MODERN CHEMISTRY

WITH ITS PRACTICAL APPLICATIONS

BY

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PREFACE

In preparing this book for use in secondary schools, I have endeavored to look at the science from the viewpoint of the students themselves. The fault with many texts upon the same subject is that the position of the learner has been disregarded; the books have been encyclopædic; they have presented a great number of facts as a skeleton or framework, but this skeleton has not been clothed with muscle and animated with life. No more fascinating subject finds a place in the curricula of our secondary schools, yet to the average student chemistry is too often but an irksome task.

In the present work I have omitted much that is often given in an elementary text, while at the same time entering more into that detail which gives lively interest to the subject. It has been my aim to show, whenever possible, the practical application of the science to the everyday affairs of life; in other words, to emphasize industrial and commercial chemistry. At the same time the fundamental principles of the science have not been forgotten; on the contrary, they have been emphasized even more than is usual in an elementary chemistry. This has been rendered possible by the omission of much that can never be either of interest or of value to the beginner.

Recognizing the fact that science must be taught inductively by experiment, some authors have assumed that the student must gain all his knowledge of chemistry in this way. No greater mistake could be made. The science has been hundreds of years in reaching its present development, and much must be accepted by the student without any effort to work it out for himself. In this text a large amount of experimental work is given, sufficient to meet the requirements of all our best colleges. The experiment is always supplemented by notes and suggestions which enable the student to draw proper conclusions, and give him such information as he cannot hope in his limited time to gain for himself. It will be noticed also that the laboratory directions are largely in the form of questions, so as to compel even the least energetic students to secure the benefits of personal investigation. This plan is always followed except in cases where the student would be in danger of going astray.

To the pedagogical treatment of the difficult parts of the science I desire to call attention. The subject has been presented much in the same way as in my own classes, where the method has met with success. Beginning with the study of that most familiar of substances, *Water*, the text enters into a discussion of its composition and then proceeds to a detailed statement of its constituents. This work is prefaced merely by a short chapter connecting the science of Chemistry with that of Physics and by one chapter upon *Valence*. This somewhat difficult subject of *Valence* is introduced so early in the book in order to avoid many difficult questions that must arise when it is deferred. Although introduced early in the book, *Valence* is treated in so simple a way and with so many graphic illustrations that the student can hardly fail to grasp its meaning.

I recognize the demands, coming from all higher institutions of learning, for more quantitative work, and believe I have fully met all such requirements. The student of the subject, as taught hitherto, has been in danger of coming to the conclusion that very little in chemistry is exact; whereas nothing could be further from the truth. The pupil is shown this by the series of quantitative experiments which have been carefully worked out in the laboratory. For this work I have sought to make use of such apparatus only as may be or should be found in any secondary school.

To the regular text is appended detailed instruction for various laboratory manipulations, preparing solutions, etc. A chapter has also been added for the benefit of any who may desire to continue along qualitative lines the work introduced at various places in the text.

I desire to acknowledge, with gratitude, the valuable suggestions offered by Professor Irving P. Bishop, of the State Normal School, Buffalo, and Professor M. D. Sohon, of the Boys' High School, New York City, both of whom have read the book critically in manuscript; furthermore, I wish to say that to many of my students of the past I am indebted for descriptions, original with them, and more appropriate than any I have found in any text. To Dr. Paul Schweitzer, for many years Professor of Chemistry in the Missouri State University, the true friend of the student, to whom I owe much for his great sympathy and encouragement, and his words of fatherly advice, I desire to express especial gratitude. Finally, I acknowledge with pleasure the help and inspiration I have gained in my private study and research from the writings of those who have been permitted to drink long and deep from this fountain of science.

TO THE TEACHER

It is not expected that everything given in the text will be demanded of the pupil, unless possibly in reviews. Some of the manufacturing processes, for example, I have deemed of sufficient importance and interest to be given; yet it may seem best in the judgment of the instructor to omit these.

The experiments, as a rule, may be performed by the students, and apparatus is suggested which most schools will be able to provide. The number of pupils will determine to some extent what experiments should be performed by the teacher and what by the students themselves. If the classes are small, so that the teacher can give very close personal attention, the pupils may attempt almost all; on the other hand, if the classes are large, it may be necessary for the teacher to perform some of the more difficult and dangerous experiments himself. On pages 355 to 380 will be found many useful suggestions to the student for the care and manipulation of apparatus, making up of solutions, etc. These should be read before the student begins his work in the laboratory, and frequent reference should afterward be made to them.

It is presumed that a school year of nine or ten months will be given to the work in this text, but by omitting some of the less important elements, much of the theory and many of the practical applications of chemical science may be obtained in five or six months. Besides the various chapters devoted to the fundamental laws of chemistry, special study should be given to the following elements and a few of their important compounds: hydrogen, oxygen, nitrogen, fluorine, chlorine, bromine, iodine, carbon, sulphur, sodium, calcium, zinc, lead, and iron.

MODERN CHEMISTRY

CHAPTER I

INTRODUCTION

1. With what is Chemistry concerned? — Nature presents herself in ever-changing forms, and to one who is not familiar with these variations she is a mystery. The untaught inhabitant of the tropics, who has never been beyond the confines of his native state, taken to a colder climate would see no relation between the snowflake or the icy covering of our northern rivers and the rain-drop as it falls upon his native hills. To him they are entirely different substances.

2. So the diamond, the filling of the ordinary "lead" pencil, and the coal that we burn in our furnaces seem altogether dissimilar, and yet they are practically the same thing. Likewise the emery with which the seamstress sharpens her needle and the mechanic his tools, and such valuable stones as the oriental emerald and the ruby, though seemingly so different, have really the same composition. The purpose of the science of chemistry is the investigation of the objects that lie all about us in nature, the study of their composition and of their relations to one another, the explanation of the various phenomena in connection with them, and the ability to apply this knowledge to practical uses.

3. Importance of the Subject. — A knowledge of chemistry adds a charm to many of the common things of life, clothing them with new beauty. Later it will be noticed that the science of chemistry enters into all or nearly all of the great manufacturing industries of the world, and that without the application of its laws and principles all such enterprises would result in failure. Whether studied, therefore, for its intellectual or for its practical value, it is of the greatest importance.

MATTER, THEORIES — PHYSICAL AND CHEMICAL CHANGES

4. Some Theories of Matter. — There have been men in all ages who believed that all substances whatsoever might be resolved back into one particular kind of matter; that by subjecting this matter to different conditions an endless variety of modifications would result. To illustrate: here is a bar of steel; by submitting it to varying processes it is made into saws, knives, needles, watch-springs, pens, and thousands of other articles. It is claimed that in the same manner the one elementary substance, in undergoing different treatments by the forces of nature, appears in the endless variety of substances about us. It has never been possible, however, for those who hold this view to prove it by any experiments. Neither does it seem that the phenomena of nature require or even admit of any such explanation.

5. Elements. — What seems a more reasonable view, and one that has come nearer to demonstration, is that matter is composed of a large number of simple substances, and that these combined in different ways produce an infinite number of substances. According to this view there are about seventy-five simple substances, called *elements*, which cannot be, or at least never have been, divided into two or more simpler substances. Numerous experiments of every character, by means of the strongest sisting of two elements, sodium and chlorine, always in the ratio of 46 to 71 by weight. Likewise, water is a compound, containing one part of hydrogen to eight of oxygen.

8. Divisibility of Matter. — Physics teaches us that matter is anything that occupies space, and that all matter is divisible. But where does this divisibility end? We do not know. A single crystal of a dark purple solid known as potassium permanganate will very perceptibly color several gallons of water. To do this, it must be divided up until its particles are diffused throughout the entire volume of the water, or into so many parts that the numbers are beyond our comprehension. Though we cannot fix an absolute limit to the division of matter, we assume it to be the *molecule*.

9. The Theory of Molecules. — A molecule is the smallest particle of matter that can exist alone, or in the case of a compound body, the smallest particle that can exist without destroying the identity of the substance. Thus, the smallest portion of common salt to be conceived of still contains the two elements mentioned, sodium and chlorine, and is a molecule. In the same way the smallest particle of water would contain both hydrogen and oxygen, and always in the same ratio. If, now, by any means we can break up these salt or water molecules into their two constituents, we no longer have a compound body, but two simpler substances or elements.

10. Atoms. — These constituent parts of a molecule we call *atoms*. Even the molecules of the elements may consist of two or more atoms; in fact, they usually do. Thus, it will be seen later that a molecule of oxygen consists of two atoms; a molecule of chlorine of two atoms, and so on. It may be said, therefore, that all matter is divisible into molecules, and that these molecules are composed of still smaller particles called atoms. From the above, it will be seen that the molecule of the compound body and its constituent atoms would be very different, while the molecule of an elementary body and its atoms would be exactly alike in properties. This is illustrated in Fig. 1.

Here, *a* represents a molecule of water consisting of two atoms of hydrogen and one of oxygen. If by electricity we decompose this molecule, we shall no longer have water, but two elementary substances, hydrogen and oxygen. Likewise, *c* represents a molecule of common salt, and if this be decomposed, we shall no longer have salt, but two substances, sodium and chlorine. On the other hand, *b* represents a molecule of oxygen, and if this be decomposed, we shall still have oxygen, but in the atomic form, possessing the same physical characteristics as before.

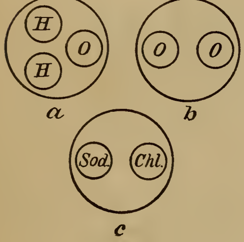


Fig. 1.

11. Physical Changes. — Matter exists in three conditions, solid, liquid, and gaseous, depending upon the relation to each other of the intermolecular forces. When the cohesion existing between the molecules is considerably greater than the repellant forces which tend to drive them apart, the substance exists in the form of a solid. When the converse of this is true, and the molecules tend to be driven farther and farther from each other, the substance is then in the form of a gas. When the repellant and attractive forces are about at an equilibrium, the substance exists as a liquid. It is with changes of molecular condition that physics deals, and the molecule is the basis of all physical phenomena.

Experiment 1. — Hold in the flame of the Bunsen burner a piece of tin foil, an aluminum wire, or a narrow strip of zinc; or put any one of them into a clean iron spoon and heat. What change takes place in the physical condition of the metal? Let it cool again and state what happens.

12. In this simple experiment two changes have taken place: one, the conversion of the solid into the liquid form; and second, the changing back again into the solid. We have changed the form of the substance and the arrangement of the molecules as regards one another, but the properties have remained the same.

13. Another Molecular Change. — Likewise, when a current of electricity is passed through an electro-magnet, the armature for the time being becomes a magnet; that is, its molecules have been rearranged, or so affected that they present the well-known phenomenon of attraction. When the circuit is broken, the armature loses its magnetism; in other words, its molecules have assumed their previous condition. When a body is heated, the molecules are set in more rapid vibration, and luminous bodies emit light because of this vibratory motion.

14. So throughout the domain of physics we find that all phenomena concern the molecule and molecular changes. We are all familiar with the different conditions under which water exists, and we are not surprised at the statement that fog, clouds, rain, snow, and other forms are modifications of the same substance, the only difference being in the greater or less amount of stored-up heat energy.

15. Substances exist in Three Forms. — At the same time we are not accustomed to think that nearly all substances may exist in the same three forms; as liquids, solids, and gases. We are familiar with air in the gaseous condition only; yet if we reduce the temperature of it to about 190° below zero Centigrade, it becomes a transparent liquid not very different in appearance from water, and at a still lower temperature it freezes or solidifies. In like manner carbon dioxide, an invisible gas thrown off from the lungs of all animals in breathing, if cooled, is first liquefied, and then by further reduction of temperature is converted into a beautiful white crystalline solid, very closely resembling snow.

16. Mercury and Carbon. — We are all familiar with mercury as a silvery white liquid, which may be boiled and converted into vapor at a moderately low temperature. On the other hand, in our most northern climates it frequently solidifies, and were the glacial epoch to return, under the rigors of that era we would know mercury, not as a liquid, but as a somewhat malleable solid closely resembling lead in its appearance and properties. To go still further, carbon, that we know best in the form of charcoal and coal, — one of the most refractory of substances — in an electrical furnace may be fused and made to boil, apparently like water, while in the intense heat of the sun it is converted into vapor and exists in the atmosphere surrounding that body just as water vapor does in our own.

17. All these are merely illustrations of changes in molecular condition, or are *physical changes;* and the same substance in its different forms presents at all times essentially the same properties.

Experiment 2. — Put into a small test-tube a crystal of iodine and warm gently. What becomes of the crystal? Does anything deposit farther up the tube? When the colored vapors have disappeared, warm the tube higher up. What happens?

From the above experiment we see what has been stated before, that heat converts many substances into vapors; and further, that when this heat is removed, they condense again into their previous condition. We learn, too, that the physical condition in which bodies exist is not an essential, but an incidental matter depending upon the ease or difficulty with which they are melted and vaporized.

18. Chemical Changes. — Chemical changes, on the other hand, involve, not the molecule, but the constituent parts of the molecule, the *atoms*. In every chemical change the molecule is broken up and its identity destroyed, while the atoms formerly composing it recombine to form new and different substances. Hence, when any substance is changed chemically, or when two or more substances react upon one another and undergo a chemical change, new products are formed, differing altogether in properties from the original substances.

EXPERIMENT 3. — Put into a small test-tube a little mercuric oxide and heat, gently at first, then quite strongly. Continue this for several minutes. Thrust a pine splinter, having a spark upon the end, down into the tube. What happens? Is there any evidence of something present different from air? What seems to be forming upon the cooler portions of the tube?

19. If we continue to heat long enough, the red oxide would entirely disappear, just as water does when boiled. In the latter case, however, the water might be condensed again as before, while in the present instance the mercuric oxide seems to be decomposed into two substances, — one, an invisible gas which caused the spark to burn brightly, the other a dark colored substance which condensed in small globules upon the cooler portion of the tube. Here we have a *chemical* change, one which caused the destruction of the original substance, and produced therefrom two, differing very strikingly in their properties.

20. Chemical changes are usually brought about by some physical agency, such as heat, electricity, light, percussion, etc. Innumerable instances of this kind of change might be given, but as such changes are to be studied throughout the science of chemistry, only a few will be noticed at present. As already seen, the substances produced are often very different from those used in obtaining them; for example, two or more solids may unite in such a way as to form a gaseous body, or even a liquid; two gases may form a solid or a liquid; while two liquids may combine to form a solid. Some of these will be illustrated below.

Experiment 4. — Rub vigorously together in a mortar a small crystal of potassium chlorate and an equal quantity of flowers [illegible] sulphur. Into what are the two solids converted? How is their chemical union manifest?

21. A change similar to this is seen when gunpowder is exploded, causing the three substances, of which it is a mixture, to combine, with the formation of several gaseous products.

Experiment 5. — With a few small crystals of potassium chlorate wrap in a piece of paper a bit of phosphorus; fold the ends together carefully and strike with a heavy weight as shown in Fig. 2. What are the results? What is the nature of the products formed?

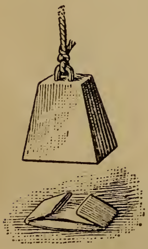


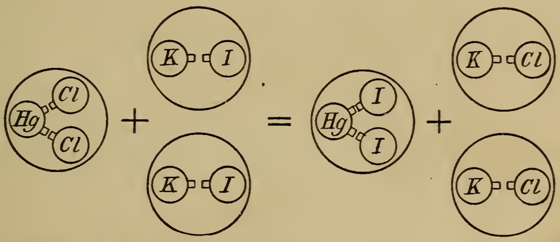
Fig. 2.

CAUTION. — In preparing for this experiment, cut the phosphorus under water, dry quickly in the folds of a filter or blotting paper, and proceed as above. Small particles of the phosphorus often fly to some distance, and a board should be set up to protect the clothing of the experimenter and of the members of the class.

Experiment 6. — Mix thoroughly a small quantity of granulated sugar with an equal amount of potassium chlorate, well powdered, and put the mixture into an iron saucer. Now by means of a pipette or glass tube drop upon it a little strong sulphuric acid. Notice that the sugar is burned, a part is converted into gaseous products, and a part left as a black residue.

22. Chemical Change by Physical Agency. — In Experiments 3, 4, and 5, the different substances were caused to combine by friction, or percussion. That is, by physical force, the molecules of the different substances were brought so close together that the *chemism*, or chemical affinity, of the atoms in the unlike substances was greater than the cohesion among the molecules, and as a result the atoms rearranged themselves to form new compounds. This may also be illustrated by the following experiment:

Experiment 7. — Put into a clean porcelain mortar a few crystals of potassium iodide, KI, and about the same amount of mercuric chloride, $HgCl_2$. Rub them together for two or three minutes; notice that the two *white* compounds react with each other to form a *bright red* mixture.



23. By the friction, the molecules of the mercuric chloride and of potassium iodide are brought so close together, that the mercury and potassium atoms exchange places, forming mercuric iodide, which is bright red in color, and potassium chloride, which is a white compound. It is simply another striking illustration of the fact already stated that chemical action brings about a change in the atomic structure, and causes, therefore, the formation of substances very different from the original.

24. Chemical Change by Chemical Agent. — In Experiment 6, the same results were brought about by the use of a chemical reagent, sulphuric acid. In all of these instances, except Experiment 7, the solid substances used were largely converted into gaseous products, and in all entirely different from the original. To show that two gases may combine to form a solid, perform the following experiment: —

EXPERIMENT 8. — Put into a beaker a few drops of hydrochloric acid, cover with a sheet of cardboard or glass, and allow it to stand a few minutes. Into another beaker put a few drops of strong ammonium hydroxide, and cover in the same way. Presently, invert the first beaker over the second, then remove the cards, so that the two gases which have filled the beakers may come into contact with each other. Notice the heavy white fumes that form. These are a white solid compound, known as sal ammoniac.

EXPERIMENT 9. — To show that two liquids by reacting upon each other may produce a solid. Numerous instances of this will be seen from time to time. Powder a gram or two of alum and an equal amount of ferrous sulphate, put both into a test-tube and add about 10 cc. of water or just enough to dissolve them readily. You will now have a nearly colorless solution. To this add slowly a little strong ammonium hydroxide. You will obtain a greenish colored, jelly-like solid, with scarcely enough water present to enable the precipitates to be poured from the tube.

25. Mixtures. — We have had the term *compound body* defined, and we must be careful to distinguish between a compound and a mixture. In the latter, the two or more substances used are not necessarily in any definite proportion, nor are they united with each other. Furthermore, as a rule, mixtures may be very easily separated by purely mechanical means.

Thus, we may put together sand and common salt in any proportion whatsoever; they do not react with each other to form a new compound, but are still sand and salt just as before being mixed. They may also be very easily separated and the salt recovered. Let the student suggest a method for doing this.

26. Gunpowder. — Gunpowder is a very familiar mixture, consisting of three substances which may be easily separated. Upon exploding, however, these three combine to form several compounds from which the original could be recovered only by difficult and expensive methods.

EXPERIMENT 10. — To separate gunpowder into its constituents. Put a gram or two of gunpowder into an evaporating dish and add a few cubic centimeters of water. After warming gently a few minutes, filter out as directed on page 00. Transfer the clear filtrate to an evaporating dish and boil slowly to dryness. While you are waiting for this, transfer the black residue upon the filter paper to a beaker and add a little carbon disulphide. Shake for a moment or two, and then decant or filter off this clear solution. *Without heating*, let it evaporate to dryness in a watch crystal or evaporating dish. What familiar substance is left? What was the appearance of the solid obtained by boiling down the solution in water? What colored residue was left after treating with carbon disulphide? Can you name the three substances?

EXPERIMENT 11. — To show the difference between a mixture and a compound of the same two elements. Put together in any proportion a small quantity of sulphur and of iron filings. Mix them thoroughly. What is the resulting color? See whether you can remove the filings by means of a magnet; owing to the presence of some moisture a little sulphur may adhere to the filings. State your results. Put the filings back into the sulphur and again mix them well. Now add 1 or 2 cc. of carbon disulphide, shake for a moment or two, and decant thoroughly upon a watch crystal or into an evaporating dish. Let the clear solution dry *without heating*, as it is very inflammable. What do you obtain? Have you effected a separation of the two?

Again mix in about equal proportions by volume, or in the ratio of 32 to 56 by weight, sulphur and iron filings; put them into the smallest test-tube you have and heat, first gently and then *very strongly*, until a bright red glow seems to go through the entire mass. After thus heating for two or three minutes, allow the tube to cool, and remove the contents; if necessary, break the tube. How does the color differ from that of the mixture at the beginning? Powder the mass, and attempt to separate the filings from the sulphur by means of a magnet as before. Can you do this? Treat a part of the dark powdered mass with carbon disulphide and determine whether you can thus remove the sulphur as you did from the mixture. State your results. From this experiment we may note several differences between the mixture of iron and sulphur that we had before heating and the compound afterward. What are they?

SUMMARY OF CHAPTER

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  Definition.
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  How different from physical.
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  How different from elements and compounds.
  Examples of mixtures.
  Method of separating.

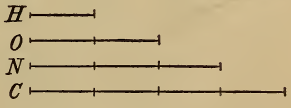
CHAPTER II

VALENCE

1. What is Valence?* — If we notice some of the common compounds of hydrogen, which we shall study, we shall see that different elements unite with a different number of hydrogen atoms. Thus, chlorine combines with one atom of hydrogen, oxygen with two, nitrogen with three, and carbon with four, as shown in the following compounds: —

Hydrochloric Acid	HCl
Water	H_2O
Ammonia	H_3N
Marsh Gas	H_4C

2. The four elements, chlorine, oxygen, nitrogen, and carbon, have the power of combining with one, two, three, and four atoms of hydrogen, respectively, and we speak of them as having a *valence* of one, two, three, and four. By valence or quantivalence we mean the *power* any element has of holding in combination the atoms of another element taken as a standard. This standard, primarily, as shown above,



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* If in the judgment of the teacher the subject of valence can be more easily grasped by the student later in the course, this chapter may be deferred until after the study of carbon and its compounds.

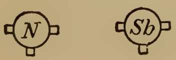
is hydrogen, and by it the valence of other elements is measured or determined. It may be illustrated in this way: suppose the first line represents the combining power of hydrogen, which is our standard. Then with this "yard stick" we will measure the combining power of the other elements. In water, H_2O, the valence of the oxygen atom is determined by applying the "yard stick," and is seen to be *two;* in NH_3 the standard is used three times, and the valence of the nitrogen atom is *three.* In the same manner the valence of the carbon atom is determined as *four.*

3. Suppose, however, hydrogen did not combine with carbon, could we still determine its valence? We are familiar with the compound, carbon dioxide. In this molecule, CO_2, the oxygen atom is used twice with the carbon atom, hence the latter must have twice the combining power of the oxygen. This has already been shown to be two, hence carbon would be four.

To illustrate roughly, we sometimes speak of the atoms as having a certain number of "bonds" or "poles of attraction," represented as below: —

Atoms with one "bond."

