bromide, the experiments for hydrogen chloride may be adapted with a little effort. Balard prepared hydrogen bromide in four ways, and you could follow his directions. As he tells us in his Memoir:

1. I exposed during some time hydrogen mixed with vapour of brome to the solar rays without observing any sensible combination; but I found that hydrogen bromide gas was produced by exposing the mixture to the flame of a taper, or still better, by introducing an ignited iron wire into the receiver which contained it.

In all these cases, the action is not propogated throughout the whole mass, as occurs with chlorine and hydrogen; the combination is produced only around the hot body which occasions it. It probably would not have so happened, if I had been able to collect and measure the vapours of brome and to have mixed them with determinate proportions of hydrogen.

2. Hydrogen iodide gas . . . [is] decomposed by brome, which is changed into hydrogen bromide, by separating the vapours of iodine; . . . this decomposition is always effected with the disengagement of heat. The volume of gas does not sensibly alter when hydrogen iodide gas is decomposed by brome. Brome acts in the same way upon the compounds of hydrogen when they are dissolved in water, and hydrobromic acid is formed at their expense.

YOUR Observations

3. Hydrogen bromide gas may be procured by decomposing the cubic crystals of potassium bromide with sulfuric acid, but the gas so obtained is often mixed with a small quantity of sulfur dioxide and hydrogen chloride gasses, which prevents the employment of this method when the hydrogen bromide is wanted perfectly pure.

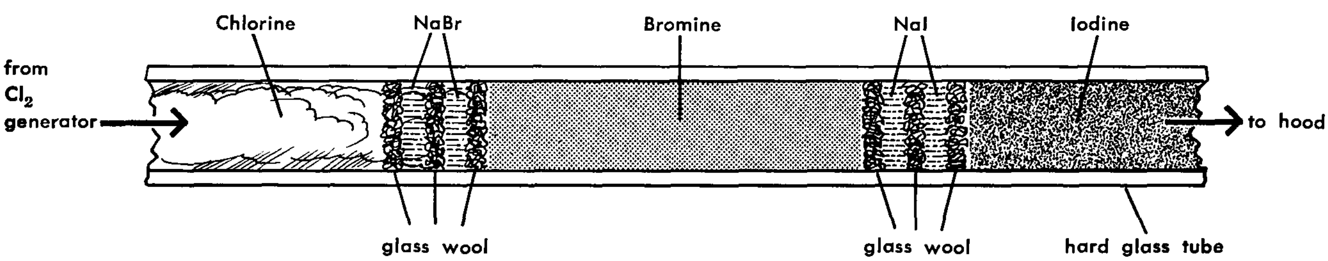
4. To obtain this gas in a state of purity, I had recourse to a process borrowed to a certain extent from that which is employed for the preparation of hydrogen iodide gas. Brome and phosphorus when put together and moistened with a few drops of water, give out an abundance of hydrogen bromide gas, which may be received over mercury. [DANGER!!! This experiment with phosphorus is dangerous and should probably be done only as a teacher demonstration.]

Hydrogen bromide gas is colourless; its taste is quite acid. When exposed to the air, it exhales white vapours, which are denser than those produced in the same way from hydrochloric acid. These vapours have a very penetrating smell and occasion violent coughing. [A WORD TO THE WISE is . . . . .]

8. Hydrogen Bromide Fountain. --- Hydrogen bromide gas is highly soluble in water and may be used instead of ammonia in the well-known ammonia fountain experiment. Use litmus as an indicator. (Hydrogen chloride gas could also be used, and, in fact, gives a more dramatic effect.) This experiment is described, among other places, in Elbert C. Weaver and Laurence S. Foster, Chemistry for Our Times, Third Edition, (New York: McGraw-Hill, 1960) page 355.

How does the hydrogen bromide (or hydrogen chloride) fountain work?

9. Replacement of Bromine and Iodine. --- Prepare plugs of glass wool with slightly moistened sodium bromide and sodium iodide, and arrange them in a large-diameter hard glass tube as shown in the figure.



YOUR Observations

Blow through the tube to be sure it is not clogged. Generate chlorine gas slowly and allow it to pass into the tube from the left side. The chlorine replaces the bromine in the sodium bromide, and a reddish vapor appears in the center of the tube. This bromine vapor in turn replaces iodine in the sodium iodide and a violet vapor appears at the right end of the tube. Warm the spaces containing bromine and iodine from time to time to keep these elements in a vapor state. This experiment clearly shows the replacement series of the halogens.

(For details of the apparatus, see Weaver and Foster (1960), page 290. The experiment is also described in Albert L. Elder, Demonstrations and Experiments in General Chemistry, (New York: Harper, 1937), page 137.)

Sources of Quotations

pages 5, 7, 9, 11 20, 21, and 22 — Balard, Antoine-Jerome, "Memoir on a Peculiar Substance Contained in Sea Water." Annals of Philosophy, 28, pages 381-387 and 411-424. (1826). ---

[In these quotations, contemporary chemical nomenclature and spelling have been substituted for that used in the time of Balard. A few other slight adaptations in language have also been made, without altering the meaning or the spirit of the original.]

The English translation in the Annals of Philosophy is taken from Balard's paper in French, which appeared in the Annales de Chemie et de Physique, (Series 2), 32, pages 337-381, (1826).

page 13 — Gay-Lussac, Louis-Joseph, "Report upon the Memoir of M. Balard Respecting a New Substance," Annals of Philosophy, 28, pages 425-426, (1826). --- Also quoted by Mary E. Weeks (see below) page 752.

page 15 — Liebig, Justus von, "Ueber das Brom" Journal für Chemie and Physik (Schweigger) 48, pages 106-108, (1826).

Reading Suggestions

WEEKS, Mary Elvira. Discovery of the Elements. Sixth Edition. Easton, Pa.: Journal of Chemical Education, 1956. [This book is indispensable supplementary reading for this Case. It is entertainingly written, authoritative, and full of pictures. The story of the discovery of bromine is told on pages 747 to 755.]

SMITH, Edgar Fahs, "Bromine and Its Discoverers, 1826-1926," Journal of Chemical Education, 3, pages 382-384, (1926).

DAVIS, Helen M. The Chemical Elements. Second Edition. New York: Ballantine Books, 1959. (No. BSF 320, paperbound, 50 cents.)

PARTINGTON, J. R. A Short History of Chemistry. Third Edition. New York: Macmillan, 1959. (also Harper Torchbook, TB 522, 1960, $1.95)

FRIEND, J. Newton. Man and the Chemical Elements. London: Charles Griffin, 1951.

BERRY, Arthur J. Modern Chemistry - Some Sketches of Its Historical Development. New York: Macmillan, 1946.

[The reports of the "discovery" - i.e., identification - of the first bromine in America may be found in the American Journal of Science, 18, pages 142-144 and 260; and ibid., 20, page 161.]