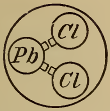
Atoms with two "bonds."



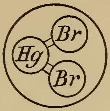
Atoms with three "bonds."

Atoms with four "bonds."

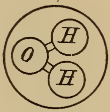
From this illustration it will be seen that an atom in the second group in combining would have two bonds by which to hold the two bonds of two individual atoms of the first.



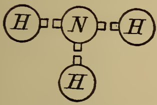
Lead Chloride.



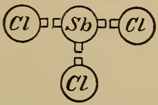
Mercuric Bromide.



Water.

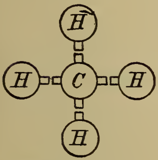


Ammonia.



Antimony Chloride.

N and Sb both have valence of *three*.



Marsh Gas.

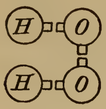
Silicon Dioxide.

C and Si, valence of four.

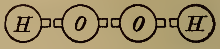
4. Such atoms as combine with one of hydrogen or its equivalent are said to be *univalent*, or are sometimes called *monads;* those which combine with two of hydrogen are *bivalent*, or *dyads;* with three, *trivalent*, or *triads;* with four, *quadrivalent*, or *tetrads;* with five, *quinquivalent*, or *pentads*.

5. Variation in Valence. — In studying a number of the compounds of any element it will be noticed that while the valence of the element in most of them is the same, there will be some compounds which show it to be different. Many of these are believed to be merely apparent exceptions and may be readily explained; while others, as yet not thoroughly understood, may be real variations. For example, the oxygen atom is always regarded as bivalent, yet we shall meet with the compound, hydrogen peroxide, H_2O_2, in which oxygen is apparently univalent.

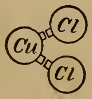
It is believed, however, that the atoms have an arrangement in the molecule which may be represented thus: —



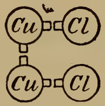
or



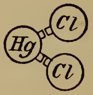
This simply means that one bond of each atom of oxygen is held by a bond of the other. In a similar way the apparent double valence of a great many other elements is explained. Thus copper and mercury, ordinarily bivalent, also form the compounds Cu_2Cl_2, and Hg_2Cl_2. But these are exactly parallel to the case above.



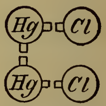
Bivalent.



Apparently Univalent.



Bivalent.



Apparently Univalent.

6. Again we shall study the two compounds of carbon, CO and CO_2, the first of which would indicate a valence of two for the atom, while in the second it would be four. The second is believed to show the true valence, and carbon monoxide is regarded as an *unsaturated* compound, that is, one in which the valence of the atom is not satisfied, or one in which a part of the bonds is not held by any other element. We may represent it thus: —

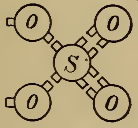
Saturated Compound.

Unsaturated Compound.

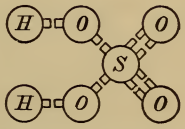
This theory is accepted because carbon monoxide very readily takes up one more atom of oxygen and forms the dioxide.

7. Double Valence. — In the examples of double valence, noticed above, the irregularity is only apparent. There are many cases, however, in which all the indications thus far would show that the valence of the atom is variable. Thus we have said the nitrogen atom is trivalent, and this is so in ammonia and nitrogen trioxide; but we shall also meet with nitrogen pentoxide, N_2O_5, in which the valence is five; the monoxide, N_2O, wherein it is apparently one, etc. There are many such variations that will trouble the student, but for our present work we shall need, as a rule, to aid us in writing formulæ and reactions, only a knowledge of the ordinary valence of the atoms.

8. Valence of Groups or Radicals. — We shall find also that many groups of atoms react in the same way as individual atoms; such groups are called *radicals*. They have combining power or valence just as individual atoms have. Thus when sulphuric acid reacts with zinc, we shall find that the group (SO_4) is not broken up; the same is true in hundreds of other instances. As it is combined with two atoms of hydrogen in H_2SO_4, and always does combine in the same way, we say its valence is two; this may be shown graphically in this way.

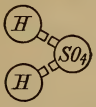


(SO_4) Group, showing two bonds unused.

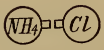


Sulphuric Acid, showing all bonds of the (SO_4) group saturated.

While we cannot prove that such is the arrangement of the atoms in the group, still it is believed to be true; at any rate it serves to illustrate how the valence of the group is two. In the same way we would show the valence of any other radical. In sal ammoniac, NH_4Cl, we find the group (NH_4) in combination with one atom of chlorine, hence its valence is one. Then if the radical (NH_4) combines with (SO_4), it must be used in the proportion of two of the former to one of the latter, thus $(NH_4)_2SO_4$.



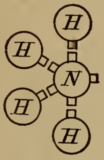
Sulphuric Acid.



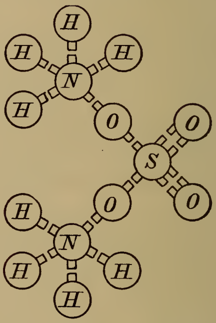
Ammonium
Chloride.

Ammonium
Sulphate.

Or we may show the same facts in this way : —



Ammonium, showing
one bond unused.



Ammonium Sulphate, showing how (SO_4)
can unite with two of (NH_4).

Exercise in Valence.* — Applying the principles set forth in the preceding paragraphs, let the student write the formulæ for the following : —

when Ba unites with I, Cl, Br, O, NO_3, CrO_4.
when Na unites with O, S, Cl, ClO_3, SiO_4, SO_4.
when Cu unites with Cl, S, SO_4, HO, O, I.
when NH_4 unites with I, PO_4, SO_4, S, HO, Br.
when Bi unites with Cl, O, S, NO_3, SO_4.

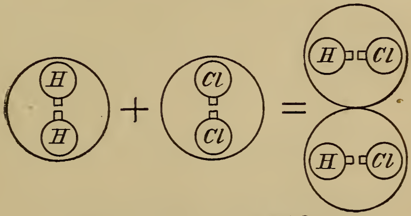
---

* Let the teacher give further exercises until the student can write with assurance the compound resulting from the union of any two of these elements or radicals.

The valence of each of the above and certain others is shown below: —

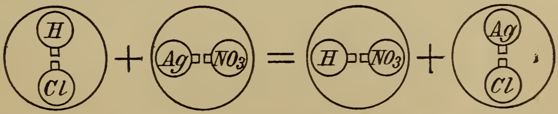
MONADS	DYADS	TRIADS	TETRADS
I	Ba	Sb	C
Br.	Zn	Bi	Si
Cl	Ca	As	(SiO_4)
F	Sr	(PO_4)	
Na	O		
K	Hg		
Li	Cu		
(NH_4)	Fe		
(NO_3)	S		
(ClO_3)	(SO_4)		
(HO)	(CrO_4)		

9. Equations. — We shall find later on that we are required often to write equations which represent the chemical action that takes place when two or more compounds are put together. We shall learn that chlorine and hydrogen, if put together in equal proportions, by a spark may be made to combine and form a compound body; we would represent this briefly as follows: —



or, $$H_2 + Cl_2 = 2\,HCl.$$

So if we put two compounds together, we would express the chemical action by a similar equation, thus: —

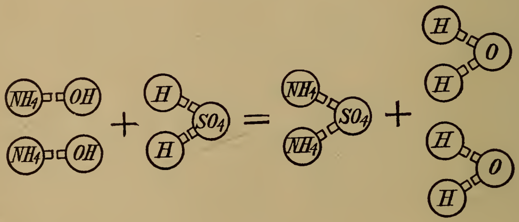


or, $$HCl + AgNO_3 = HNO_3 + AgCl.$$

It will be noticed that the first elements in the compound bodies have simply interchanged places. So, if we bring together ammonium hydroxide, NH_4OH, and sulphuric acid, H_2SO_4, we shall find a similar exchange, thus: —

$$2\,NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2\,H_2O,$$

in which we are compelled to use two parts of the NH_4OH because the group (NH_4) has a valence of only one, and there are two atoms of hydrogen in the acid to be displaced.



Exercises.* — In the same way let the student show by simple equations the changes which take place when the following compounds are put together: —

$NaBr + AgNO_3 =$

$Zn + H_2SO_4 =$

$NH_4OH + HCl =$

$HgCl + KI =$ $HgI + K$

$NH_4OH + HNO_3 =$

$Pb(NO_3)_2 + 2\,HCl =$

$BaCl_2 + H_2SO_4 =$ $BaSO_4 + 2\,HCl$

SUMMARY OF CHAPTER

Valence — Meaning of term.
Illustrations.
Classification of elements as to valence.
Synonymous terms for *univalent*, etc.
Variation in valence.
Apparent — Illustrations of.

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* Let the teacher add as many others as may seem necessary.

    Unsaturated compounds.
  Real — Illustrations of.
Valence of radicals.
  Illustrations.
Application of a knowledge of valence.
  Writing formulæ of compounds.
  Writing equations.

CHAPTER III

WATER : H_2O

1. Its Abundance. — Water is one of the most abundant substances known; it covers about three-fourths of the surface of the earth, besides existing in vast quantities in other forms. In the arctic regions in the form of an ocean of compressed snow it covers the entire surface of the land to a depth of many feet; in a similar form it caps all the loftiest mountain peaks from which great rivers of ice flow down the valleys until they are melted at the snow-line. In the form of vapor it exists in the atmosphere, invisible except when condensed in fogs, clouds, etc. In any given locality this moisture in the air varies largely at different times, but not often is there more than sixty-five per cent of what the air is able to hold. Even with this amount, however, it has been estimated that were the vapor in the air all condensed, it would form over the surface of the entire earth a layer of water five inches deep.

2. The human body is about sixty per cent water, and daily throws off through the pores and from the lungs over three pounds of moisture. Many vegetable articles of food contain eighty to ninety per cent of water, and some even more.

3. Water of Crystallization. — Water also exists in another form not so familiar as those already mentioned; that is, *water of crystallization.* A great many compounds in solidifying from their aqueous solutions take up a considerable amount of water. This does not exist in a free state like water in the pores of a sponge, or in a piece of soft wood that has been submerged for some time, but is in combination — crystallized in with the molecules themselves. Such substances in crystallizing cause the disappearance of a considerable amount of water, which may, however, usually be obtained again by subjecting the body to a greater or less degree of heat. Some astronomers even believe that the absence of water upon the moon may be accounted for by the fact that such bodies as those mentioned have taken it all up in crystallizing from their aqueous solutions. An idea of the amount contained by such substances may be gained from the following experiments.

Experiment 12. — Put into a test-tube a crystal of native gypsum and heat in the Bunsen flame. What do you see depositing upon the cooler portions of the tube? How is the crystal of gypsum affected? Repeat the experiment, using borax or alum instead of gypsum, and state results.

Experiment 13. — Expose to the air for several hours a crystal of ferrous sulphate. Notice its appearance before the exposure; how has it changed in the air?

4. Efflorescent Substances. — Many such substances as ferrous sulphate and copper sulphate, upon being exposed to an atmosphere more or less dry, give up all or part of their water of crystallization; at the same time they usually change in color and crumble to a powder. The process is the same as when the substances are heated, but not so rapid. By adding water to them the color is usually restored, and they crystallize as before. Such substances as these that give up their water of crystallization to the air are said to be *efflorescent*.

5. Deliquescent Substances. — There is another class of substances which have the power of abstracting moisture from the air or surrounding bodies, and of dissolving themselves either in whole or in part in this moisture. Such are called *deliquescent* bodies. A familiar example of these is common lime, which on being exposed to the air gradually takes up moisture, crumbles to a powder, and becomes "air-slaked." Another noted example is phosphorus pentoxide, a white solid formed when phosphorus is burned in the air or oxygen; also calcium chloride and caustic potash.

EXPERIMENT 14. — Put into a dry evaporating dish or beaker a small lump of fused calcium chloride and allow it to stand several hours or over night. Notice how it has changed. In the same way expose a small piece of caustic potash. Notice how rapidly it changes. Only a few minutes will be necessary in this case.

Common salt, stick candy, and some forms of taffy are very familiar examples of deliquescent bodies.

6. Distinguishing Characteristics of Water. — In the pure state, water is practically colorless, but when of great depth it is seen to be of a blue color. It is odorless and tasteless, but we are so accustomed to drinking impure water that when we use that which is distilled, or perfectly pure, it tastes "flat," just as unseasoned food does to those who are habituated to the use of salt, pepper, and other condiments. Pure water, on being evaporated to dryness, leaves no residue whatever, and this, in connection with the fact that it affects vegetable coloring matter in no way, is one method of testing it.

7. Solvent Powers of Water. — Pure water is seldom found, owing to its great solvent powers. To a greater or less extent it may be said to be almost a universal solvent. Even glass and similar substances immersed in water show appreciable loss after a considerable length of time. From this property result the various kinds of "hard" or mineral waters, medicinal, saline, etc. It is owing to the solvent powers of water, and the fact that evaporation leaves all mineral matter behind, that the ocean contains such vast quantities of different kinds of salt.

8. For example, in a hundred pounds of sea water, there are over three pounds of solid matter; of this the greater portion is common salt, but compounds of magnesium and calcium in the form of what are usually known as epsom salts and gypsum also occur. It has been estimated that if the ocean were of an average depth of one thousand feet, the common salt in solution would occupy a space of about three and a half million cubic miles, or a volume more than five times as great as that of the Alps. On this basis, if the depth of the ocean averages what is now claimed for it, the amount of salt surpasses in bulk our greatest mountain ranges.

9. Composition of Water. — By many of the ancients, water, along with fire and air, was regarded as an element; but about 1800 A.D. it was proved to be a compound body. There are two methods of proof, which taken together are quite conclusive.

The first proof is by *Electrolysis*.

Experiment 15. — Fill the tubes of the electrolytic apparatus shown in Fig. 3 with water slightly acidulated with sulphuric acid, the latter being added simply to increase the conductivity. Then connect the platinum electrodes with a strong battery. As the current passes through the water, bubbles of gas will be seen rising from the two strips of platinum, *P*, and from one of them considerably faster than from the other. It will be found that twice as much gas collects in one tube as in the other. These two gases, we shall learn before long, are hydrogen and oxygen. Open the stop-cock of the tube containing the greater amount of gas, and hold a lighted match to it; notice that it burns with a very pale flame. Test the gas in the other tube, using a pine splinter with a spark upon the end; notice that it bursts into a flame.

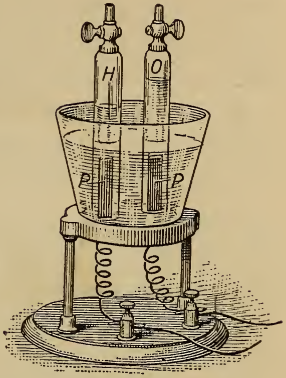

FIG. 3.

10. The second proof is by *Synthesis*.

EXPERIMENT 16. — Put into the eudiometer, Fig. 4, 8 cc. of oxygen, and twice as much or more hydrogen, the instrument being already partly filled with mercury, *M*. Hold the thumb over the open end and pass a spark from a galvanic battery. The two gases will combine with explosive force, producing water in the form of vapor. If the proportions were exactly two of hydrogen to one of oxygen, when the apparatus has become cool, there will be no gaseous residue, showing that the two unite in this proportion to form water. *A* in the figure is a cushion of air left to break the force of the explosion.

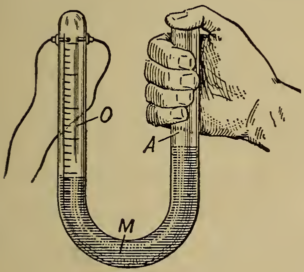

FIG. 4.

11. Conclusions. — From the above experiments we learn that water is the result of the union of two invisible gases, one of which burns with a pale flame, the other of which causes various substances to burn vigorously. We see also that from the union of the two gases, which together form a very explosive mixture, there results an exceedingly stable compound, which not only does not burn, but which has the power of quenching thirst and of overcoming the greatest fires. These two gases were given the names, *hydrogen* and *oxygen*.

12. We noticed also in the proof by analysis, that the hydrogen was given off in volume double that of the oxygen, and further, that in mixing the two gases for the synthetic proof we caused them to unite in the same ratio. From these experiments we may conclude that the composition of water by volume is two parts of hydrogen to one of oxygen, a fact which we represent by the expression H_2O.

13. Analysis by Other Methods. — The analysis of water may be effected by means other than electricity. For example, if a current of steam is made to pass through a tube containing charcoal or coke heated red hot, the steam is decomposed ; the oxygen combines with the carbon of the charcoal, forming an oxide of carbon, and at the same time the hydrogen is set free.

14. Synthesis by Other Methods. — In a similar way the synthesis of water may be effected. If a current of hydrogen is passed through a tube containing some metallic oxide, heated to redness, for example, copper oxide, the oxygen is removed from the compound by means of the hydrogen, and water is formed and may be collected.

EXPERIMENT 17. — Into *a* of the small bulb-tube put a little black oxide of copper, and weigh both tube and oxide carefully. Next fill a U-shaped tube with lumps of calcium chloride, weigh and quickly connect with the other tube. Now pass a current of hydrogen, generated as on

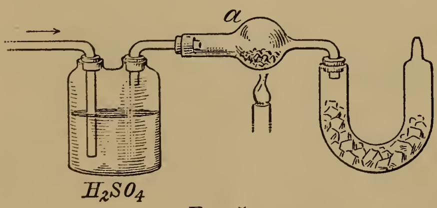

FIG. 5.

page 39, over the copper oxide, heated to redness. The hydrogen should first be dried by passing through sulphuric acid or over calcium chloride. After some time, disconnect the apparatus, and weigh the U-tube; the gain in weight will represent the amount of water produced. When the bulb-tube is cool, weigh it: the loss will represent the amount of oxygen removed. Subtracting the weight of the oxygen from the weight of water found will give the amount of hydrogen. Allowing for errors, this should give eight parts of oxygen to one of hydrogen, by weight.

From this experiment we are able to conclude as to the quantitative composition of water, just as by the others we learned of the volumetric. The action of hydrogen in thus removing oxygen from an oxide is called *reduction.*

$$\text{Water}\begin{cases}\text{By volume: Hydrogen, 2; Oxygen, 1.}\\ \text{By weight: Hydrogen, 1; Oxygen, 8.}\end{cases}$$

SUMMARY OF CHAPTER

Water — Various forms in which it occurs.
  Water of crystallization.
    Meaning of term.
    Examples of substances containing it.
    Proof of its presence by experiment.
  Efflorescent substances.
  Deliquescence — Meaning of term.
        Illustrations.
  Some special characteristics of water.
Composition of water — Proof of.
  a. By analysis — Details of work.
        Apparatus used.
  b. By synthesis — Explanation of process.
        Drawing of apparatus.
  Composition by weight.
    Proof by experiments.

CHAPTER IV

HYDROGEN : H = 1

1. **History.** — The term *hydrogen* is from two Greek words, which mean *water producer*, and the gas is so named because this element enters so largely into the composition of water. It was first isolated in quantities sufficient for experiment by Cavendish in 1766, and on account of its combustibility was called by him *inflammable* air.

2. **Where found.** — Hydrogen is seldom found uncombined, though its chemical affinity for most substances is not very marked. It exists abundantly in composition — water being the most important example ; it enters into nearly all organic compounds ; it is given off, together with other gases, by some volcanoes ; and by the spectroscope we know that it exists in the atmospheres of the sun and of some of the stars.

3. **Methods of obtaining Hydrogen.** — We have seen already in Experiment 15 that hydrogen may be obtained by the electrolysis of water. This gives a very pure gas, but does not produce it rapidly enough for ordinary experimental purposes. Just as electricity has the power of decomposing water, so do certain metals. When iron is exposed to moisture, we say it *rusts;* in reality, it takes up a certain amount of oxygen from the water and sets free a corresponding amount of hydrogen.*

---

* **Rust** is an oxide of iron ; that is, a compound of iron and oxygen, represented by the formula Fe_2O_3. The chemical change which

4. Decomposition of Water. — Again, there are some metals, like calcium, a constituent of common limestone, which have the power of decomposing water at the boiling point, setting free a part of the hydrogen and forming at the same time a compound, such as lime water. The chemical action may be expressed by the following equation : —

$$Ca + 2\,H_2O = Ca(OH)_2 + H_2.$$

5. There are two common metals, sodium and potassium, which decompose water rapidly at ordinary temperatures. Of these, the second acts much more violently, generating almost instantly sufficient heat to ignite the hydrogen given off from the water and volatilizing a portion of the metal itself. This is seen in the violet color which is imparted to the flame. That sodium is setting free a combustible gas in the same way may be shown by bringing a lighted match close to the metal, when the hydrogen will be ignited as it was spontaneously with potassium.

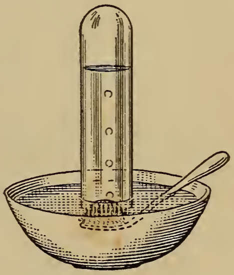
FIG. 6.

EXPERIMENT 18. — Fill a test-tube with water and invert it over a trough or basin of water, as shown in Fig. 6. Put into a wire gauze spoon, or wrap in a piece of flexible wire

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probably takes place when iron is thus exposed may be expressed as follows : —

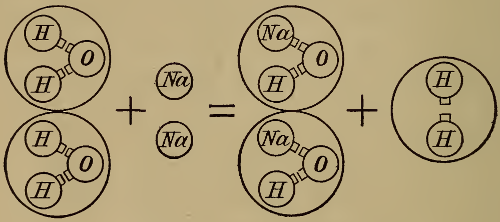
$$2\,Fe + 6\,H_2O = 6\,H + Fe_2O_3,\ 3\,H_2O,$$

in which Fe_2O_3 is rust. Likewise, if iron filings be heated red hot, and a current of steam slowly passed over them, the filings take up the oxygen from the steam and are converted into an oxide of iron, Fe_3O_4, differing somewhat from rust, while hydrogen is set free. The following equation expresses the chemical changes that take place : —

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2.$$

cloth, a small piece of sodium and hold under the mouth of the tube. Bubbles of gas will rapidly form, will rise into the tube and displace the water. Test the gas obtained to see whether it acts as did the hydrogen obtained by electrolysis in Experiment 15. Does it seem to be the same kind of gas? Sometimes, before putting the sodium into water, it is treated with a small quantity of mercury, whereby the rapidity of the action is greatly decreased.

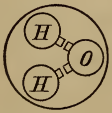
6. Caustic Soda. — The chemical change which has taken place in the above experiment may be expressed as follows: —



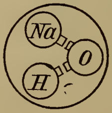
or, as it is usually and most simply written, —

$$H_2O + Na = NaOH + H.$$

The graphic equation above shows that in each molecule of water one atom of the hydrogen is replaced by one of sodium, represented by Na, and that thus a new compound, NaOH, called caustic soda or sodium hydroxide, is formed. In other words, the water molecule becomes one of caustic soda, thus: —



becomes



7. Tests to show Change. — We can easily prove that the solution has acquired new and very different properties. Dip into it a strip of red litmus paper, and the paper is instantly turned blue; or add to it one drop of a solution of phenol phthalein, and the whole will turn a beautiful red.

8. Other Methods of obtaining Hydrogen. — The above methods of obtaining hydrogen, while of interest, are too expensive where considerable quantities are needed for experimental work. All acids contain hydrogen, and just as some metals decompose water, so certain others act with acids. .

9. Laboratory Method. — In obtaining hydrogen for laboratory purposes this is the plan usually pursued. The metal used is generally iron or zinc, and the acid, sulphuric or hydrochloric.

Experiment 19. — Fit to a flask a cork doubly perforated. Through one of the holes insert a delivery tube, and through the other a thistle tube which extends nearly to the bottom of the flask. Put into the flask several pieces of granulated zinc made by pouring the metal in a molten condition into cold water. Add water until the zinc is nearly covered, and then pour in slowly a small quantity of strong sulphuric acid. After allowing the first gas which comes over to escape, because it is mixed with air, collect several bottles over water as described on page 362 and preserve for experiments a little later. The action may be hastened by adding a little copper sulphate to the flask a few minutes before the acid is introduced.

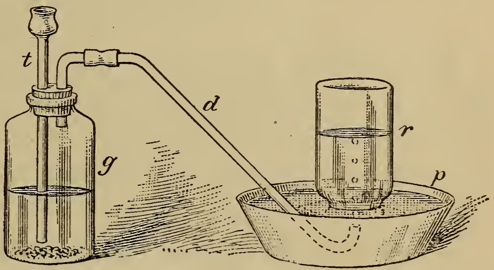
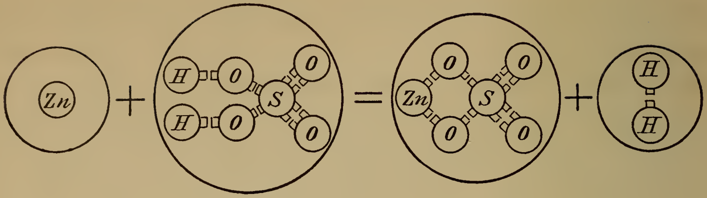


Fig. 7. — Hydrogen Apparatus.

p = pan.
g = generating flask.
t = thistle tube.
r = receiving flask.
d = delivery tube.

10. Results of the Experiment. — The chemical change that takes place in the above preparation of hydrogen may be graphically represented as follows: —



From this it is seen that the atom of zinc has driven out or replaced two atoms of hydrogen in the sulphuric acid, H_2SO_4, and has entered into combination, while the two hydrogen atoms have been set free and now exist as a hydrogen molecule; further, it is seen that the sulphuric acid has been converted into a compound known as zinc sulphate. Usually we express these facts thus: —

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Zinc sulphate is a white compound which collects upon the zinc, and would soon cover it so completely as to stop the chemical action; the water, however, being added dissolves it as fast as formed, and leaves a clean surface exposed to the acid.

11. Method of obtaining Large Quantities.—When hydrogen is desired in very large quantities, as in filling balloons, iron, being cheaper, is used instead of zinc. The gas thus obtained is somewhat less pure, but it is not on this account specially objectionable. Large vessels or retorts are used, which are lined with lead, a metal which is not affected by dilute sulphuric acid. The hydrogen obtained is passed through water and lime to purify it, after which it is transferred to the balloon.

12. Mond's Method. — This method, although it has thus far been used only to a limited extent, promises to give satisfaction. We have seen that when steam is passed over red-hot charcoal the former is decomposed just as when passed over red-hot iron (page 37) and two similar products are formed, both gases; thus, —

$$H_2O + C = H_2 + CO.$$

The apparatus may be represented conventionally as follows: —

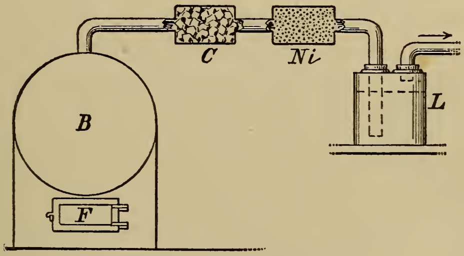


FIG. 8. — Mond's Method.

F is a furnace, *B* the boiler in which the steam is generated, *C* a tube containing lumps of coke which are heated red hot by a gas furnace beneath, *Ni* a tube containing powdered metallic nickel, *L* an apartment containing lime water. The steam passing through *C* is decomposed as stated above; the mixture of hydrogen and carbon monoxide formed here passes over the nickel, also heated red hot. In this tube a part of the carbon unites with the nickel, and carbon dioxide is formed. This mixed with the hydrogen passes on through the "washer" *L*, containing lime water, which absorbs the carbon dioxide, leaving the hydrogen comparatively pure. The reactions in the different parts of the process may be shown as follows: —

$$H_2O + C = H_2 + CO \text{ (in the coke tube).}$$

$$H_2 + 2\,CO + Ni = NiC + H_2 + CO_2 \text{ (in the nickel tube).}$$

$$H_2 + CO_2 + Ca(OH)_2 = H_2 + CaCO_3 + H_2O \text{ (in the ``washer'').}$$

The nickel carbide formed is readily converted back again into metallic nickel by heating in the air, so that it may be used over and over.

13. Characteristics of Hydrogen. — The following experiments will illustrate well the most striking peculiarities of hydrogen: —

EXPERIMENT 20. — Remove one of the bottles of hydrogen from the water, keeping it inverted, and thrust up into it a burning candle. Notice whether the candle continues to burn in the gas; notice also what happens as you remove it again. Can you see anything burning at the mouth of the bottle?

EXPERIMENT 21. — To show the lightness of hydrogen. Bring a bottle of the gas, *a*, mouth downward, up close to another inverted bottle, *b*, of about the same size. Then gradually tip the hydrogen bottle, *a*, as shown in Fig. 9, just as you would pour water from one vessel into another, only in a reverse order. Now test both bottles to learn which contains the hydrogen. State the results.

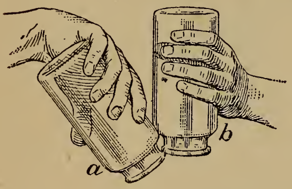


FIG. 9. — Upward Decantation.

EXPERIMENT 22. — Start the generator again, and replace the delivery tube with one which has been drawn to a fine jet. Let the gas flow a few minutes until the air is all expelled, and then ignite it.

14. CAUTION. — A mixture of air and hydrogen is *very explosive*, and before lighting the jet a towel should be wrapped about the generating flask. It will do equally well to inclose the flask in a pasteboard box as shown in the figure.

When first lighted, how does the hydrogen burn? How does it soon change? This is due to the sodium in the glass, which colors the flame. A burning jet of hydrogen is sometimes called the "philosopher's lamp." Does the gas burn with much heat? Hold a clean dry bottle or test-tube over the flame. Do you see any deposit forming upon the upper part of the tube? What is it? Now try several tubes and bottles of different sizes in the same way; notice the different pitch of the "singing tones" produced. When the tube is thus sounding, notice the flame carefully. Can you explain the tones produced?

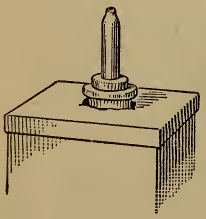


FIG. 10. — Hydrogen Jet in Box.

Experiment 23. — Allow a jet of hydrogen from a generator working rapidly to strike against a platinum sponge. State the results.

Experiment 24. — The hydrogen pistol shows the explosiveness of a mixture of air and hydrogen.* Load the pistol by pouring into it a small bottle of hydrogen, as shown in Experiment 21, and fire by bringing a flame to the touch-hole. A loud explosion should follow.

Experiment 25. — Hydrogen soap-bubbles — to show lightness of hydrogen. For success in this experiment a good soap solution is necessary. To a little soft water add a few shavings of castile or other good soap, and when dissolved add about one-third as much glycerine as soap solution. Shake well. Now attach to a delivery tube, from which is flowing a current of hydrogen, a clay pipe, or even an ordinary spool; dip into the soap solution, and let the bubble form in the usual way. Detach from the pipe by a gentle jerk and notice whether the bubble rises or falls. Touch a light to one of the bubbles. What happens? This experiment is sometimes made more striking by filling the bubble with a mixture of hydrogen and oxygen, which, when touched with a flame, explodes violently.

15. CAUTION. — The greatest care must be taken to avoid bringing the flame near the delivery tube, lest the whole mixture be exploded with serious results.

Experiment 26. — To show the presence of hydrogen in oils, alcohol, etc. We have already seen that when hydrogen burns, water is produced. This is true whether we have hydrogen free, or in the form of compounds. Light a small candle and hold over it a cold beaker. Notice the water condensing upon the cooler portions of the beaker. In the same way try a small spirit lamp. State the results.

16. Conclusions from our Work with Hydrogen. — By the above work with hydrogen we have learned that it is a colorless gas; is without odor if pure, and very light.

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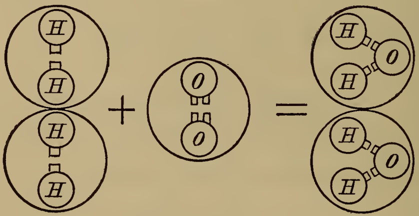
* The pistol may easily be made from a small tin can. With an awl punch a hole in the side of the can near the bottom, and for a bullet use a cork snugly fitted to the mouth of the can. When a light is brought to the touch-hole, several seconds may elapse before the explosion follows, but the experiment almost invariably succeeds.

Its density is but little more than one-fifteenth that of air. It is this which causes it to diffuse so rapidly, and renders it valuable for filling balloons. A liter of the gas weighs .0896 g. It is very inflammable, and burns with a pale, almost non-luminous flame. As noticed above, the hydrogen flame from a glass jet has a yellow color, but this is due to a compound of sodium in the glass, just as the hydrogen arising from the sodium on the water burned with a yellow flame. The heat of this flame is intense, as is seen by the rapidity with which the glass jet becomes red hot. When hydrogen burns in the air or in oxygen, water is the only product, the union being expressed by the following equation: —



or, $2\,H_2 + O_2 = 2\,H_2O$.

17. Combination of Hydrogen with Other Substances. — The explosiveness of hydrogen when mixed with oxygen has already been noticed. One of its most remarkable properties is that of being absorbed or *occluded* by certain metals. By finely divided platinum the absorption is so rapid that the metal becomes red hot, and the jet of hydrogen is quickly ignited. Likewise, if a piece of spongy platinum be lowered into a mixture of hydrogen and oxygen, the rapid absorption in a short time causes sufficient heat to explode the mixture.

At the usual temperature, hydrogen has very little affinity for most substances. As will be seen in Experiment 65, it explodes violently when mixed with chlorine, either on the approach of a strong light or by means of a spark. It unites vigorously with oxygen also on the application of a flame, but a light has no effect.

18. Liquid Hydrogen. — Hydrogen is one of the most difficult gases to reduce to the liquid condition. This has been accomplished, however, by reducing the temperature to −205° C., and allowing it to escape rapidly from a pressure of 180 atmospheres into a vacuum. At the same time this space is surrounded by a temperature of −200° C. Considerable quantities have been obtained in this way. In April of the year 1900, Dewar even succeeded in solidifying the gas. He surrounded liquid hydrogen with liquefied air, and then by a pump caused so rapid an evaporation of the hydrogen that he soon obtained the remainder in a white, opaque solid.

19. Uses of Hydrogen. — As a gas it has but few practical uses. Its suitability for filling balloons has been mentioned, but in such cases it is generally used in a very impure form, mixed with various hydro-carbons given off with the hydrogen in the later distillation of coal. In the *nascent* state, that is, at the instant it is set free from some compound, it has great chemical activity and has the power of reducing many metals from their compounds. This use has already been seen in the passage of hydrogen over copper oxide, and will be further illustrated in our work with silver, iron, and other metals.*

---

* The use of hydrogen in an automatic cigar-lighter is occasionally seen. As shown in the figure, a small glass cylinder has a cubical block, *a*, of porcelain in the bottom: upon this rests an inverted glass cylinder, *c*, with a tubular neck and stop-cock, *s*; above this jet is supported a platinum sponge, *p*; under the small cylinder upon the porcelain block is

SUMMARY OF CHAPTER

- Hydrogen — Origin of term and meaning.
- Occurrence of hydrogen.
- Methods of making hydrogen.
  - By decomposing water.
    - With sodium or potassium.
    - Describe method and apparatus.
    - Chemical action — Proof of, by experiment.
  - By decomposing acids.
    - With zinc.
    - Draw apparatus and explain method.
  - Commercial methods.
    - For filling balloons.
- Characteristics of hydrogen.
  - Experiments to illustrate.
    - Density.
    - Inflammability.
    - Explosiveness, etc.
  - Liquid hydrogen.
- Uses of hydrogen.
- Special points.
  - Explain the hydrogen pistol.
    - Philosopher's lamp.
    - Singing flame.

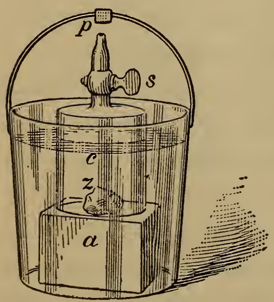


Fig. 11.

placed some zinc, *z*, and in the outer cylinder diluted sulphuric acid. As the acid and zinc react upon each other, hydrogen fills the inverted cylinder, forces out the acid, and the action ceases. If now the stop-cock is opened, the hydrogen flows out of the jet, the acid reënters, and the generation of gas continues. As already seen, the hydrogen jet is quickly ignited by the platinum. When the customer has lighted his cigar, the stop-cock is again turned, and the action soon ceases. It ought to be said, perhaps, that such apparatus is of more interest as a novelty than as of real lasting utility.

CHAPTER V

OXYGEN, COMBUSTION, OZONE

Oxygen: O = 16

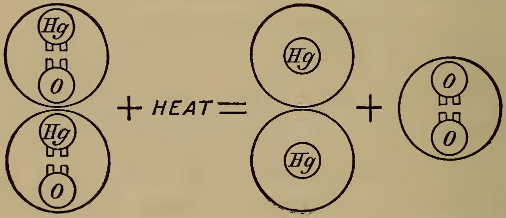
1. Its Discovery. — The term *oxygen* is derived from two Greek words, meaning *acid-former*, and was given to this element because it was believed to be essential to the production of all acids. Oxygen was discovered by Scheele in 1773, but he did not publish his discovery until 1775; and as in the meantime Priestley had isolated the same gas and had published an account of his experiments, the latter is generally given the credit.

2. Abundance of Oxygen. — Oxygen is found in the atmosphere in large quantities, uncombined, constituting about one-fifth of the whole. It has been estimated that there is in the atmosphere alone over two and a half million billions of pounds. A liberal estimate of the amount used annually in respiration, and all forms of combustion, is about two and a quarter billion pounds. At this rate, in a century the entire world would use only one ten-thousandth part of the whole. At the same time it must be remembered that plant life is pouring the oxygen back again into the air, so that there is no danger of the equilibrium being destroyed. Oxygen also forms by weight eight-ninths of water, and being absorbed by the same, exists therein in considerable quantities in a free state. It is this free oxygen which is breathed by fishes. On account of its great affinity for other substances, it is found in combination with nearly all known elements, and forms in this way about 45 to 50 per cent of the earth's crust.

3. How to produce Oxygen. — As a matter of historical interest, the method employed by Priestley is still sometimes used. It is as follows: —

Experiment 27. — Place in a hard-glass test-tube about a half gram of mercuric oxide, HgO, and heat strongly. Notice the change in the appearance of the oxide. Insert into the tube a pine splinter with a spark upon the end. What happens? What do you notice collecting upon the sides of the tube? What substances have therefore been obtained by heating this oxide?

4. Explanation. — The heat used has served to decompose the molecules of mercuric oxide into their constituent parts, thus: —



or,
$$2\ HgO + heat = 2\ Hg + O_2.$$

The two molecules of red oxide of mercury have yielded two molecules of mercury, one atom in each, and one molecule of oxygen, having two atoms. By continuing the operation the entire amount of the red oxide would disappear, while the deposit of mercury upon the sides of the tube would gradually increase.

5. Other Methods of obtaining Oxygen. — The above method, though of interest, furnishes too limited a quantity of oxygen for practical purposes. A better and more common way is to heat potassium chlorate, $KClO_3$, with manganese dioxide, MnO_2.

EXPERIMENT 28. — Mix together in a good-sized test-tube, or small flask, 1 or 2 g. of potassium chlorate and half as much manganese dioxide. Support upon a ring-stand with a wire screen protection, as shown in the accompanying figure, and attach the cork and delivery tube. Heat gently at first, and then more strongly, but moderately, so as to regulate the flow of gas and not let it become too rapid. Allow the first that comes over to escape, then collect several bottles of the gas over water as you did the hydrogen, and use for the following experiments. Save the contents of the flask for further use.

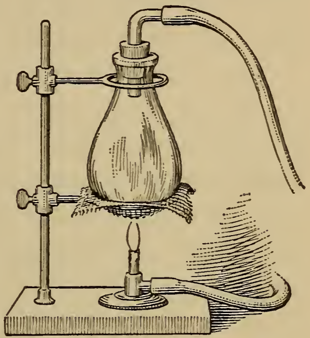


FIG. 12.

EXPERIMENT 29. — Slip a sheet of glass or paper under a small bottle of oxygen, and place it in an upright position upon the table. Now plunge into the oxygen a taper, or pine splinter, with a spark upon it. Do you obtain the same results as before in the case of the oxide of mercury?

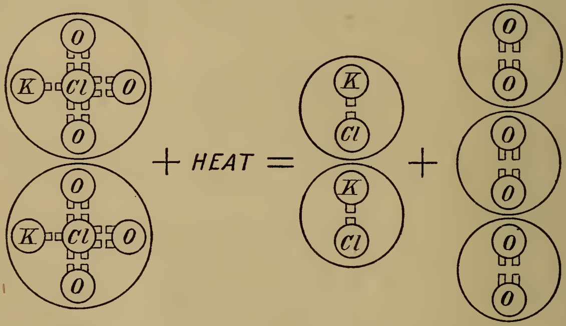
EXPERIMENT 30. — Into another bottle of oxygen lower a deflagrating spoon containing some burning sulphur; does it burn any differently than in the air? If no deflagrating spoon is at hand, the student can prepare one by hollowing out the end of a short stick of gas carbon, or of crayon, and attaching a wire handle of suitable length.

EXPERIMENT 31. — Fasten a piece of soft or bark charcoal to a stout iron wire, hold it in the burner flame until it begins to glow, then plunge into a jar of oxygen. If the charcoal is soft, the results will be very striking. Describe them.

EXPERIMENT 32. — Twist together three or four fine iron wires, fasten to the end a small pine splinter, or warm and dip into sulphur and ignite. Plunge quickly into a large jar of oxygen which contains about an inch of water in the bottom. Describe the results. Do you see anything falling to the bottom of the bottle? A knife-blade or watch-spring may be thus burned, by first drawing the temper and using a larger amount of kindling material.

Experiment 33. — Put into a deflagrating spoon a small piece of phosphorus, ignite it, and thrust into a large jar of oxygen. Describe the combustion and the fumes that fill the jar. These are phosphorus pentoxide, a substance mentioned under *deliquescent* bodies.

6. The Chemical Action. — In preparing oxygen as above from potassium chlorate and manganese dioxide, the latter remains unchanged at the close of the experiment. What has really taken place, then, is the same as in the use of the mercuric oxide. The heat has simply decomposed the molecules of potassium chlorate, setting free the oxygen and leaving behind a new compound containing only potassium and chlorine, called potassium chloride. The change may be shown thus: —



The two molecules of potassium chlorate shown here have each given up three atoms of oxygen, which have combined to form three molecules of oxygen, while two molecules of potassium chloride remain behind. These facts are more usually written thus: —

$$2\ KClO_3 + \text{heat} = 2\ KCl + 3\ O_2.$$

7. Effect of the Manganese Dioxide. — If potassium chlorate be used alone, instead of mixing with manganese dioxide, as we did above, the same results are obtained, but considerably more heat is required. Apparently, therefore, manganese dioxide has simply acted *by its presence*, or, as it is called, by *catalysis*. It is believed, however, that the dioxide is first converted into another compound, which at the temperature present is unstable, and that this in breaking up yields oxygen and the dioxide again.

EXPERIMENT 34. — To prove that the manganese dioxide remains unchanged and that potassium chloride is formed. To the residue in the flask in Experiment 28, add about 50 cc. of water, let it stand a few minutes, shaking occasionally, warm gently and then filter. Boil this clear filtrate to dryness in an evaporating dish. While this is proceeding, add a little water to the black residue on the filter paper once or twice to wash it, throw the water away, and let the black residue dry. When the solution in the evaporating dish is perfectly dry, scrape it out, mix with a little fresh manganese dioxide, transfer to a test-tube, and heat. Do you observe any indication of oxygen being given off? If not, we may conclude under the present circumstances that the oxygen was all removed in the previous heating, and that the white solid residue is KCl, potassium chloride, and not potassium chlorate, $KClO_3$.

When the black residue on the filter paper is dry, mix with it a little potassium chlorate, transfer to a test-tube and heat. Is oxygen given off readily? What proof? Is there any reason for believing that the black residue is still manganese dioxide?

8. The Proof by Weighing. — It will be well to try an experiment by which the facts discovered in preceding experiments may be proved. Such is the following experiment.

EXPERIMENT 35. — Put into a test-tube or flask about a gram of potassium chlorate, put it upon the scales and balance it with shot or sand in a small box. Now add about a half gram of manganese dioxide, and then weigh carefully. As the box and shot counterbalance the flask and potassium chlorate, the weights added show at once the amount of dioxide used. Now connect a delivery tube and heat to drive off the oxygen. When the operation is complete, known by the fact that the gas no longer bubbles up through the water, remove the delivery tube from the water, and let the flask cool. When cold, add a few cubic centimeters of water to dissolve the potassium chloride, then filter and wash the black residue as before. When *thoroughly* dry, weigh the residue and filter paper and subtract the weight of the paper. The latter may be obtained by weighing ten of them, or, if the balance is not very delicate, a hundred, and then taking the fractional part. Does the weight of the black compound now agree with its weight before heating?

9. Commercial Methods of making Oxygen. — Most of these methods consist in abstracting oxygen from the air by using a substance which when heated or when under pressure will absorb oxygen, and then when cooled or when the pressure is removed will again give it up. One of the best known of these methods is *Brin's*, which consists in using barium oxide, BaO, as the chemical agent. When gently heated in the air, it takes up an additional amount of oxygen, forming barium dioxide, BaO_2, thus, —

$$BaO + O = BaO_2.$$

If, now, the heat is increased, the barium dioxide is unable to retain the additional atom of oxygen taken from the air and gives it up again, thus, —

$$BaO_2 + \text{heat} = BaO + O.$$

Or, if the pressure under which the barium dioxide was formed is decreased, the same results follow at considerably less expense.

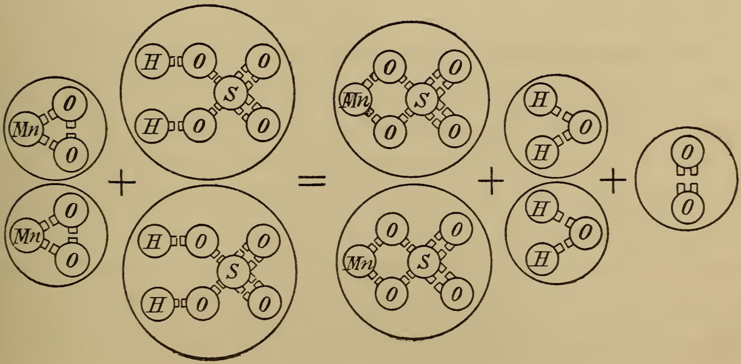
10. Motay's Method. — The principle of this is about the same as that of Brin's, but different substances are used. Manganese dioxide and caustic soda, when heated moderately in a current of air, form a compound which at a higher temperature is again decomposed, yielding up the oxygen previously taken from the air.

11. Other Methods. — These are not important as a means of producing oxygen for commercial or experimental purposes, but the principle underlying them is involved in a number of the processes of chemistry with which we shall deal later, and should consequently be understood. It will be noticed that in all the methods of preparing oxygen used above, we have employed substances containing a large per cent of that element. There are several other substances of similar composition which may be made to furnish oxygen. Thus, manganese dioxide, MnO_2, potassium dichromate, $K_2Cr_2O_7$, and potassium permanganate, $KMnO_4$, when heated with sulphuric acid, H_2SO_4, will yield oxygen.

Experiment 36. — Put a half gram of manganese dioxide into a test-tube and add about a cubic centimeter of sulphuric acid. Warm gently, collect a small bottle of the gas, and make the usual test for oxygen. What are the results?

It will be found that the dichromate and the permanganate act in a similar way, except that the quantity of gas obtained is considerably greater. The chemical action may be shown thus: —

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$



In a similar way the reaction of potassium dichromate and sulphuric acid upon each other may be shown;

$$K_2Cr_2O_7 + 4\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,O,$$

and of potassium permanganate and sulphuric acid,

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O.$$

See pages 322, 325, for application of this property of the above substances.

12. Characteristics of Oxygen. — Oxygen is an odorless, colorless gas, a little heavier than air, the weight of a liter being 1.43 g. As already noted it is slightly soluble in water, and upon this fact depends the life of aquatic animals, which abstract this free oxygen from the water. It may be liquefied by extreme cold and pressure. This was first accomplished about a quarter of a century ago by Cailletet and Pictet, who succeeded in preparing a small quantity at great cost. At present it is made in almost any amount by first liquefying air and then allowing the nitrogen to boil out. (See page 100.)

13. Peculiarities of Liquid Oxygen. — In the liquid condition oxygen is of a pale blue color and boils at about − 180° C., a few degrees higher than the boiling point of nitrogen. It presents many striking peculiarities; a rod of carbon heated red hot and plunged into the liquid oxygen at a temperature 180° below zero burns vigorously, while a stout iron wire similarly heated is rapidly consumed with a brilliant display of sparks. Cotton rags saturated with it and confined in a cylinder, when ignited, explode so violently as to burst tubes made of iron or brass.

14. Chemical Affinity of Oxygen. — The strongest chemical property of oxygen is its affinity for other substances. This was seen in the rapidity of combustion of the various ignited substances when placed in an atmosphere of oxygen. From these experiments it is not difficult to see what would be the results were the air undiluted oxygen. The smallest spark would be sufficient to start the fiercest conflagration, while our stoves, furnaces, etc., would be rapidly consumed, accompanied by a most brilliant display of sparks.

15. Uses of Oxygen. — As is well known, oxygen is absolutely necessary for life. It is absorbed by the blood through the walls of the air-cells of the lungs and carried by the red corpuscles to all parts of the body. Here it unites with the waste material, burning it to carbon dioxide and other compounds, and at the same time warming the body. The carbon dioxide is carried back to the lungs, from which it is thrown off into the air. In cases of asphyxiation pure oxygen is sometimes used as a restorative, but ordinarily, if breathed for any length of time, the temperature of the body rises owing to the increased destruction and consumption of tissue, and general feverish symptoms follow. A limited number of experiments by the author show that small animals, such as mice, when placed in an atmosphere of pure oxygen soon exhibit great activity, followed by apparent relaxation and complete exhaustion. Experiments have also shown that animals in oxygen under pressure would very quickly die, as if the gas in this condition were an active poison.

EXPERIMENT 37. — Into a hard-glass tube, *T*, the weight of which is known, supported in a ring-stand as shown in Fig. 13, put 2.5 g.

of potassium chlorate. Let the tube, *f*, just reach through the cork of *A*, while the tube, *c*, extends nearly to the bottom. *B* needs no cork, but those in *A* and *T* should be of rubber and fit air-tight. Heat the contents of the tube gradually and then strongly until the water is no longer forced from *A* into *B*. Allow the tube to cool, and weigh. The loss will represent the oxygen expelled. Measure carefully the water in *B*. This will represent the volume of oxygen at the pressure and temperature of the room. For methods of reducing this to standard conditions, see page 96.

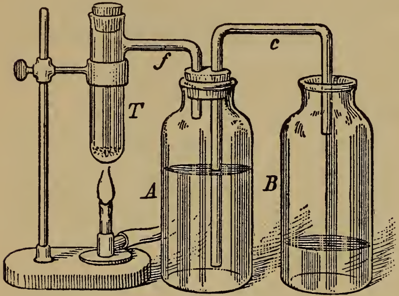


Fig. 13. — Apparatus to use in finding the Weight of Oxygen.

Suppose the tube weighs 15 g.; then

$$\text{tube} + KClO_3 = 17.5 \text{ g., before heating;}$$

$$\text{tube} + KCl = m \text{ grams, after heating;}$$

$$17.5 - m = \text{wt. of oxygen expelled.}$$

Volume of H_2O in $B = n$ cc., or what is the same, n cc. of oxygen at existing temperature and pressure, and by calculation, n', at standard conditions. Then n' cc. weigh $(17.5 - m)$ grams, from which the student can easily find the weight of one liter or 1000 cc. This should be 1.43 g. Let the student determine what is his per cent of error.

By similar methods, the weight of a liter of various other gases, insoluble in water, may also be determined.

16. Oxidation and Combustion. — When any substance combines with oxygen to form a new compound, it is said to be oxidized, and the process is known as *oxidation*. This may be slow or rapid. When it takes place so rapidly as to be accompanied by heat and light, the process is called *combustion*. To illustrate: when a piece of iron is exposed to the air in the presence of moisture, it soon becomes covered with *rust*, which is really an oxide of iron; in other words, the iron has been *oxidized.* Again, when we tipped the iron wires with sulphur and ignited it, they were rapidly consumed in the jar of oxygen with much heat and considerable light. This was *combustion.* A pile of brush will gradually decay, or oxidize, without any perceptible heat, but by setting it on fire we quickly destroy it by the process of combustion.

17. Combustible Substances and Supporters of Combustion. — Substances which thus burn in oxygen or its diluted form, the air, are said to be *combustible*, while the substance in which they burn is called a *supporter* of combustion. Thus, when a jet of hydrogen burns in a jar of oxygen, the former would be spoken of as the combustible substance, and the latter as the supporter of combustion. It is true, however, that if we thrust a delivery tube from which a current of oxygen is issuing, up into a jar of hydrogen which is burning at the mouth, as seen in Fig. 14, the jet of oxygen will be seen to burn in the atmosphere of hydrogen, just as before the hydrogen did in the oxygen. Yet in view of all the facts it seems better to adhere to the statement previously made, that it is really the hydrogen which burns, and the oxygen which supports the combustion.

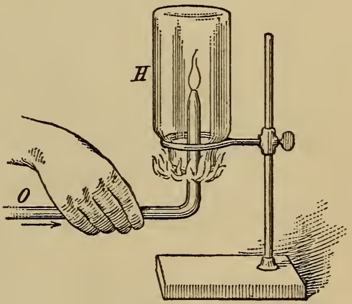


Fig. 14.

18. Kindling Temperature. — It is well known that some substances ignite much more readily than others. This, chemically speaking, simply means that some combine with oxygen at a lower temperature, or much more readily, than do others. Thus, substances like alcohol and many oils need but little heat to ignite them; phosphorus, likewise. Pine wood needs a higher temperature, and hard wood still higher. The point at which any substance takes fire is said to be its *kindling temperature.*

19. What is a Flame? — A flame is simply burning gas. Whenever a substance will not burn with a flame, it is because there is either no gas present or there is nothing which may be converted into a gas. For example, when a lamp burns, the oil drawn up through the wick by capillary attraction is volatilized by the heat, and it is the burning of this gas that makes the flame. On the other hand, charcoal and the hardest natural coals do not burn with a flame, because previous heating has driven out all the gaseous products. However, they may be heated sufficiently to be partially converted into carbon monoxide, a gas which burns with a pale blue flame.

20. The Oxy-hydrogen Blowpipe. — This is a lamp arranged for burning hydrogen thoroughly mixed with oxygen, and affords one of the hottest flames known. Its construction will be understood from the figure, which gives a sectional view. The inner tube, *m*, is connected with the oxygen tank, and the outer, *n*, with the hydrogen. In this way, as the inner tube is somewhat shorter, the gases become thoroughly mixed before leaving the tube at *E*, hence the combustion is perfect. The pressure should be so regulated as to furnish twice as much hydrogen by volume as oxygen. This blowpipe is used for melting very refractory substances. It is also used espe-

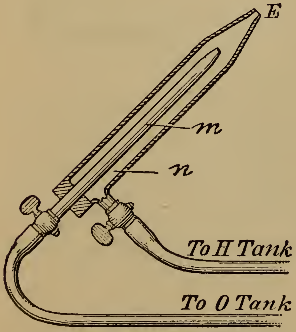


FIG. 15. — The Oxy-hydrogen Blowpipe.

cially in furnishing light for stage effects, stereopticon views, and for illuminating moving floats in street parades given after dark. When used for these purposes the almost non-luminous blue flame is allowed to strike upon a stick of prepared lime supported in a socket just in front of the blowpipe. This is often called the calcium or Drummond light, and is of dazzling whiteness, rivaling the electric arc light.

OZONE

21. Its Discovery. — This substance, on account of its peculiar odor, was named from a Greek word which means *to smell.* It was first observed in passing electrical sparks through a tube of oxygen, and is always noticeable when an electric discharge takes place in the air.

22. What is Ozone? — For some time it was regarded as a compound body, but is now known to be simply a condensed form of oxygen. Quite a number of substances, such as sulphur and phosphorus, appear in a form other than the usual one: this is known as the *allotropic*, a word which means simply *another form.*

23. Methods of obtaining Ozone. — It is impossible to prepare ozone in large quantities in a pure condition, because by the best methods only a small per cent of the oxygen used is converted into its allotropic form. Usually not over one or two per cent is obtained, and under the most favorable circumstances only about twenty per cent. In the ordinary methods of making oxygen, ozone is almost always obtained in appreciable quantities. One of the easiest methods of preparing it is given in the following: —

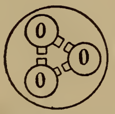
EXPERIMENT 38. — Scrape a stick of phosphorus perfectly clean, put it into a bottle, and add water sufficient to cover about half of it. In a few minutes the presence of ozone may be detected by suspending in the bottle a strip of white paper moistened with a solution of potassium iodide and starch. The paper will turn decidedly blue. A solution of potassium permanganate treated with strong sulphuric acid also gives the test for ozone, along with the oxygen thus evolved.

24. Ozone in the Air.—Ozone is believed to exist in appreciable quantities in the atmosphere, being produced mainly by electrical discharges. Its presence in dwellings is never perceptible, and scarcely ever in large cities, but in the country a strip of starch paper exposed to the breeze for some time shows the characteristic blue color.

25. How Ozone differs from Oxygen.—As already stated, it is a condensed form of oxygen. Experiment has shown that if a given amount of ozone is decomposed so as to form ordinary oxygen, the volume increases one-half; that is, 100 cc. of ozone would become 150 cc. of oxygen. On the other hand, if a closed volume of oxygen be subjected to a silent discharge of electricity so as to convert a portion of it into ozone, a corresponding decrease of volume takes place.

26. For example, suppose 150 cc. of oxygen be thus treated, and that 30 cc. are converted into ozone. It is found that by absorbing this ozone so as to separate it from the remaining oxygen, and again setting it free, there are only 20 cc. of ozone, while but 120 cc. of oxygen remain. If, however, this 20 cc. of ozone be heated strongly, so as to convert it into oxygen again, we shall find the volume increases to 30 cc. The molecule of ozone therefore would differ from that of oxygen, in that it contains three atoms of oxygen, while the other has only two. This is shown in the accompanying figure.

Molecule of Oxygen.



Molecule of Ozone.

From this it naturally follows that ozone is 50% more dense than oxygen.

27. Properties of Ozone. — The properties are also different from those of oxygen. Its odor has already been mentioned. If placed in a long glass tube, so as to give considerable depth, it is seen to have a blue tinge. It readily destroys the color of such vegetable solutions as indigo and litmus and quickly attacks such metals as mercury and silver, which remain unchanged in the air and which are even unaffected by oxygen when heated. We have seen its effect upon potassium iodide above. Free iodine always turns starch blue. In the test made, the ozone united with the potassium in the potassium iodide to form an oxide with the metal, and the iodine was thus set free. In the same way if a drop of ammonium hydroxide be let fall into a jar of ozone, a dense white cloud forms, owing to the fact that a white solid compound of ammonia is formed, thus: —

$$2\,NH_4OH + O_3 = NH_4NO_2 + 3\,H_2O.$$

28. Liquid Ozone. — Ozone may be liquefied at ordinary atmospheric pressure by reducing the temperature to −106° C., — a point considerably higher than that at which oxygen liquefies. Ozone is also a very unstable body, changing back readily into oxygen; an illustration of this is seen in the fact that if a quantity of ozone be suddenly compressed and heated, it explodes with violence. It is because of this instability that ozone is so strong an oxidizing agent. The nascent oxygen liberated, if inhaled, attacks the mucous linings, causing an irritation somewhat like that of dilute chlorine. More than this, headache soon follows, if much ozone is inhaled, even though diluted with considerable quantities of oxygen.

TABULAR VIEW OF DIFFERENCES

Oxygen	Ozone
Colorless.	Blue.
Odorless.	Peculiar odor.
Density; slightly heavier than air.	Density; considerably heavier than air.
Two atoms in molecule.	Three atoms in molecule.
Strong oxidizer.	*Very* strong oxidizer.
Liquefies at − 180° C.	Liquefies at − 106° C.
Stable.	Unstable.

29. Uses of Ozone. — It is believed to have a beneficial effect in destroying disease germs and in oxidizing decaying organic matter.

30. Isomeric and Polymeric Bodies. — Just as ozone is another form of oxygen, so we shall find that phosphorus and certain other elements present allotropic forms as unlike the usual forms as oxygen and ozone. When we come to the study of compound bodies we often find two substances not at all alike in properties, which, upon analysis, are found to contain exactly the same elements united in exactly the same ratios. Thus aldehyde and oxide of ethylene both have the same composition, represented by the formula C_2H_4O, but their properties are very different. Such substances are said to be *isomeric*.

31. Sometimes while they have the same percentage composition, the vapor density of one will be several times that of the other. Thus acetylene is C_2H_2, and benzine C_6H_6. In each case the carbon is $\frac{12}{13}$, or 92.3 per cent, of the molecule; but the molecular weight of one is three times that of the other. Such substances are said to be *polymeric*.

HYDROGEN DIOXIDE: H_2O_2

32. Composition. — This is a compound which in some of its characteristics resembles ozone. In composition it is most like water, having one additional atom of oxygen. It is believed to exist in the air in minute quantities, and some of the effects attributed to ozone may be due to hydrogen dioxide.

33. How to obtain It. — For experimental purposes it is usually prepared by treating barium dioxide with dilute sulphuric or hydrochloric acid.

EXPERIMENT 39. — Add to about a gram of barium dioxide a little water, and then dilute sulphuric or hydrochloric acid. Stir for a moment or two with a glass rod.

To prove the presence of hydrogen dioxide, add a few drops of potassium dichromate and about a half cubic centimeter of ether, and shake well. The hydrogen dioxide forms a blue solution with the dichromate, which is taken up by the ether and thus concentrated within little space.

34. Some of its Peculiarities. — Like water, it is a colorless liquid, but is thicker or sirupy, and has a bitter taste. It is very unstable, decomposing at all temperatures into water and oxygen; it is therefore a good bleaching agent, the bleaching being done by the *nascent* oxygen. Like ozone, it readily tarnishes silver and decomposes potassium iodide, giving in the same way a test with starch paper. It is soluble in water, and thus diluted it will bleach the skin, but when concentrated it burns or blisters it.

35. Uses. — This compound, more usually sold under the name hydrogen peroxide, is now manufactured very cheaply, and is used to a considerable extent as a bleaching agent, especially for hair and feathers. It is used largely by dentists and in surgery as an antiseptic, and to some extent in cleansing oil paintings and engravings.

SUMMARY OF CHAPTER

- Discovery of oxygen.
  - Meaning of term.
- Abundance of oxygen — Various forms in which it occurs.
- Methods of preparing oxygen.
  - Priestley's method.
  - Ordinary method.
    - Chemicals and apparatus used.
    - Chemical changes involved.
      - Proof of these changes — Experimental.
      - Proof by weight.
  - Other methods.
    - Character of substances used.
- Characteristics of oxygen — Compare with hydrogen in
    - Color, odor, density, combustibility.
    - Power of supporting combustion.
    - How would you distinguish the two?
    - Some peculiarities of liquid oxygen.
- Uses of oxygen.
- Special.
  - Meaning of terms *combustion*, *oxidation*, *flame*, *kindling point.*
  - Illustration of the terms.
  - Description and drawing of oxyhydrogen blowpipe.
    - Uses for it.
  - Ozone — Meaning of the word.
    - What is its relation to oxygen?
    - Methods of obtaining.
    - Compare with oxygen, showing differences.
    - Value of ozone.
  - Hydrogen dioxide — Formula.
    - Compare with water in properties.
    - Uses for the compound.

CHAPTER VI

CHEMICAL NOTATION, SYMBOLS, FORMULÆ, EQUATIONS, PROBLEMS

1. Symbols. — The student will have noticed that in chemistry we frequently employ a short-hand method of expressing the different elements and their compounds. Thus we have seen that hydrogen is represented by H, oxygen by O, and so on. These are called *symbols.*

2. Their Form. — Frequently, the symbol of an element is its initial letter; often, however, this is the same for a number of elements, as for example, carbon, calcium, cadmium, copper, etc. In such cases, the most common usually is designated by the initial letter; another by the first and second letter, as Ca, calcium; another by the first and some other distinctive letter, as Cd for cadmium. Frequently, the first or the first and second letters of the Latin term for the same substance are used, as Cu for copper, from *cuprum.* In like manner, sulphur, silicon, selenium, silver, are designated by the symbols S, Si, Se, and Ag (from the Latin *argentum*). The Latin has furnished a number of the symbols of the common elements: thus, sodium, Na (*natrium*), potassium, K (*kalium*), iron, Fe (*ferrum*). The symbol, Hg (*hydrargyrum*), for mercury is from the Greek.

3. Strict Meaning. — Strictly speaking, the symbol of an element not only represents that element, but a definite amount of it; that is, one atom. Hence, to speak of an element by using its symbol when we mean an indefinite amount is unscientific and should not be practiced.

4. Formulæ. — As the elements are represented by symbols, so compound bodies are by *formulæ;* that is, by an aggregation of symbols. Compounds are usually named by simply combining the terms representing the elements entering into the composition, the more electropositive being placed first; thus, potassium iodide consists of two elements, potassium and iodine. The formulæ are always arranged in the same way: thus, KI, potassium iodide; KCl, potassium chloride. It will be seen, therefore, that as a symbol represents an atom of an element, so a formula represents the smallest amount of a compound body, a molecule.

5. Sub-figures. — When the elements enter into composition, in other than a single atom of each, that fact is indicated by putting a small figure below and at the right of the symbol; thus, H_2O, the formula for water, indicates that there are two atoms of hydrogen in the molecule, and, H_2O_2, for hydrogen peroxide, indicates that there are two atoms of each. These sub-figures are sometimes appended to a group of elements, in which case the group is inclosed in parentheses and the figure placed outside; for example, lime-water, or calcium hydroxide is $Ca(OH)_2$. This might also be written CaO_2H_2, but the former method is preferable, as will be seen later. If we desire to indicate more than one molecule of a substance, this is done by prefixing a coefficient to the formula. Thus, 2 HCl indicates two molecules of hydrochloric acid; 5 H_2O, five molecules of water.

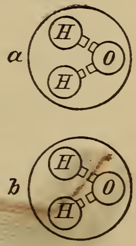
6. Radicals. — By a radical we mean a group of elements which in most chemical reactions seem to hold together, but which do not by themselves form a distinctive compound. For example, (HO) seen in the formula for lime-water is a radical known as *hydroxyl*, which enters into a great many compounds. Again, (NH_4) is a group called *ammonium*, which is very common, and ordinary ammonia water is NH_4OH, composed of two radicals (NH_4) and (OH), *not* written NH_5O, because of this fact.

7. **Reactions.** — Equations in chemistry which show the chemical changes that take place when two or more substances react with each other are called *reactions*. We have already seen a number of these; thus: —

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2;$$

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

8. The first indicates that two atoms of sodium uniting with two molecules of water will produce two molecules of caustic soda and two atoms or one molecule of hydrogen. Another thing must be noticed, and that is that every atom appearing in one member of the equation must also be found in the other. Thus, the two atoms of sodium are seen in the second member of the equation in the two molecules of caustic soda, the four atoms of hydrogen in the water appear partly in the caustic soda and partly as free hydrogen; likewise the two atoms of oxygen in the water are found in the caustic soda. It must be borne in mind that a coefficient before a formula multiplies every symbol in that formula. Thus, $2\,KClO_3$ means that there are two atoms of potassium, K; two of chlorine, Cl; and six of oxygen. This will be seen from the following illustration: —



a represents a molecule of water containing two atoms of hydrogen and one of oxygen; *b* represents a second molecule having the same composition. Taking both together, or two molecules of water, $2\,H_2O$, we see there are four atoms of hydrogen and two of oxygen.

9. Atomic Weights. — We cannot think of matter without assigning to it some weight. So the atoms of the elements, though the smallest conceivable portions of matter, are assumed to have definite weights. Hydrogen, being the lightest of substances, is taken as the standard,* and its atomic weight is assumed to be *one*, or by some, as *one micro-crith.* Of course, a weight as small as this has never been determined, and is therefore merely an abstract idea; but something is necessary for comparison. When we speak of the atomic weight of an element, therefore, we simply mean its density compared with hydrogen. Thus, we say the atomic weight of oxygen is 16, of carbon, 12; we mean that these elements are, respectively, sixteen and twelve times as heavy as hydrogen, or, if one cubic foot of hydrogen weighs a gram, one cubic foot of oxygen will weigh sixteen grams.

10. Molecular Weight. — By *molecular weight* we mean the sum of the weights of the atoms entering into the composition of the molecule. For example, H_2O represents a molecule of water; the two atoms of hydrogen weigh 2, the one of oxygen, 16, or all together, 18. The molecular weight of water is therefore 18. Now if we examine any chemical equation, we will find that the sum of atomic weights in one member must equal the sum of those in the other member. Take the following: —

$$Na + H_2O = NaOH + H,$$

and substituting the atomic weights as given in the table on page 9, we have

$$23 + (2 + 16) = (23 + 16 + 1) + 1, \text{ or } 41 = 41;$$

and this must always be so in any true reaction.

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* There has long been a controversy whether Hydrogen, H = 1, or Oxygen, O = 16, should be the standard. The latter is increasing in favor.

11. Writing Equations. — A chemical equation is valuable in that it shows at once in concise form not only the substances which enter into the reaction, but also the products formed, and the exact amount of each. At first the student will experience some difficulty in completing even the simpler reactions, but it soon becomes a very easy matter. In writing the second member, always put down first the product or products that you know are produced, and then note what remains. There will usually form of the remaining elements some compound that is familiar, so that the ordinary reaction becomes very simple. Thus, suppose we are preparing ammonia from ammonium chloride, NH_4Cl, and caustic soda, $NaOH$.

$$NH_4Cl + NaOH = \begin{cases} NH_3 \text{ (product we know is produced)} \\ \quad \text{remaining H, Na, Cl, H, O, from} \\ \quad \text{which water, } H_2O \text{ and NaCl, form.} \end{cases}$$

12. Practical Value of the Equation. — Having determined by experiment the products that are formed in any chemical reaction, and having therefrom written the equation, we can readily ascertain the amount of each product that will be formed from a certain amount of another; or if required to produce a definite quantity of any body, we can calculate what it will be necessary to use in obtaining it. This is very important to the manufacturer, and only by paying the closest attention to this point can he hope to succeed. To illustrate, suppose we are required to determine how much zinc will be necessary for the preparation of 50 g. of hydrogen. We would first write the equation, showing the preparation of hydrogen: —

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

In the table we find the atomic weight of zinc is 65; looking at the reaction, then, we would see that 65 parts of zinc by weight produce, when reacting with the acid, 2 parts of hydrogen. The gas obtained is therefore $\frac{2}{65}$ by weight of the metal used.

$$\text{Then,}\quad 50\text{ g.} = \tfrac{2}{65}.$$

$$\tfrac{1}{65} = \tfrac{1}{2}\text{ of } 50\text{ g.} = 25\text{ g.}$$

$$\tfrac{65}{65} = 65 \times 25\text{ g.} = 1625\text{ g. of Zn.}$$

Problem 1. — How much sulphuric acid is it necessary to put with 260 g. of zinc in preparing hydrogen?

Using the same reaction as above, we find first the molecular weight of H_2SO_4, which is 98. We see then that 65 parts of zinc unite with 98 of acid, or the acid used is $\frac{98}{65}$ of the metal.

$$\text{Then,}\qquad \tfrac{98}{65}\text{ of } 260\text{ g. Zn} = \frac{98 \times 260}{65} = 392\text{ g. } H_2SO_4.$$

Some prefer to solve such problems by proportion, thus: —

The wt. of the Zn : wt. of acid : : wt. of Zn in g. : wt. of acid in g.; or, 65 : 98 : : 260 : x.

$$x = \frac{98 \times 260}{65} = 392.$$

Problem 2. — In using 260 g. of zinc in preparing hydrogen, how much zinc sulphate, $ZnSO_4$, will be obtained?

Problem 3. — How many grams of oxygen may be obtained from 450 grams of potassium chlorate?

Problem 4. — How much caustic soda will be produced in preparing 10 g. of hydrogen by using metallic sodium and water?

SUMMARY OF CHAPTER

Symbols and formulæ — Difference between them.
Composed of what.
Exact meaning of each.

Radicals.
  Meaning of the term.
  Illustrations.

Atomic and molecular weights.
  Meaning of the terms.
  Illustrations.

Chemical equations.
  Value of.
  Problems.

CHAPTER VII

NITROGEN AND ITS COMPOUNDS

NITROGEN: N = 14

1. History. — Nitrogen, meaning *niter producer*, was given this name because of its being an important constituent of saltpeter, often called *niter*. It had previously been called *azote*, a term which meant that it would not support life.

2. Where found. — As already stated, nitrogen constitutes about four-fifths of the air, and is uncombined. It also exists in various compounds, such as saltpeter, potassium nitrate, KNO_3, and Chile saltpeter, sodium nitrate, $NaNO_3$. It also enters into the composition of many vegetable and animal products, and in their decomposition is given off into the air in the form of ammonia, NH_3.

3. How to prepare Nitrogen. — As nitrogen exists so abundantly in a free state in the air, this is the best source from which to obtain it. Any method by which we can remove the oxygen and leave the nitrogen will do. For this purpose phosphorus is generally used.

EXPERIMENT 40. — Cover a large flat cork with a coating of plaster of paris and float it upon a pan or basin of water. A small iron saucer serves well instead of the cork. Put upon it a small piece of phosphorus and ignite. Quickly place over the burning phosphorus a large wide-mouthed jar. Notice that the water gradually rises in the jar to take the place of the consumed oxygen, and that in a few minutes the white fumes are absorbed by the water. Owing to the expansion caused by the heat some bubbles of air almost always escape in the early part of the experiment.

If the phosphorus is not ignited, but the combination with the oxygen is allowed to take place slowly, this loss may be avoided, but several hours are required. Sometimes it is more convenient to use a deflagrating spoon instead of a cork; if so, the handle must be bent V-shaped, so as to bring the phosphorus above the water even after it has risen in the jar. Notice about how much the water rises. When the fumes have all disappeared, lift the jar and put a burning candle up into the gas. What happens? Compare it with similar tests with oxygen and with hydrogen.

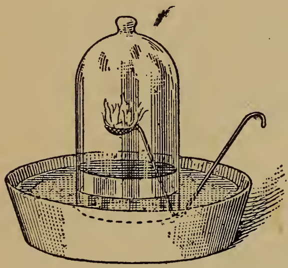

FIG. 16.

4. **Other Ways of preparing Nitrogen.** — The method already given, while the easiest and most commonly used, does not give as pure nitrogen as may be obtained in some other ways. If a current of air be made to stream slowly over a tube containing copper turnings heated to redness, the oxygen will combine with the copper, forming copper oxide, and the nitrogen will remain. Then if this is allowed to bubble through a bottle of lime-water, the carbon dioxide will be absorbed, and we shall obtain a fairly pure nitrogen. The illustration will show the method.

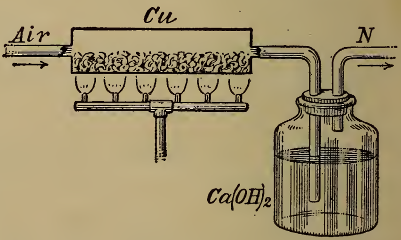

FIG. 17. — Nitrogen, prepared by passing Air over Copper.

Nitrogen may also be obtained by heating certain compounds containing it.

Experiment 41. — Into a small flask put 1 or 2 g. of sal ammoniac, NH_4Cl, and the same amount of sodium nitrite, and add about 30 cc. of water. Heat gently and cautiously, and collect the gas over water as you did oxygen and hydrogen. Test the gas for nitrogen. What are your conclusions?

5. **Peculiarities of Nitrogen.** — From the experiments made the student will notice that the gas has no color; it is odorless, lighter than air, will neither burn as does hydrogen, nor support combustion as does oxygen. It has no affinity for other substances at ordinary temperatures. It will combine with red-hot magnesium in the absence of oxygen, and with oxygen when a discharge of electricity takes place, both of which methods have been used in preparing argon from its mixture with atmospheric nitrogen. It will not support respiration any more than it will combustion, and is one of the most inactive substances known. This inactivity, or feeble chemical affinity of nitrogen, is the reason for the instability of many of its compounds, as seen in the explosiveness of gunpowder and nitroglycerine.

6. **Use of Nitrogen.** — The use of nitrogen, except in the form of many valuable compounds, seems to be simply to dilute the oxygen of the air as already stated.

Compounds of Nitrogen

7. In an indirect way nitrogen forms a large number of compounds, many of which are very valuable. Among these we shall first consider ammonia.

8. **Ammonia, NH_3.** — As already stated, ammonia is one of the products formed in the decomposition of nitroge-

nous organic matter; that is, organic matter which contains nitrogen in addition to the usual carbon, hydrogen, and oxygen. It finds its way into the air from these sources, and being absorbed by the moisture of the air is brought down in the rain, and usually exists in very small quantities in cistern and river water. With these exceptions, ammonia does not occur free to any extent, but is found abundantly in certain compounds, especially sal ammoniac or ammonium chloride, NH_4Cl.

9. The commercial supply of ammonia is obtained from the distillation of coal in the manufacture of common illuminating gas. (See page 153.) The decay of organic matter, attended by the formation of ammonia, occurs as follows: when the nitrogenous matter decomposes, the former arrangement existing among the atoms of carbon, oxygen, nitrogen, and hydrogen is broken up, and in the rearrangement the nitrogen and hydrogen unite to form ammonia.

10. Ammonia prepared from Coal. — In the distillation of coal the process is really the same, but more rapid, and ammonia is one of the impurities given off with the hydrocarbon gases. These are all passed through a tank filled with water, which absorbs the ammonia and forms an aqueous solution, known as aqua ammonia or ammonium hydroxide. This, more or less impure, is drawn off at intervals and treated with hydrochloric acid, which converts it into a salt of ammonia, ammonium chloride, NH_4Cl, as shown by the following reaction: —

$$NH_4OH + HCl = NH_4Cl + H_2O.$$

11. Then by treating this chloride with some strong alkali like caustic potash or soda, and heating, ammonia is again liberated, and being passed into water, produces the aqua ammonia of commerce. The following shows the reaction which takes place: —

$$NH_4Cl + KOH = NH_3 + KCl + H_2O.$$

12. On account of its cheapness, slaked lime, $Ca(OH)_2$, a compound very similar in properties to caustic potash or soda, is ordinarily used with the sal ammoniac to liberate the ammonia. The reaction is seen below: —

$$2\ NH_4Cl + Ca(OH)_2 = 2\ NH_3 + CaCl_2 + 2\ H_2O.$$

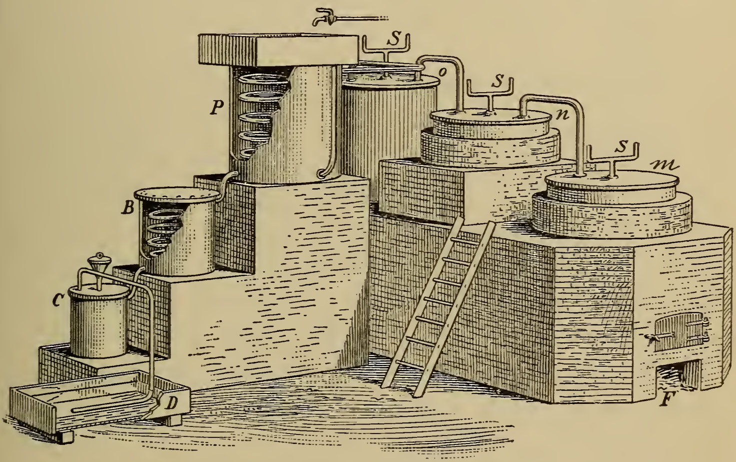

FIG. 18. — Preparation of Ammonia.

m, *n*, *o*, cylinders containing solutions of impure ammonium chloride, as obtained from coal-gas factories, mixed with lime; *S*, *S*, *S*, stirrers to keep the lime from settling; *F*, furnace to heat the mixture and expel the ammonia; *P*, *B*, condensers for cooling the ammonia gas; *C*, cylinder of pure water to absorb the ammonia and thus form aqua ammonia; *D*, trough of acid to combine with any fumes escaping from *C*. In this trough, if hydrochloric acid is used, there would form ammonium chloride.

EXPERIMENT 42. — To illustrate the preparation of ammonia. Put about a half gram of sal ammoniac, NH_4Cl, into a test-tube and add to it about 1 cc. of water, then a little caustic soda or potash solution, and heat gently. Is there any gas given off having an odor? Hold in the mouth of the test-tube a piece of moistened red litmus paper and note the effects. Try also a piece of turmeric paper in the same way. How is it affected?

Experiment 43. — To about 2 g. of ammonium chloride in a tube or flask add 1 or 2 cc. of slaked lime, made by adding a little water to some lime; adjust upon a ring-stand and attach a delivery tube. Warm the flask gently and collect a jar of the gas by upward displacement, as described in appendix. To tell when the flask is filled, hold near the mouth a piece of red litmus paper, as in the preceding experiment. Keeping the bottle inverted, insert a burning taper up into the bottle. Does ammonia burn? Does it support combustion?

13. Peculiarities of Ammonia. — Ammonia is a colorless gas having a strong pungent odor, and if inhaled in considerable quantities produces strangulation and fills the eyes with tears. It is lighter than air, having a density of 0.59; it will not support combustion, nor burn in the air; but in oxygen a jet if ignited will continue to burn for some time with a yellow flame. It has remarkable affinity for chlorine, as will be seen when we come to study that gas. It also combines readily with hydrochloric acid, forming dense white fumes. This will be noticed if two bottles, one of each, be opened close together. It is well shown also in the following experiment.

Experiment 44. — Put into a bottle two or three drops of strong hydrochloric acid and cover with a glass or paper. Now fill another bottle with ammonia gas and invert over the bottle containing the acid. Remove the cover separating the two and notice the results.

14. Solubility in Water. — Ammonia is very soluble in water, as the following experiments will show.

Experiment 45. — Fill the bottle again with ammonia gas as before and place it mouth downward into a basin of water. Let it stand two or three minutes and notice whether the water rises in the bottle.

15. Ammonia Fountain. — The most striking illustration of the solubility of ammonia in water is the "ammonia fountain."

Experiment 46.— Fit to a round-bottomed flask or strong bottle, of a gallon capacity or more, a rubber cork through which passes a long glass tube that will reach half way to the bottom of this flask and nearly to the bottom of another similar one. Draw out the upper end to a jet. Fasten in position or hold over the lower bottle or jar as shown in the figure. To the water in the lower flask add a few drops of some acid and a little litmus solution, or a few drops of phenol-phthalein solution. Now fill the upper flask with ammonia as in Experiment 44, or by warming gently a solution of strong aqua ammonia — the latter will be much quicker — and collecting by upward displacement as before. When well filled, quickly insert the cork and long jet-tube and support upon the other flask of water, as shown in Fig. 19. In a few seconds the water will begin to rise in the tube, owing to the gradual absorption of the ammonia, and will soon flow into the upper flask. The absorption then will be very rapid, and the water will be forced up, forming a beautiful fountain. As it enters the upper flask it will change in color, owing to the effect of the ammonia upon the litmus or the phenol put into the solution.

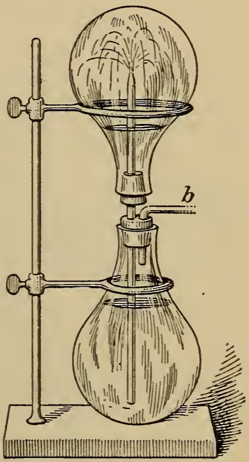

Fig. 19. — Ammonia Fountain.

16. Effect of Heat on the Solubility of Ammonia. — At 0° C. one liter of water will absorb about 1150 liters of ammonia. As the temperature rises, the amount absorbed rapidly decreases. This is seen in the fact that if a few cubic centimeters of aqua ammonia in a flask be warmed gently, the gas bubbles out so rapidly that the liquid seems to be boiling vigorously when it scarcely feels more than warm to the hand.

17. Effects of Platinum and Charcoal on Ammonia. — If a small flask containing strong ammonium hydroxide be warmed gently, and a spiral of platinum wire previously heated to redness be held in the neck of the flask, the wire will continue to glow for a considerable time. Ammonia is also absorbed rapidly by charcoal.

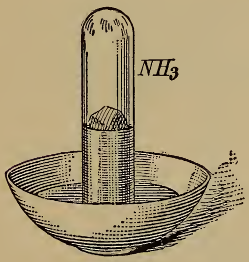

FIG. 20.

EXPERIMENT 47. — To show absorption of ammonia by charcoal.

Fill a large test-tube with ammonia and place it inverted over an evaporating dish containing a quantity of mercury, as shown in the figure. Slip under the tube a piece of charcoal. In two or three minutes the mercury will begin to rise in the tube to fill the space formerly occupied by the gas.

18. Uses of Ammonia. — Immense quantities of ammonia are manufactured and used annually. For cleansing purposes and for softening or "breaking" water it is found in almost every household. In a medicinal way it is used as a restorative in cases of fainting, and overdoses of chloroform and other anæsthetics. Considerably diluted it is employed in neutralizing the effects of acids upon the clothing or upon the hands and face; in a similar way, by inhaling it cautiously, it will counteract the effects of chlorine, bromine, sulphur dioxide, and similar irritating gases.

19. As a Refrigerant. — Perhaps the most extensive use of ammonia is as a refrigerant in the manufacture of ice. The principle underlying this process is as follows: Ammonia may be readily liquefied by moderate pressure; if this pressure is suddenly removed, very rapid evaporation takes place, producing a low degree of cold.

Experiment 48. — To show the freezing of water by rapid evaporation. Put upon a block of wood a few drops of water, and upon this a watch crystal. Into the crystal pour 1 or 2 cc. of carbon disulphide, and blow a current of air by means of a blowpipe across the liquid. By the time the disulphide is all evaporated the crystal will be frozen tightly to the block. Lift the block by taking hold of the crystal.

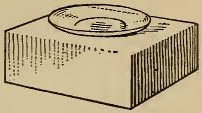

Fig. 21.

20. Manufacture of Ice. — It is upon the same principle that ice is manufactured. The first apparatus for this purpose was devised by Carré, and is shown in the accompanying figure. (I) *a* is a tank containing strong ammonia water, underneath which a fire is placed. This causes the ammonia to bubble out of the water very rapidly, whereupon it flows over into *b*, and there liquefies by its own pressure, the water surrounding it keeping it cool. *c* is a cylinder of pure water fitting into *b*.

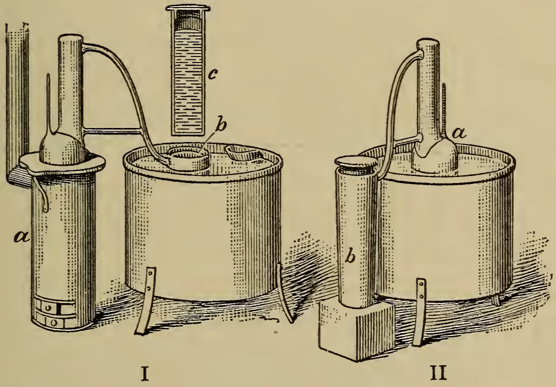

Fig. 22. — Carré's Apparatus.

21. After a half hour or so, when the ammonia has about all been driven out of the solution in *a*, the position of the two, *a* and *b*, is reversed (II). A partial vacuum forms in *a* as it cools, the ammonia in *b* begins to evaporate to fill the vacuum, and as fast as it flows over into *a* is absorbed by the water there. The rapid evaporation is thus kept up for a considerable time, and the cylinder *c*, containing pure water surrounded by the ammonia chamber *b*, has its contents frozen.

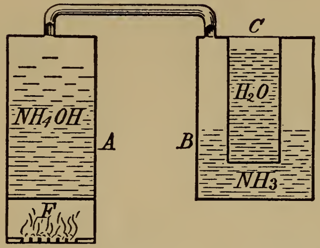

FIG. 23. — Cross-sectional View of Carré's Apparatus.

22. Manufacture of Ice for Commerce. — The first ice machines used for the manfacture of ice upon a large scale were made upon this principle. At present, however, instead of creating a vacuum by cooling *A*, pumps are used to remove the vapor from *B* as fast as it forms. This causes, as in the other class of ice machines, a rapid evaporation and a consequent cooling of the adjacent water.

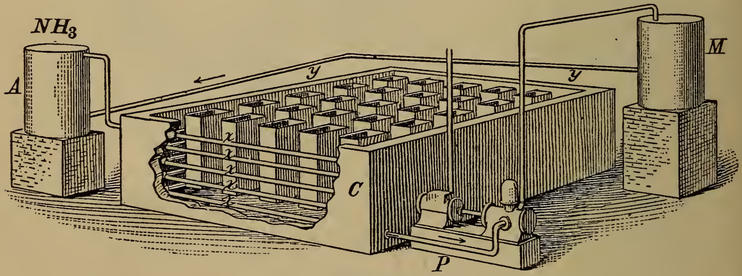

FIG. 24. — Modern Ice Plant.

23. Figure 24 will show the essentials of the improved methods of ice manufacture. *A* is a strong cylindrical tank containing liquid ammonia. *C* is a large rectangular vat filled with strong salt water, through which are coiled a series of pipes, *xx*, which connect with *A*. Through the top of this vat are let down oblong galvanized iron boxes containing the water to be frozen. They are thus surrounded by the salt water through which the ammonia pipes, *xx*, pass. *P* is a pump worked by steam, which is continually exhausting the pipes and keeping up a rapid evaporation in *A*. The pump, at the same time that it exhausts *xx*, is also condensing the ammonia again in the tank *M*, from which, at intervals, it is allowed to flow back again by the pipe *y* into *A*. In this way the ammonia is used over and over without appreciable loss. The rapid evaporation lowers the temperature of the salt water in *C* below the freezing point of pure water, and in from 36 to 60 hours the ice is ready to be drawn from the boxes.

24. Oxides of Nitrogen. — There are five of these compounds, though not all are of much importance. They are : —

Nitrous Oxide, Laughing Gas, or Nitrogen Monoxide,	N_2O
Nitric Oxide, Nitrogen Dioxide, ...	N_2O_2
Nitrous Anhydride, Nitrogen Trioxide, ...	N_2O_3
Nitrogen Peroxide, Nitrogen Tetroxide	N_2O_4
Nitric Anhydride, Nitrogen Pentoxide, ...	N_2O_5

The formulæ for the second and fourth, for the sake of simplicity, are frequently written NO and NO_2.

25. Nitrous Oxide. — This is ordinarily called "laughing gas." It has been stated already that many of the compounds of nitrogen are unstable. So, if we heat ammonium nitrate, NH_4NO_3, it first melts, then begins to boil, and is decomposed to form nitrous oxide and water, thus : —

$$NH_4NO_3 + \text{heat} = N_2O + 2\ H_2O.$$

Experiment 49. — Put into a test-tube 1 or 2 g. of ammonium nitrate, attach a delivery tube, and suspend upon an iron ring-stand. Heat moderately and collect two or three small bottles of the gas over warm water. Be careful not to heat so strongly as to cause a vigorous ebullition, lest some of the impurities always present in the nitrate may be carried over and thus vitiate the nitrous oxide. When two or three bottles of the gas have been collected, remove the cork and notice the odor. Has the gas any color? Test a bottle of it with a glowing pine splinter as you did the oxygen. What are the results? Try also a small piece of phosphorus ignited; how does it burn?

26. Peculiarities of Nitrous Oxide. — Laughing gas is colorless, somewhat heavier than air, having the odor of sugar when being heated or slightly burned. It is soluble to a considerable extent in cold water, will not burn, but supports the combustion of most bodies nearly as well as oxygen. Upon the human system it acts as an intoxicant, producing first a sense of hilarity, and afterward unconsciousness. Because of this fact it is frequently used in a purified form as an anæsthetic in dentistry. It is easily liquefied by cold and pressure, and is generally used in this form.

27. Nitric Oxide, N_2O_2. — This gas is almost always one of the products formed when a metal is treated with nitric acid.

Experiment 50. — Into a flask put 2 or 3 g. of copper turnings, and make connections as for collecting oxygen over water. Add a few cubic centimeters of nitric acid, somewhat diluted. What kind of fumes first fill the flask? Notice that they disappear, being carried over and dissolved in the water. Collect three or four bottles of the gas. What can you say of its color and density? Test it to learn whether it will burn. Try a blazing pine splinter, also a burning candle in the gas; do they continue to burn? Try also in a deflagrating spoon a *well-ignited* piece of phosphorus; what results? Can you explain?

28. Peculiarities of Nitric Oxide. — As seen above, it is a colorless gas, heavier than air, is non-combustible and a non-supporter of ordinary combustion. It is noticed, however, that substances which burn with great heat, such as phosphorus, sodium, and the like, continue to burn in nitric oxide with great brilliancy. The reason is apparent. Ordinary air is about 20 per cent oxygen; nitric oxide is about 50 per cent oxygen; such bodies therefore as have sufficient heat in burning to decompose the gas continue to burn more brilliantly, while those which kindle at a low temperature have not the power to use the large proportion of oxygen present.

29. Affinity for Oxygen. — The strongest chemical property of the gas is its great affinity for oxygen. This is seen whenever it is allowed to escape into the air, brown fumes of nitrogen tetroxide being formed.

Experiment 51. — Into a bottle of nitric oxide inverted over a basin of water, pass slowly a current of oxygen. This may be generated in a test-tube by using a small amount of potassium chlorate and manganese dioxide, or by treating the latter with sulphuric acid. Notice how the colorless gas changes; what else happens?

30. One molecule of nitric oxide unites with one of oxygen, O_2, as follows: —

$$N_2O_2 + O_2 = N_2O_4.$$

If two or three drops of carbon disulphide be put into a bottle of nitric oxide and allowed to stand a few minutes, or until the disulphide vapor has filled the bottle, on the approach of a flame the mixture of gases will burn with a brilliant flash, pale violet in color.

31. Nitrous Anhydride, N_2O_3. — The term, *anhydride*, means *without water*, and is applied to certain oxides, which, when water is added to them, form acids; that is, the anhydride is the acid *without the water.* Such oxides were formerly called acids, and carbon dioxide is sometimes even now spoken of as carbonic acid ; but all true acids contain hydrogen, and theoretically at least are formed by adding water to the oxide or anhydride. Nitrogen trioxide is thus the anhydride of nitrous acid, and is of interest to us only because of this fact. Thus : —

$$N_2O_3 + H_2O = 2\ HNO_2.$$

In this case if the oxide is passed into water it is readily absorbed, forming nitrous acid, as shown by the reaction.

Experiment 52. — Into an evaporating dish put a little starch, and with a little water rub it to a thick paste. Transfer this to a test-tube into which you have put about 2 cc. of nitric acid. Attach a delivery tube and let the end dip into 15 or 20 cc. of water in a bottle or flask. Heat the starch in the test-tube for some time, or until the fumes are given off readily. What color are they? When the gas ceases to come over, test the solution in the bottle with blue litmus paper to learn whether it is acid in character. You should thus obtain nitrous acid from the brown fumes of nitrogen trioxide which were driven off.

Let us test it to determine. Put one or two cubic centimeters of the solution into a test-tube and add a few drops of a solution of ferrous sulphate, made by dissolving a crystal of the salt in water. Does it turn brown in color? If so, nitrous acid is indicated.

32. Instability of Nitrous Acid. — Although it is characteristic of nitrogen compounds to decompose readily, nitrous acid is more unstable than most of the others. In fact, it breaks up of its own accord at ordinary temperatures.

Experiment 53. — Put a part of the nitrous acid prepared above into a test-tube, and when it has been standing a few minutes, or when gently warmed, hold a sheet of white paper behind the tube and notice carefully whether brown fumes are being given off. Continue to heat gently for a few minutes, or until these do not seem to appear, and test with blue litmus paper. Is the solution still acid? If so, test a part of it to determine whether it is still *nitrous* acid. If it is, warm it a little longer and test again. If not, test it for *nitric* acid. This is usually done thus: To about 1 cc. of the solution to be tested add about as much strong sulphuric acid; shake the two together and cool well by holding the tube in a stream of cold water.

Next prepare a fresh solution of ferrous sulphate, and pour it very cautiously upon the solution to be tested so as not to mix them. To do this it will be necessary to hold the two tubes almost in a horizontal position, as shown in the figure, and let the ferrous solution run slowly upon the other. Set aside the tube in a vertical position and let it stand for a few minutes, when a dark brown ring should have formed at the junction of the two liquids. The test requires considerable care, but is very satisfactory when well done. The test is not distinctive, however, if nitrous acid is present, as this also will form a ring; but the latter ring is usually much broader and forms much more quickly. A simpler plan is to drop a crystal of ferrous sulphate into the solution to be tested, and then pour down the side of the tube upon it a little sulphuric acid. A brown ring forms about the ferrous sulphate.

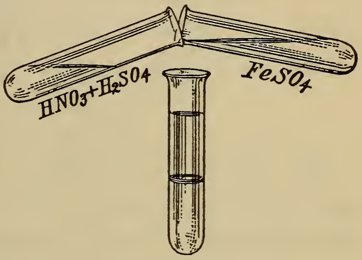

FIG. 25.

33. Nitrogen Tetroxide, N_2O_4. — This gas is of little importance, yet it is one frequently seen in the action of nitric acid upon metals in the presence of air. We noticed that when nitric oxide was exposed to the air it quickly turned brown. So when a metal is treated with ordinary nitric acid, the nitrogen dioxide at first formed quickly unites with oxygen from the air and forms the brown fumes of nitrogen tetroxide. For experimental purposes it may be prepared directly by heating almost any nitrate.

34. Characteristics of Nitrogen Tetroxide. — It is at ordinary temperatures a brownish red gas, heavier than air, having a very offensive suffocating odor; is non-combustible and a non-supporter of ordinary combustion. It is soluble in water, as may be seen by inverting a bottle of it over water. The brown fumes will disappear and the water will rise in the bottle.

35. Nitrogen Pentoxide, N_2O_5. — The only fact of interest in connection with this compound is its relation to nitric acid, of which it is the anhydride. Hence it is often called *nitric anhydride.* The relation is exhibited in the following reaction: —

$$N_2O_5 + H_2O = 2\ HNO_3.$$

36. Nitric Acid, HNO_3. — When a strong electrical discharge takes place in the air, as in the case of violent thunder storms, small quantities of the nitrogen and oxygen are caused to unite, forming nitrogen oxides, which dissolved in the falling rain form nitric acid. This is sometimes in appreciable quantities. Compounds of nitric acid, such as sodium and potassium nitrate, are found in abundance, especially the former. These salts are now known to be produced by the action of certain bacteria upon nitrogenous matter, and in some countries the sodium nitrate needed is prepared by introducing these bacteria.

37. Formation of Nitric Acid. — Nitric acid may be obtained by decomposing any nitrate with sulphuric acid.

Experiment 54. — Put into a retort 4 or 5 g. of sodium nitrate, $NaNO_3$, cover with concentrated sulphuric acid, and insert the long neck of the retort into a flask surrounded with ice and salt, as in Fig. 26. Instead, the retort may be connected with a short Liebig condenser, kept cool by a stream of water. Apply a moderate heat to the retort; nitric acid will distil over and condense in the receiver. The reaction may be represented in two ways, according to the amount of Chile saltpeter used: —

$$2\ NaNO_3 + H_2SO_4 = Na_2SO_4 + 2\ HNO_3.$$

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

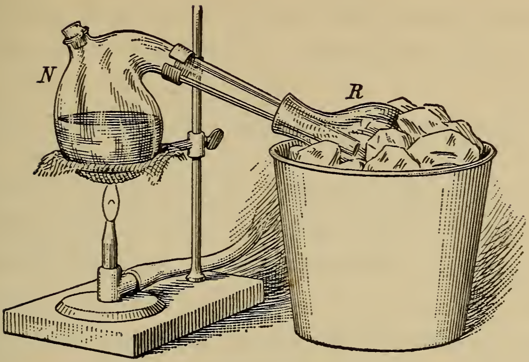

FIG. 26. — Preparation of Nitric Acid.

38. It will be remembered that we prepared ammonia, a volatile compound, by treating a salt of ammonia with caustic lime, a compound of similar properties which is not volatile. In exactly the same way nitric acid may be easily expelled from a liquid by heating, while sulphuric acid cannot be. The latter, therefore, simply takes the place of the former in combination with the metal, and the nitric acid boils out and condenses in the receiver. This is shown in the above reactions.

39. Characteristics of Nitric Acid. — *Aqua fortis*, as this acid is frequently called, is colorless when pure, though, owing to impurities present, it is generally slightly yellowish in color. It is a volatile acid and gives off fumes which are very irritating. It colors the skin and finger nails yellow, and the color is intensified rather than removed by the application of ammonia. Like other strong acids, it attacks all organic matter, rapidly destroys the fibres of clothing, and the discoloration of the cloth cannot be removed by the application of any alkali, as is the case with other acids. Though a comparatively stable compound, a flask of it exposed to bright sunlight, or heated, soon becomes filled with a brownish gas, nitrogen peroxide, N_2O_4, and oxygen. This is seen in the following reaction: —

$$2\ HNO_3 + \text{heat} = O + H_2O + N_2O_4.$$

On account of this property of giving up a part of its oxygen with moderate ease it is frequently used as an oxidizing agent. This is seen in the following experiments: —

Experiment 55. — Warm slightly a little turpentine in an evaporating dish and pour upon it some strong or fuming nitric acid. Usually only a copious evolution of fumes is the result, but sometimes the oxidation is so rapid that the whole mass bursts into a flame.

Experiment 56. — Heat in an iron spoon a few small pieces of charcoal; when red hot drop quickly into a beaker containing some strong nitric acid. Notice that the charcoal continues to glow for some little time, owing to the oxygen obtained from the acid; notice also that brown fumes fill the beaker. Upon a small quantity of warm strong nitric acid in an evaporating dish, drop a *very small* piece of phosphorus. Notice that it is instantly set on fire, and small particles are thrown out in all directions.

Experiment 57. — To a little tin-foil in a test-tube add some strong nitric acid and heat. Notice that the metal is not dissolved, but converted into a white solid, which is really an oxide of tin in combination with water, SnO_2, H_2O. By heating, the water is evaporated and the oxide remains.

40. Uses of Nitric Acid. — Nitric acid finds a great many uses in the laboratory, frequently as an oxidizing agent, as will be seen from time to time. It is used considerably in the manufacture of sulphuric acid, which will be described later, and in making nitro-glycerine and other explosives.

41. Aqua Regia. — This is a mixture of nitric and hydrochloric acids in the proportion of one of the former to three of the latter, and is so named because it will dissolve gold, the "king of the metals." It is the strongest solvent known, and attacks several metals which are unaffected by single acids.

42. Nitro-glycerine and Dynamite. — Nitro-glycerine is prepared by treating glycerine with a mixture of fuming nitric and sulphuric acids. It is in the form of a liquid, and hence not convenient for uses under all circumstances. Dynamite differs from nitro-glycerine in that it contains about 25 per cent of siliceous or infusorial earth. It is, therefore, more convenient and less liable to explode by accident. Guncotton is a similar compound which is prepared by treating cotton wool with nitric and sulphuric acids. It is, therefore, not very different from nitro-glycerine in composition. It has the advantage of being perfectly safe when wet, and is, therefore, kept damp when carried on board men-of-war. In this condition it is exploded by igniting with a small charge of fulminating mercury. Its combustion is five hundred times as rapid as that of the best gunpowder. The heavy charges now used for torpedoes give an impact that no man-of-war can withstand. All of these explosives, as well as gunpowder, are valuable because of the great instability of the nitrates present or formed in the preparation of them.

ARGON: $A = 40$?

43. Its Discovery. — For some time previous to the discovery of argon, in 1894, it had been observed that nitrogen obtained from the atmosphere was heavier than that from its compounds. In that year Lord Rayleigh and Professor Ramsay observed that, by passing atmospheric nitrogen over red-hot magnesium, a small residue was obtained which could not be made to enter into combination. This residue was the new gas now called Argon.

Its name comes from the Greek word *argon*, which means *idle* or *inactive*.

44. Characteristics of Argon. — This element is an odorless, colorless gas, somewhat heavier than air, constituting about eight-tenths of one per cent of the atmosphere. As far as is known it is a perfectly inert substance, hitherto resisting all attempts to make it enter into combination. No compounds of the gas being known, it is impossible to assign it a positive atomic weight, but it is believed to be about forty.

SUMMARY OF CHAPTER

Origin of the term *nitrogen*.
Abundance of the element and of certain compounds.
Easiest method of preparing nitrogen.
  What is the purpose of the phosphorus?
  The source of the nitrogen?
  Would a candle do as well as phosphorus? Why?
Two other ways of preparing nitrogen.
  Chemical action in each case.
Characteristics of nitrogen.
  Compare with oxygen and hydrogen — How similar — How different.
  How test each?
Compounds of nitrogen.
  Ammonia — How formed in nature.
    Old method of preparing "hartshorn."
    Present source of ammonia.
    Wherein are these three methods similar?
    Characteristics of ammonia.
      Experiments to illustrate these.
    Uses.
      Experiments to illustrate the most important.
      Carré's ice machine.
      Present ice machines,

- Oxides of nitrogen.
  - Names and formulæ.
  - Most important. Why?
  - Method of preparing this one.
  - Use — Physiological effects.
- Acids of nitrogen.
  - Names and formulæ.
  - Anhydride of each — Meaning of.
  - How distinguish each by test.
  - Preparation of nitric acid.
  - Characteristics and uses of.
  - Aqua regia.
  - Explosives — Explanation of their explosive character.

CHAPTER VIII

THE ATMOSPHERE

1. What it is. — We are living at the bottom of an ocean as wonderful as the watery one that washes the shores of our continent. The atmosphere covers the entire earth to a depth variously estimated at from fifty to two hundred miles. Some of the recent investigators believe that, in an extremely attenuated form, the air extends through space, even reaching and commingling with the atmospheres of other planets. Centuries ago the air was regarded as one of the elements, just as water was, and the other gases, as discovered, were all called *air;* for example, hydrogen was known as *inflammable air*, carbon dioxide as *fixed air*, etc. So the perfumes that were exhaled from various flowers were regarded as *air*, slightly changed in some unknown way.

2. Constituents of the Air. — We know now that the air is not an element, but a mixture of several substances. Three of these, nitrogen, oxygen, and argon, are constant, but the watery vapor and carbon dioxide vary from time to time. Many efforts have been made to learn whether the air is a compound of oxygen and nitrogen, mixed with the other constituents named. Analyses have been made in all parts of the world, thousands of feet above the earth, in the crowded cities, on the North and South American prairies; but though the proportion of the gases, 79 of nitrogen to 21 of oxygen, by volume, is found in all cases approximately the same, yet the variation is too great to permit one to believe that they are united to form a compound. The argon constitutes about 1 per cent of what has usually been taken as nitrogen, or about 0.8 per cent of the air. The carbon dioxide varies somewhat, but seldom amounts to more than three or four parts in 10,000, except in poorly ventilated rooms. The aqueous vapor varies greatly. When the air contains all it is able to hold, it is said to be *saturated*, or to contain 100 per cent. Ordinarily, however, the humidity is not above 60 to 70 per cent. The amount may be estimated by passing a certain volume of air through a tube filled with calcium chloride and noting the increase of weight.

3. Diffusion of Gases. — We find that the air contains five gases, of densities ranging all the way from eight to forty times that of hydrogen. Were it not for the law of diffusion, we should find the argon, perhaps, nearest the ground The next above this, forming a layer twelve feet or more deep, would be the carbon dioxide; then the oxygen, nitrogen, and water vapor, in the order named. Such conditions would be fatal to all animal life. As it is, however, owing to the constant circulation of the atmosphere and the rapid diffusion of gases, no more carbon dioxide is found close to the surface of the earth than hundreds of feet above. Two or three exceptions to this ought to be noted, among them the deadly Upas Valley, where the carbon dioxide is exhaled from volcanic sources more rapidly than diffusion can carry it away.*

4. **Boyle's Law.** — Many years ago Boyle discovered and formulated the law, which now bears his name, that the volume of a gas, the temperature remaining constant, varies inversely as the pressure. In other words, if we double the pressure, the volume decreases by half; or if we lessen the pressure by half, the volume becomes twice as great. In the accompanying figure we have 10 cc. of the gas, *a*, under the pressure of the atmosphere, simply confined by the mercury in the bottom of the bent tube; if now we pour in more mercury at the open end, the volume of *a* will constantly decrease, and when we have added as much as corresponds to the pressure of an additional atmosphere, the volume will have decreased to 5 cc.

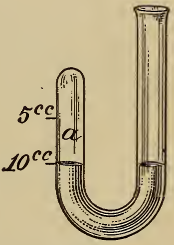

FIG. 27.

5. **Standard Pressure.** — Atmospheric pressure is measured by the barometer, which at sea level stands about 30 in. high. In chemical calculations, however, we use the metric system, and the equivalent of 30 in. is 760 mm. Hence when we say that a gas is under *standard* pressure, we mean 760 mm.

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* This valley is located in the island of Java, is about a half mile in circumference and thirty-five feet deep, surrounded at no great distance by hills. The bottom is comparatively smooth and is devoid of vegetation. Loudon, in describing his visit there, says that "skeletons of human beings, tigers, pigs, deer, peacocks, and all sorts of birds" are to be seen everywhere, bleached by the exposure till they are as white as ivory. A fowl thrown in died in one and a half minutes.

Problem. — 500 cc. of oxygen under standard pressure would be how much under 750 mm.? As the pressure has decreased, the volume would have increased. We would solve then by the following proportion: —

$$V : V' :: P' : P;$$

or

$$500 \text{ cc.} : x :: 750 : 760.$$

$$x = ?$$

If desired, this problem may be solved without using a proportion. As the pressure has decreased, we know that the volume will be correspondingly increased; that is,

$$V' \text{ will equal } \tfrac{760}{750} \text{ of } V;$$

or

$$V' = \tfrac{760}{750} \times 500.$$

$$V' = ?$$

2. What volume would 300 cc. of hydrogen, at 750 mm. pressure, occupy at 780 mm. pressure?

3. 25 liters of air at 380 mm. pressure, would be how many at 5 atmospheres' pressure?

6. Law of Charles. — Just as heat causes solids and liquids to expand, so it affects gases. In the case of the latter the rate of expansion is practically constant, and is in the *Law of Charles* stated thus: *The pressure remaining constant, all gases expand or contract uniformly under the same increase or decrease of temperature.* This has been studied carefully, and it has been proven that for an increase or decrease of 1° C., a volume of gas expands or contracts $\frac{1}{273}$ of the volume it occupies at 0° C. To illustrate, suppose we have in a vessel 273 cc. of oxygen at 0° C. If by any means the temperature is raised to 10° C., the volume would increase $\frac{10}{273}$ of 273 cc. or 10 cc., and would occupy 283 cc. It obviously follows from this that were the law to hold true, and were the gas reduced to a temperature of 273° below zero, it would disappear entirely. However, all gases thus far tried become liquids before reaching this low temperature, so that the law no longer applies.

7. Absolute Zero. — From the fact that a gas would disappear entirely at 273° below zero, according to the *Law of Charles*, – 273° has been called *absolute zero*, the point at which the molecules of a body would have no *vis viva*, or absolutely no heat energy. This point has never yet been reached, though recent investigators have approached within a few degrees of it. It is necessary to have a clear understanding of what is meant by the absolute zero, as it is used in making all calculations for correction of the volume of gases for temperature.

8. The Absolute Thermometer. — In Fig. 28 we have the Fahrenheit, Centigrade, and *Absolute* thermometers represented in *F*, *C*, and *A*, respectively. It must be remembered that the last is not a thermometer really in existence, but serves merely for illustration. The boiling points on the three are marked 212°, 100°, and 373°; the freezing points 32°, 0°, and 273°. The *absolute* zero therefore would be the same as – 273° on the Centigrade, as the degrees on these two are of the same size. Let us apply this in a problem.

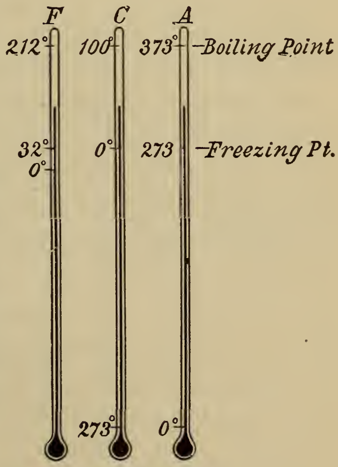


FIG. 28.

PROBLEM. — 500 cc. of oxygen at 0° C. would occupy what volume at 25° C.?

Expressing Charles's Law in the form of a proportion, we would have

$$V : V' :: t : t',$$

in which V and t represent the volume and temperature of the gas at the beginning of the experiment, and V' and t' at the end; and it must be remembered that t and t' always mean *absolute* temperatures. Applying this to the problem, we see that $t = 0°$ C., or 273° A., and $t' = 273 + 25$, or 298° A. Substituting, we have:—

$$500 : V' :: 273 : 298.$$

$$V' = \frac{298 \times 500}{273}.$$

Problem 2. — What volume would 250 cc. of gas at 20° C. occupy at − 10° C.?

Here, $t = 20°\text{ C.} = 273 + 20 = 293°\text{ A.}$

$t' = -10°\text{ C.} = 273 - 10 = 263°\text{ A.}$

$V = 250\text{ cc.}$

Substituting, $250 : V' :: 293 : 263.$

$$V' = \frac{250 \times 263}{293}.$$

Problem 3. — If 400 cc. of hydrogen is heated from − 15° C. to 30° C., what volume would the gas then occupy?

Problem 4. — What would be the result in problem 2, if at the same time the barometer fell from 760 mm. to 740?

This may be solved by first finding the value of V', as shown above at the temperature t', and substituting this in the proportion for determining V' under P' pressure. Suppose, in problem 2 above, $V' = 225 +$, then solving for pressure, we would have

$$V'' = \tfrac{760}{740} \text{ of } 225 + ;$$

or $$V' : V'' :: P'' : P' ;$$

or $$225 : V'' :: 740 : 760.$$

$$V'' = \frac{225 \times 760}{740}.$$

Or the problem may be solved by using a compound proportion:—

$$250 : x :: \left\{\begin{matrix} 273 + 20 : 273 - 10 \\ 740 : 760 \end{matrix}\right. ;\quad 293 \times 740x = 263 \times 760 \times 250.$$

Problem 5. — 500 cc. of gas under 4 atmospheres and at − 25° C. would have what volume at 760 mm. and at 20° C.?

Let the teacher furnish a number of similar problems for practice.

9. Weight of Air. — The weight of a liter of air may easily be found by the following experiment: —

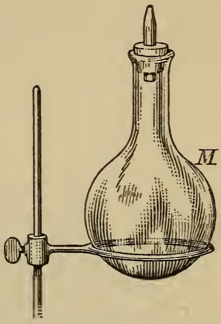


Fig. 29.

Experiment 58. — M in the figure is a flask of about 500 cc. capacity. Fit to it a cork with a glass tube somewhat drawn out, as shown. Put into the flask about 50 cc. of water and boil for several minutes, so as to expel all the air. Immediately remove the cork and insert another, not perforated. When the flask has cooled to the temperature of the room, weigh the whole. Suppose this to be m. Remove the cork, thus allowing the air to enter, and again weigh flask and cork. Suppose this to be n. The gain in weight,

$$n - m = \text{wt. of air in flask.}$$

To determine the volume of the air contained, take a graduated flask, or cylinder, and fill the flask M with water. Suppose this to be r cc. Then

$$r \text{ cc. of air weighs } n - m \text{ grams,}$$

from which the weight of 1000 cc. = 1 liter may be determined.

10. Liquefaction of Air. — The air is so well known that it is not necessary to say anything regarding its properties. At the present time, however, considerable attention is being given to it in the liquid form. A large number of experiments with it have been made by Dewar, Pictet, Linde, Tripler, and others, with a view to ascertaining its properties and practical value. It is said that the first ounce of liquid air ever produced cost about $3000 and the next pint about $80; with improved methods, however, it may now be prepared for a few cents per gallon.

11. Dewar's Bulbs. — Dewar has invented a double-walled glass globe in which liquid air may be kept for a number of hours with little loss; here in this country it is often shipped several hundred miles in large double-walled tin cans, heavily lined with felt, but at the expense of 20 to 40 per cent of the liquid. The Dewar bulbs vary somewhat in construction, but the general plan is the same in all. Into the space between the inner and outer walls of the globe, a drop or two of mercury is introduced; the air-pump is then attached, and a vacuum of very high degree obtained. As the air is pumped out, the mercury vaporizes and fills the space. When liquid air is introduced into the inner globe, the mercurial vapor is condensed upon the outer surface of the inside flask, and forms a perfect mirror. Thus we have not only a vacuous chamber, but also a mirror to prevent the access of heat rays to the liquid air, and the insulation is well nigh perfect. A modified form of this Dewar bulb, holding about two gallons, is now used for shipping liquid air. The insulation is so perfect that the liquid may be kept two weeks with little loss. It is obvious that the ordinary closed tank is unsuitable on account of the high pressure which would soon obtain.

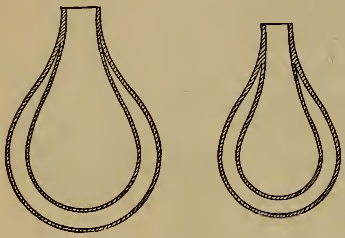
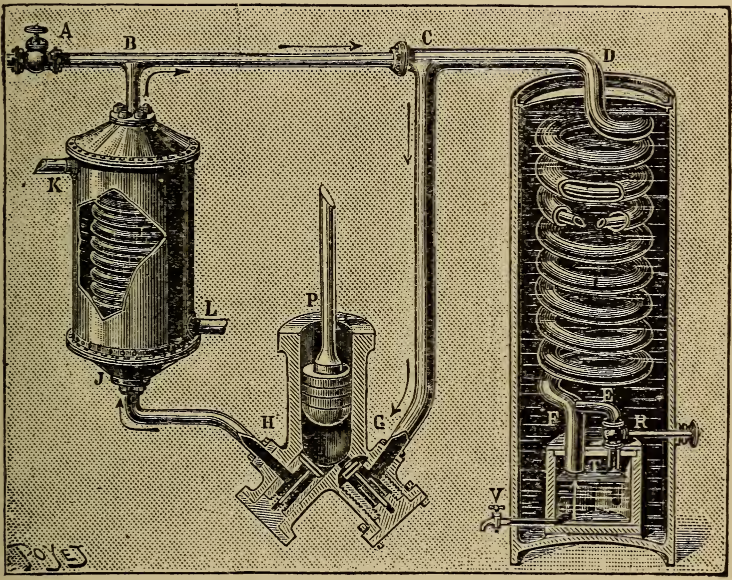


Fig. 30. — Dewar's Bulbs.

12. Linde's Apparatus. — The plan used for liquefying air may be understood from the accompanying figure, which represents the apparatus used by Linde. *P* is a pump which, when the piston is raised, opens a valve at *G* and allows the air from *D* to enter; as the piston descends, the valve *G* closes and *H* opens. The air is thus forced up through the coils in the tank *J*, kept cold by running water, and passes on through *B*. At *C* the pipe *B* enters within a larger one, and continues thus until at the point *E* it again emerges. The ingoing current of air flows through the inner pipe under pressure and issues from a small aperture at *R* into a chamber, *T*, under low pressure. As expansion is a cooling process, the air is thus reduced in temperature; at the next stroke of the piston the vacuum formed in the pump again opens the throttle valve at *G*, and the cooled air in *T* flows back through the outer pipe, back through *D*. As this operation is constantly repeated, the outgoing current being cooled by its expansion into *T*, continually lowers the temperature of the ingoing current, until finally liquid air will trickle down into the chamber *T*, and may be drawn off at *V* much the same as water from a reservoir.



Used by Courtesy of the Scientific American.

Fig. 31. — Linde's Apparatus for liquefying Air.

13. Effects of Liquid Air upon Certain Substances. — It is found that such articles as rubber, beefsteak, eggs, etc., immersed in liquid air, become exceedingly brittle; while an ordinary tin cup dipped into the liquid and dropped upon the floor breaks into fragments like glass. All these effects are due to the intense degree of cold of the liquid air, and not to any chemical action.

14. As the boiling point of nitrogen is lower than that of oxygen, the former boils out the more rapidly, and in a short time a vessel of liquid air, freely exposed, will contain almost pure liquid oxygen. If into this a red-hot iron rod be thrust, it will burn vigorously, notwithstanding the fact that the temperature of the surrounding liquid is nearly 1700° C. below the melting point of iron. It should be said, however, that the two are probably not in contact, but that a layer of gaseous oxygen next to the iron rod supports the combustion. Felt, saturated with liquid air, burns explosively, and if confined in metal tubes, bursts them with violence.

15. Practical Uses of Liquid Air. — Numerous applications for liquid air have been suggested, but as yet these are in the experimental stage. Among them may be named the following: (1) as a substitute for compressed air; (2) as a refrigerant; (3) in blasting; (4) in surgery for removing diseased tissues without the use of the knife; (5) as a smoke consumer, and for burning garbage in cities.

SUMMARY OF CHAPTER

- Composition of the atmosphere.
    - Old ideas of the air.
    - Present ideas.
    - Explanation of uniformity of composition.
- Boyle's Law — Statement of.
    - Meaning of term *standard pressure*.

Charles' Law — statement of.
    Meaning of term *absolute zero.*
    Problems.
Density of air.
    Methods of finding weight of one liter.
Liquefaction of air.
    Present method.
    Dewar bulbs.
    Effects of liquid air.
    Suggested uses.

CHAPTER IX

THE HALOGENS

1. Members of the Group. — The term *halogen* is from two Greek words, meaning *salt producer*, and is given to this group of elements because with the metals they form a large number of salts. The group includes *fluorine*, *chlorine*, *bromine*, and *iodine*. The first two are gases, the third a liquid, and the fourth a solid. They possess properties very similar to each other, differing in degree rather than otherwise. It will be found that as the atomic weights increase, the chemical activity decreases.

FLUORINE: F = 19

2. Characteristics. — Fluorine is an element which had not been prepared until a few years ago. It is a greenish-colored gas, of a very irritating odor, and readily attacks almost all substances. By extreme cold and pressure it has been liquefied, and when in that condition loses much of its chemical activity. It is of little practical value, and is considered only because of one or two compounds which it forms.

3. Compounds of Fluorine. — There is only one compound of this element in which we are specially interested, and that is hydrofluoric acid, HF. It is prepared by treating fluor spar, calcium fluoride, with strong sulphuric acid, the reaction being —

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\ HF.$$

Hydrofluoric acid is a very irritating, colorless gas, which readily dissolves or corrodes glass, and hence is sometimes used in glass etching.

Experiment 59. — Warm a sheet of glass 3 or 4 in. square by holding it at some height above the burner flame, and drop upon it a few shavings of paraffine. Move the glass about so as to distribute the melted wax evenly, and allow it to cool. Now with a sharp pencil or stylus draw any desired figure in the wax, being sure to cut through to expose the glass. Lay this face down over a lead saucer,* into which you have put about 2 g. of calcium fluoride and as much strong sulphuric acid. Support upon a ring-stand and warm for a minute *very* gently, so as not to melt the wax. In a few minutes the etching should be completed. This can be determined by testing with the point of a knife blade, when the glass will feel rough where the figure was drawn in the wax. When the experiment is finished, the paraffine may be removed with a dull knife or by immersing in warm water.

Chlorine: Cl = 35.5

4. History. — Chlorine, the most important element of the halogen group, was first prepared by Scheele in 1774, in treating black oxide of manganese — the same compound we have used in preparing oxygen — with hydrochloric acid. He did not know, however, that he had discovered a new element, but supposed it to be a com-

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* Instead of the lead saucer a small evaporating dish may be used. If so, notice whether it also is attacked on the inside by the hydrofluoric acid.

pound of oxygen and hydrochloric acid, and called it *dephlogisticated marine acid air*. Hydrochloric acid was then called *marine acid*. Later, when chlorine was found to be an element, it was given its present name from the Greek word *chloros*, meaning *green*.

5. How found. — Because of its great chemical affinity, chlorine, like fluorine, is never found uncombined. Its most widely distributed compound is common salt, $NaCl$, which is found in extensive deposits in nearly all parts of the United States, and constitutes a large per cent of the solids held in solution in the ocean.

6. How to prepare Chlorine. — For laboratory purposes the simplest way of preparing chlorine is that used by its discoverer, by treating manganese dioxide with hydrochloric acid and warming gently.

EXPERIMENT 60. — Into a good-sized test-tube or generating flask put 1 or 2 g. of manganese dioxide and about 2 cc. of hydrochloric acid. Attach a delivery tube and warm gently. Collect two or three bottles of chlorine by downward displacement, as described on page 362, and preserve for future experiments in studying its properties.

7. The reaction that takes place in preparing chlorine as above may be indicated thus: —

$$MnO_2 + 4\ HCl = Cl_2 + MnCl_2 + 2\ H_2O.$$

From this we see that only half the chlorine, in the hydrochloric acid used, is obtained free, the other half having united with the manganese to form manganese chloride, a compound which has no application in the arts. An immense quantity of chlorine is used every year in the manufacture of bleaching powder, and cost of production is a very important consideration. The method described above is, therefore, not strictly followed commercially, but is so modified that the manganese chloride is converted into the dioxide again. This is much cheaper, and is known as the Weldon process.

8. The Weldon Process. — In the preparation of chlorine for manufacturing processes, *pyrolusite*, a natural ore of manganese and an impure form of the dioxide, is treated with hydrochloric acid in large stone tanks. When the chlorine is no longer given off, any excess of acid in the residual liquor is neutralized with common limestone, finely powdered. The reaction may be represented thus :—

$$\begin{aligned} &MnCl_2 + H_2O + 2\ HCl + CaCO_3 \\ &\qquad = MnCl_2 + CaCl_2 + CO_2 + 2\ H_2O. \end{aligned}$$

$$\left(\begin{array}{l}\text{Residual liquor and excess}\\ \quad\text{of acid}\end{array}\right) + (\text{limestone}) = \left(\begin{array}{l}\text{mixture manganese and cal-}\\ \quad\text{cium chloride in water.}\end{array}\right)$$

Therefore, we now have a mixture of manganese chloride and calcium chloride in solution. Next, lime water, prepared by treating ordinary lime with water, is added.

$$CaO\ (\text{lime}) + H_2O = Ca(OH)_2\ (\text{lime water}).$$

This precipitates the manganese in the form of the hydroxide, $Mn(OH)_2$, thus : —

$$\left.\begin{array}{r}MnCl_2\\ CaCl_2\end{array}\right\} + Ca(OH)_2 = Mn(OH)_2 + 2\ CaCl_2.$$

Now by heating this and at the same time passing a current of air through the solution, the manganese hydroxide, $Mn(OH)_2$, is converted into the dioxide, thus : —

$$Mn(OH)_2 + O\ (\text{air}) = MnO_2 + H_2O.$$

The calcium chloride, being very soluble, remains in solution. The mixture is now allowed to flow into settling basins, where the dioxide is slowly deposited as a dark-colored ooze, known as *Weldon's mud.* This is now ready to be passed again into the stills for a second treatment with hydrochloric acid.*

9. The Chemical Changes in the Above Method. — By studying the reaction

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2,$$

we see that the oxygen in the manganese dioxide has been set free from the manganese and has united with the hydrogen in the acid; or, as we sometimes say, the chlorine has been set free by the oxidation of the hydrogen with which it was combined. In like manner other substances, besides manganese dioxide, may be used with hydrochloric acid in preparing chlorine. In every instance the principle is the same: the oxygen is first set free, and, combining with the hydrogen in the acid, liberates the chlorine. Let us prove this.

EXPERIMENT 61. — Treat a few crystals of potassium chlorate, $KClO_3$, a substance from which we obtained oxygen, with a little hydrochloric acid. Warm very gently if necessary to start the action, and then remove the test-tube from the flame. Notice the rapid evolution of gas. With the chlorine thus obtained we have also an oxide of chlorine, ClO_2, as seen in the reaction

$$4\,KClO_3 + 12\,HCl = 4\,KCl + 9\,Cl + 3\,ClO_2 + 6\,H_2O.$$

Add to this a few cubic centimeters of water, which will give a yellowish solution known as *euchlorine* or *chlorine water.* Preserve it in a dark-colored, tightly stoppered bottle.

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* It perhaps ought to be stated that a small excess of lime water usually remains mixed with the precipitated manganese hydroxide. When the current of air is passed through the solution, this lime water, $Ca(OH)_2$, is also oxidized; that is, converted into lime, CaO. Weldon's mud, therefore, contains besides the manganese dioxide, a small amount of lime.

10. It will be remembered that we prepared oxygen also by using potassium dichromate. If now we treat this compound with hydrochloric acid, chlorine is obtained as in the other instances.

11. Practical Application of this Principle. — In all the above methods the chlorine is set free by bringing into contact with hydrochloric acid some highly oxygenized substance which will give up a part of its oxygen to unite with the hydrogen of the acid. Hence was conceived the idea of using atmospheric oxygen as the most economical source of supply.

12. Deacon's Process. — This idea is applied in Deacon's process. Theoretically the reaction that takes place according to this method is as follows : —

$$2\,HCl + O = H_2O + Cl_2.$$

In reality, however, the process is not so simple. In the preparation of oxygen from potassium chlorate and manganese dioxide, we have seen that the latter compound remains unchanged. It acts, as was said, by *catalysis*, in a manner not thoroughly understood, causing the potassium chlorate to yield up its oxygen at a temperature much lower than would otherwise affect it.

13. The Catalytic Agent. — In Deacon's process for the preparation of chlorine some catalytic agent is necessary, because a mixture of oxygen and gaseous hydrochloric acid, when heated, is only slightly decomposed. As a catalytic agent some such compound of copper as the sulphate or the chloride is used. Clay balls or bits of brick are saturated with the copper solution and placed in an iron pipe called the *decomposer*. Through this the mixed gases, air and hydrochloric acid, previously heated to about 500° C., are made to pass. The acid is oxidized and the chlorine set free. The chemical action of the cuprous chloride, Cu_2Cl_2, is not thoroughly understood; but it is believed that two or three reactions take place, in the course of which cupric chloride, $CuCl_2$, is formed, which at the temperature present is unstable and gives up a part of its chlorine, leaving cuprous chloride again.

14. Another Method of preparing Chlorine. — Another method is frequently employed in the laboratory instead of the first one given.

Experiment 62. — Into a test-tube put a small quantity of common salt, $NaCl$, mixed with a little manganese dioxide, and about a cubic centimeter of sulphuric acid. Warm gently. Is there any evidence that chlorine is being generated?

15. Comparison of the Two Methods. — We shall find that when common salt is heated with sulphuric acid they react with each other, forming hydrochloric acid. That is what we have done in this case. We see by comparing the two reactions,

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2$$

and

$$MnO_2 + \overbrace{2\,NaCl + 2\,H_2SO_4} = MnSO_4 + Na_2SO_4 + 2\,H_2O + Cl_2,$$

that in the first case we treated the dioxide directly with hydrochloric acid, but in the second indirectly by the use of two substances, which in reacting prepare the hydrochloric acid needed. It will be seen, however, in the second instance that all the chlorine is set free, while in the first only one-half.

16. It is probable that in the second case the reaction is a little more complicated, perhaps as follows: —

First, a part of the sulphuric acid reacts with the common salt, forming hydrochloric acid, thus: —

$$2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO_4.$$

Then another part reacts with the manganese dioxide also present, setting free oxygen, as we have seen before, thus: —

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

Then this nascent oxygen immediately attacks the hydrochloric acid present, oxidizing it and liberating the chlorine, thus: —

$$2\,HCl + O = H_2O + Cl_2.$$

Putting these three reactions together, we would have

$$2\,NaCl + 2\,H_2SO_4 + MnO_2 = MnSO_4 + Na_2SO_4 + 2\,H_2O + Cl_2.$$

17. Experiments with Chlorine. — With the chlorine prepared make the following experiments in study of its properties: —

Experiment 63. — Note the color of the gas; the odor. Put a burning match into a bottle of chlorine; try also a burning candle. State the results. Does the gas burn? Does it support combustion?

Experiment 64. — To show its chemism for certain metals. Sift into a bottle of chlorine, by means of a fine wire-gauze spoon, some powdered metallic antimony; try in the same way metallic arsenic. Describe the results.

Experiment 65. — To show the chemism of chlorine for hydrogen. In a room partially darkened, fill a strong bottle with chlorine and hydrogen, mixed. Wrap a towel about it, ignite a piece of magnesium ribbon, and bring it toward the mouth of the bottle. A violent explosion is the result. Bright sunlight has the same effect. Try also the following experiment to show the same fact.

Experiment 66. — Attach a jet to a hydrogen generator, *H*, and when it has been in action long enough to expel all the air, ignite it, and insert into a jar of chlorine, *C*, as shown in Figure 32. Does it continue to burn? How does the flame change in appearance? What becomes of the green gas? After a few moments add about 1 or 2 cc. of water to the gas, and shake well. Drop into the solution a piece of blue litmus paper; what is indicated? It is best to dry the hydrogen by passing through a drying tube, *D*, filled with calcium chloride.

Experiment 67. — To show affinity of chlorine for hydrogen in compounds of the latter. Into a jar of chlorine thrust a narrow slip of blotting paper which has been moistened in moderately warm turpentine. State the results. Turpentine consists of carbon and hydrogen, $C_{10}H_{16}$. What has the chlorine really done?

Experiment 68. — Practical application of the preceding experiment. Into a jar of chlorine pour a few cubic centimeters of any solution containing organic colors, as litmus, logwood, or carmine. Shake it up and notice the effects.

Experiment 69. — With the same purpose as in Experiment 68. In another jar of chlorine, suspend a piece of blue or pink calico moistened with water. Try another similar piece without moistening it. Are the results different?

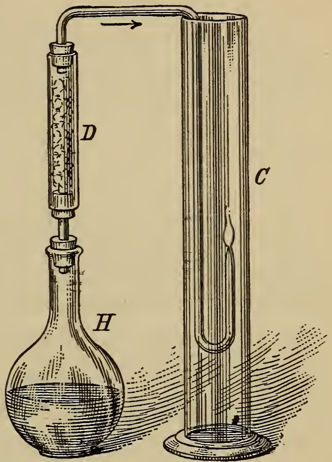

Fig. 32.

Experiment 70. — To show affinity of chlorine for ammonia. Attach to a small flask, into which you have put 25 or 30 cc. of strong aqua ammonia, a delivery tube with jet attached. Warm the flask gently as in preparing ammonia for the "fountain," Experiment 46, and insert the tube into a bottle well filled with chlorine. What happens? What becomes of the chlorine?

18. Characteristics of Chlorine. — Chlorine is a greenish yellow gas, with a very irritating odor, producing temporarily a catarrhal affection of the nasal passages. It is somewhat soluble in water, forming a solution yellowish in color, with the characteristic odor of chlorine. This solution is, however, unstable, as the chlorine gradually combines with the hydrogen of the water to form hydrochloric acid, while the oxygen is set free. Chlorine is about two and a half times as heavy as air and does not support ordinary combustion. It will be found, however, that sodium and phosphorus, when well ignited, burn vigorously in an atmosphere of chlorine.

Experiment 71. — Put a small piece of sodium, heated in a deflagrating spoon until it takes fire, into a bottle of chlorine. State results. Notice the white deposit of common salt that forms. In the same way try a piece of phosphorus, without first igniting it. State results.

19. Chemical Affinity of Chlorine. — From our experiments in oxygen we learned that considerable heat was necessary to effect its rapid union with any other element. The iron wire, the sulphur, and the phosphorus, all had to be raised to the kindling point. In the case of chlorine we find that union often takes place at ordinary temperatures, showing its chemism to be far greater. Thus arsenic and antimony sprinkled into the gas took fire spontaneously, as did also the phosphorus and the turpentine. In the latter case the chemical action is due to the affinity between the hydrogen in the turpentine and the chlorine; the same remarkable affinity of these gases for each other was also seen in exploding the mixture of the two by means of light, and in the hydrogen jet which continued to burn in the chlorine.

20. Chlorine as a Solid. — If a saturated solution of chlorine water be surrounded by a mixture of ice and salt, in a few minutes yellowish crystals of chlorine hydroxide, represented by the formula $Cl, 5\,H_2O$, are formed throughout the liquid. Chlorine may be liquefied at $-34°$ C. under ordinary atmospheric pressure, or at 0° with a pressure of six atmospheres. In this condition it is of a bright yellow color. It has also been solidified by reducing to 102° below zero, and in this form closely resembles the liquid in color.

21. Uses of Chlorine. — Chlorine is used to a considerable extent in the extraction of gold from its ores, because it is a good solvent of that metal. A large amount of that now used for this purpose is put up at the factories in the liquid form in steel cylinders lined with lead, and then shipped wherever desired.

22. As a Bleaching Agent. — Chlorine is a powerful bleaching agent, but acts indirectly. We noticed that dry calico was but little affected by chlorine. The reason for this is that chlorine in its great chemism for hydrogen abstracts it from the water, and the nascent oxygen unites with the coloring matter of the cloth, converting it into colorless compounds; whereas in the dry cloth there was comparatively little moisture to furnish the necessary oxygen.

23. Its most extensive use in manufactures is in bleaching cotton and linen goods and paper pulp. Here, however, it is used in the form of bleaching powder. This is a compound, which when treated with dilute acid readily gives up its chlorine. The following diagram will illustrate the method employed in bleaching cloth.

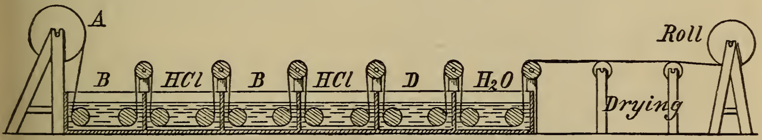

Fig. 33. — Cloth-bleaching Apparatus.

The cloth is seen in a roll at *A*; from here it passes down under rollers at the bottom of the vat *B*, which contains bleaching powder in water, next up over rollers and down into a second vat containing dilute hydrochloric acid, into a third vat with bleaching powder, and so on until the cloth is sufficiently bleached. The excess of chlorine must now be removed, or it will attack the fibers of the cloth and make them weak. To prevent this the cloth is drawn through another vat, *D*, containing an *antichlor;* that is, a solution which combines with the chlorine still present and forms such compounds as will not attack the fibres. For this, sodium hyposulphite is frequently used. Then, after passing through a vat of water for washing, the cloth comes out pure and white.

Chlorine is also used to some extent as a disinfectant, but generally in the form of bleaching powder for this purpose also.

HYDROCHLORIC ACID, HCl

24. History. — This acid, sold usually under the name *muriatic* acid, has been known for four centuries, and was formerly called *spirit of salt.* Later it received the name of *marine* acid.

25. Where found. — It is found uncombined only in very small quantities. It is said to exist in the stomach and to aid digestion, and is sometimes emitted from volcanoes in eruption.

26. How to prepare Hydrochloric Acid. — The method of preparation has already been suggested in one of the experiments for making chlorine.

EXPERIMENT 72. — Into a generating flask put about 2 g. of sodium chloride, $NaCl$, and cover with moderately dilute sulphuric acid. The action will be seen to begin immediately, but it is better to warm gently. Collect two or three bottles of the gas by downward displacement and preserve for a study of the properties. Keep them covered to prevent diffusion. The bottle is full when a moistened piece of blue litmus paper held near the mouth is quickly turned red.

27. Manufacture on a Large Scale. — The method illustrated by this experiment is really the one used in preparing hydrochloric acid on a large scale. It is nearly all obtained as a by-product in the manufacture of soda crystals preparatory to the making of soap. Like many other valuable articles of commerce, it was at one time allowed to go to waste as of no value.

28. In the manufacture of sodium carbonate, common salt was treated with sulphuric acid as above, and the gas obtained was allowed to escape from the flues. But being heavier than the air it settled to the ground, destroying vegetation and rendering all life in the neighborhood almost unendurable. In some places it was produced so abundantly as to corrode even the tools of workmen. It thus became so great an evil that laws were passed prohibiting any manufacturer from allowing the escape of such gas, just as the consumption of coal smoke is demanded in most large cities to-day. An attempt was also made to conduct the gases into streams of water, but this resulted in the death of animals living in the streams.

29. Finally uses were found for the acid, and then plans were thought of and efforts made to save and use it. The gas is conducted into towers filled loosely with coke, down which water is allowed to trickle slowly. In this way the gas is practically all absorbed, and there results a moderately strong aqueous solution of hydrochloric acid. Sometimes the gases are conducted through large Woulff bottles partly filled with water, where solution is effected in the same way.

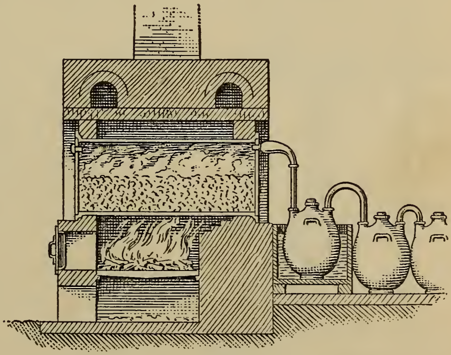

Fig. 34. — Hydrochloric Acid Factory.

The reaction that takes place may be represented as follows: —

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

If, however, the heat is increased, a larger amount of hydrochloric acid is obtained by using the same amount of sulphuric acid with more salt. Thus: —

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$

30. Experiments with Hydrochloric Acid. — Many characteristics of hydrochloric acid may be learned by the following experiments: —

Experiment 73. — Into a bottle of the gas collected above put moistened pieces of blue and red litmus paper. How are they affected? Lower a candle into the bottle. What happens? Will the gas burn?

Experiment 74. — To show the solubility of the gas in water. Add to a bottle of hydrochloric acid gas a little water and shake for a moment. Hold a piece of moistened blue litmus paper within the bottle. Is it affected? Drop it into the solution. What happens? What has the water done? Has the solution any taste?

Experiment 75. — Purpose same as the preceding. This is a repetition of the "ammonia fountain" experiment. In preparing for it one or two additional points should be noticed. It is better to use apparatus somewhat smaller than before, and the gas must be collected by downward displacement. The lower flask in this case had better be fitted with a two-hole rubber cork, through one of which the long tube passes. Through the other should be passed a short tube bent at right angles, as shown in the figure accompanying.

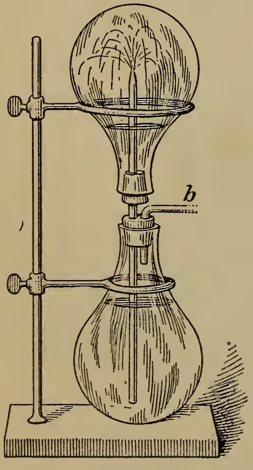

Fig. 35. — Hydrochloric Acid Fountain.

When the flask is well filled with gas, make the connections all tight, then blow through the bent tube *b* to start the flow. Otherwise it will be necessary to wait several minutes before the water will enter the upper flask. The experiment works well, but will be more attractive if the water is colored by litmus or some vegetable solution which will change color upon absorbing the acid in the upper flask. A drop or two of ammonia and a few of phenol phthalein in the water serve excellently. The deep purplish red solution becomes perfectly colorless as it enters the upper flask.

31. Characteristics of Hydrochloric Acid.—Hydrochloric acid is a colorless gas, somewhat heavier than air, and has a very irritating odor. It neither burns nor supports combustion; it turns blue litmus paper red, and is very soluble in water. At 0° C. 1 liter of water will dissolve about 500 liters of hydrochloric acid gas. So great is its affinity for moisture that whenever it escapes into damp air, heavy, white clouds appear.

32. The commercial acid, which is simply an aqueous solution of the gas, contains about 32 per cent of acid. Very dilute solutions of hydrochloric acid may be concentrated by heating until the solution contains 20 per cent of acid, but the process can be carried no further. On the other hand, very strong acid, if exposed to the air, or if heated, loses strength.

33. Hydrochloric acid has great affinity for ammonia; if a bottle of hydrochloric acid and a bottle of ammonia remain undisturbed side by side for some time, they become thickly coated about the top with ammonium chloride, a white salt formed by the union of the two gases.

34. Uses of Hydrochloric Acid. — The chief use of this acid is in the preparation of chlorine for the manufacture of bleaching powder. It is also used very largely in all chemical laboratories as a reagent, in gas works to neutralize the ammonia solutions drawn off from the "washer," and in the preparation of various chlorides.

BROMINE: Br = 80

35. Where found. — Because of its great chemical activity, bromine, like chlorine, does not occur free, but is found in sea water and in salt wells combined with other substances. Its discovery dates from the year 1826, when Balard found it in sea water.

36. Commercial Supply. — The greater part of the commercial supply of bromine is obtained from Germany and the United States. The greater amount used in this country comes from Pomeroy Bend, Ohio, where there are a large number of salt wells. Bromine appears there in the form of magnesium and sodium bromide. The salt water from these wells is boiled down to a certain extent, the common salt ($NaCl$) crystallizing out, while the other compounds remain in solution. This residue is known as the "mother liquor." The next step in the process is to put the solution into stills hewn out of solid rock, adding to it manganese dioxide and sulphuric acid. The whole is then heated by steam introduced into the liquid through pipes. Bromine distills over and is condensed under water.

37. Formerly bromine was expensive, but, owing to cheaper methods of production, the price has been so reduced that many of the salt works no longer prepare it. The method of preparation described above is illustrated in the following experiment: —

EXPERIMENT 76. — Into a test-tube put a few small crystals of sodium or potassium bromide, add a little manganese dioxide, and cover with sulphuric acid. Warm slightly and notice the dark red gas given off. What other gas have we prepared that resembles this somewhat? Describe the odor. How does it affect the eyes? Try its bleaching effects upon a moistened piece of calico or litmus paper. How does it compare with chlorine in this respect? Does anything condense upon the cooler portion of the tube? What is its physical condition? Its color?

38. Laboratory Method of obtaining Bromine. — If some bromine is desired for class experiments, it may be prepared as above. Attach a delivery tube and conduct the gas into cold water. As soon as the water is saturated, the bromine will condense in the bottom of the jar. It may then be obtained from the water by a separating funnel, or by pouring into a burette and drawing off the heavier liquid as needed for experiment. Preserve both the bromine and the water.

39. The reaction that takes place is the same as in the preparation of chlorine by a similar method, thus: —

$$2\ KBr + 2\ H_2SO_4 + MnO_2 = K_2SO_4 + MnSO_4 + 2\ H_2O + Br_2.$$

40. Another Method. — Sometimes another method is used when the purpose is merely to determine whether bromine is present in a solution. In this process the bromine is set free from its compound by the use of chlorine.

Experiment 77. — To the solution supposed to contain bromine add a little chlorine water as prepared in Experiment 61. If bromine is present, the solution should turn darker in color, due to the liberation of the bromine by the chlorine. Which does this experiment show to have the greater chemism? To prove that this color is due to the presence of free bromine add about a half cubic centimeter of carbon disulphide, shake well, and allow it to settle. If free bromine is present, the disulphide will be turned brown from the fact that it has taken up all the free bromine in the solution.

41. Characteristics of Bromine. — Bromine is a dark reddish brown liquid. It is the only non-metallic element that is a liquid. It is very volatile, giving off at all temperatures heavy brown fumes. At seven degrees below zero it solidifies. It has a very disagreeable odor, and attacks not only the throat and nostrils, but also the eyes. It differs from chlorine in that the odor is more sickening, and it was this fact that gave to the element the Greek name *bromos*, meaning *offensive odor*.

42. The vapors are non-combustible, yet, like chlorine, they allow of the continued combustion of a jet of hydrogen. As the hydrogen burns, the *red* vapors gradually disappear, and *colorless* hydrobromic acid gas takes their place. Powdered arsenic, sifted into the vapors, burns, and a small bit of antimony dropped upon liquid bromine burns brightly, and the heat generated by the chemical action melts the metal, which spins around upon the surface like sodium upon water. Bromine is soluble to a considerable extent in water, and if the temperature of such a solution is reduced by surrounding it with a freezing mixture, light brown crystals of *bromine hydroxide* separate, as did the crystals of chlorine hydroxide under similar circumstances.

43. Experiments with Bromine. — Let the teacher prove the above facts by experiments with bromine before the class.

EXPERIMENT 78. — Place a small piece of phosphorus in a deflagrating spoon and put it into a jar of bromine vapor. Allow it to remain a few minutes. Does it burn? Compare bromine with chlorine in this regard.

EXPERIMENT 79. — To test the bleaching effects of bromine upon colored solutions. Pour into a bottle a little bromine vapor, and add a few cubic centimeters of logwood, litmus, or carmine solution. Shake it up. Notice the effect upon the color.

44. Uses of Bromine. — The principal use of bromine is as a disinfectant. It is also used in organic work in chemistry and in the preparation of some dyes. For organic colors it is a strong bleaching agent, though not as active as chlorine. There are also several compounds which have application in medicine. Of these magnesium bromide, $MgBr_2$, and potassium bromide, KBr, are the most important; the former is found in the water of many mineral springs and is regarded as of medicinal value; the latter is used as a sedative in the case of nervous headache. A third compound, silver bromide, AgBr, is used in photography for sensitizing various printing papers.

IODINE: I = 127

45. The Source of Supply. — Until within recent years, the iodine of commerce was obtained from certain varieties of sea-weeds. These weeds were collected in large quantities and burned, and the ashes treated with water to dissolve out the sodium carbonate which was wanted for making soap. If such sea-weeds are burned at a low temperature, the iodine will remain in the ashes in the form of sodium and potassium iodide. From these it can be obtained as shown below.

46. The greater part of our present supply of iodine comes from Chile. There is a desert in that country many square miles in area, where are found vast deposits of sodium nitrate mixed with considerable quantities of soil and small amounts of iodine compounds. This mixture is treated with water, which dissolves out the sodium nitrate and the iodides; the solution is then evaporated till the sodium nitrate crystallizes out, as in the manufacture of bromine in Ohio, leaving the iodine compounds still in solution. The residual solution, called the "mother liquor," is treated with manganese dioxide and sulphuric acid, and gently heated.

47. Preparation for Commerce. — When treated as above, from the mother liquor, violet fumes of vaporous iodine are given off abundantly; they are passed over into cool chambers, where they condense. To further purify the iodine, it is resublimed at a low temperature and condensed in a series of conical-shaped flasks (see Fig. 36).

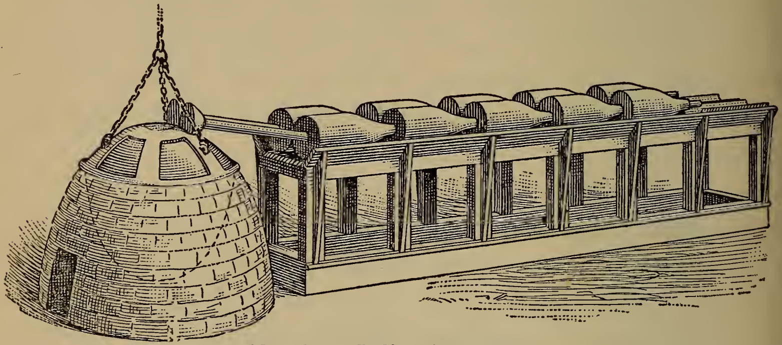

Fig. 36. — Iodine Apparatus.

At the left is a small brick furnace, in the upper part of which is an oven. The iodine to be purified is placed in the oven, and gently heated. The final reaction in the separation of the iodine is the same as in the case of the bromine and chlorine.

$$2\ NaI + 2\ H_2SO_4 + MnO_2 = Na_2SO_4 + MnSO_4 + 2\ H_2O + I_2.$$

The essential features of this method of preparing iodine may be shown by the following experiment: —

Experiment 80. — Into a small test-tube put a crystal or two of potassium iodide, add a little manganese dioxide, and cover with sulphuric acid. Warm gently; notice the fumes that are given off and what condenses upon the cooler portion of the tube.

48. Another Method of preparing Iodine. — The following method is employed to some extent in France in obtaining iodine from the ashes of sea-weeds. It is also the usual method pursued in the laboratory in testing for iodine. The plan consists simply in adding free chlorine to the iodine solution, whereby the latter is liberated from its compounds. As a commercial method it is open to the objection that if too little chlorine is added, not all of the iodine is liberated, and if too much, a portion is redissolved.

Experiment 81. — To a solution containing iodine in combination add a few drops of chlorine water. What change in color takes place? This indicates free iodine, as may be proven by adding starch paste solution. The starch will turn blue, as it did with ozone.

49. Experiments with Iodine. — Many characteristics of iodine may be learned from the following experiment: —

Experiment 82. — Put a small crystal of iodine into a test-tube and warm gently. What happens? Describe the color and odor of the vapors. Hold a piece of moistened starch paper near the mouth of the test-tube; how is the starch affected? Close the mouth of the tube with your finger and notice the stain that is formed. See whether you can remove it by moistening with caustic potash or ammonia.

50. Characteristics of Iodine. — Iodine is a solid of a dark bluish black color, with a metallic luster. At ordinary temperatures it is somewhat volatile, and when gently heated it is readily converted into vapors of a beautiful violet color. It was from this fact that the element received its name, *iodine* being derived from a Greek word which means *violet.* The odor of the vapors resembles somewhat that of dilute chlorine, but is less irritating. It has the power of turning the skin yellow, but the stain may be removed by treatment with some alkali. It has feeble bleaching properties, and turns starch paste blue. This is so delicate a test that one part of iodine in several hundred thousand of water will be clearly shown. Its affinity for phosphorus is so strong that if a crystal of iodine be dropped upon a small piece of phosphorus, the latter will be ignited almost instantly.

51. Solvents for Iodine. — Among the better solvents for iodine are chloroform, ether, alcohol, carbon disulphide, and a solution of potassium iodide.

Experiment 83. — Put a crystal of iodine into a test-tube with a little cold water. Shake for a moment or two, and then pour off a part of it into another tube and test with starch paste to determine whether any has dissolved. What are your conclusions? Warm the remainder; what indications are there that the iodine is dissolving? Test the solution again with starch paste, or with carbon disulphide, thus: add about a half cubic centimeter of the disulphide to the iodine solution, and shake well. Notice the beautiful violet color imparted to the disulphide.

Try alcohol also as a solvent. Before testing the solution with starch or carbon disulphide, dilute until pale yellow in color. What are the results? Try in the same way a solution of potassium iodide upon an iodine crystal, and state results.

52. Uses for Iodine. — In the form of a tincture, or alcoholic solution, iodine is used to a considerable extent in medicine to prevent the spread of eruptive diseases, like erysipelas, in skin affections, sore throat, and the like. In the compound iodoform it is used by physicians as a deodorant and disinfectant. As potassium or sodium iodide it is frequently used as a reagent in the laboratory, and to a limited extent in making aniline dyes. In these various ways 300 tons or more are used annually.

53. Some Comparisons. — It has probably been observed that the same method is used in preparing chlorine, bromine, and iodine. Notice the following reactions: —

$$\begin{array}{l|l}
\mathrm{Cl} & \mathrm{MnO_2} + 2\,\mathrm{H_2SO_4} + 2\,\mathit{NaCl} = \mathrm{MnSO_4} + \mathrm{Na_2SO_4} \\
 & \qquad + 2\,\mathrm{H_2O} + \mathit{Cl}_2. \\
\mathrm{Br} & \mathrm{MnO_2} + 2\,\mathrm{H_2SO_4} + 2\,\mathit{NaBr} = \mathrm{MnSO_4} + \mathrm{Na_2SO_4} \\
 & \qquad + 2\,\mathrm{H_2O} + \mathit{Br}_2. \\
\mathrm{I} & \mathrm{MnO_2} + 2\,\mathrm{H_2SO_4} + 2\,\mathit{NaI} = \mathrm{MnSO_4} + \mathrm{Na_2SO_4} \\
 & \qquad + 2\,\mathrm{H_2O} + \mathit{I}_2.
\end{array}$$

SUMMARY OF CHAPTER

Meaning of term *halogen*.

Names, symbols, and atomic weights of the halogens.

Comparison of the halogens.

- *a.* Method of preparing.
- *b.* Physical condition at ordinary temperatures; at lower temperatures.
- *c.* Color.
- *d.* Odor.
- *e.* Density.
- *f.* Chemical activity.
- *g.* Bleaching powers.
- *h.* Affinity for certain substances, as hydrogen, phosphorus, etc.
- *i.* Uses.
- *j.* Hydrogen compounds.
  - Compare hydrofluoric and hydrochloric acids as to —
    1. Method of preparation.
    2. Characteristics.
    3. Uses.

Special points for study.

Method of etching glass.

What kind of substances may be used instead of manganese dioxide in preparing chlorine? Why?

Proof of this by experiments.

Practical application of this.

Compare these two methods of making chlorine: —

1. $MnO_2 + HCl$.
2. $MnO_2 + NaCl + H_2SO_4$.

How similar? How different?

Explain how chlorine bleaches. Write the equation. Source of commercial supply of hydrochloric acid.

Tests for bromine and iodine with carbon disulphide — compare results.

Method of obtaining and purifying iodine.

Describe experiments which illustrate chief properties of chlorine, bromine, and iodine.

Solvents for chlorine, bromine, and iodine.

CHAPTER X

ACIDS, ALKALIES, AND SALTS

1. **Neutralization.** — There are a great many substances which, if put together, have the power of destroying the characteristic properties of each other.

EXPERIMENT 84. — To show this fact, put into an evaporating dish about 10 cc. of dilute hydrochloric acid and dip into it a small piece of blue litmus paper. Notice that it is changed to red. Now add slowly, stirring all the time with a glass rod, a solution of caustic soda, until the litmus paper *just* turns blue again; then add one drop of hydrochloric acid. You ought now to have a solution that will not affect either red or blue litmus paper. Boil this solution to dryness. What is the appearance of the solid thus obtained? Taste it. Does it seem familiar? Dissolve it in a little water and test with both red and blue litmus paper. Is the paper affected? Now boil a little hydrochloric acid to dryness. Does it leave a residue? Examine a specimen of solid caustic soda and compare with the white solid obtained above. Are the two solids the same? Do they both affect litmus in the same way?

2. From this experiment we see that the acid and the caustic soda, on being put together, have both lost their characteristic properties and have reacted to form a new substance having the properties of neither. In other words, they have *neutralized* each other.

3. **Bases.** — Such substances as have the power of neutralizing the properties of acids are called *bases.* This was shown in Experiment 84 above. We have already seen that the compound of any element with oxygen is called an *oxide;* many of the oxides combine with water to form

water oxides, or, to use the ordinary term, which is from the Greek, *hydroxides* or *hydrates*. We have seen also that some oxides or *anhydrides*, when united with water, form acids, as, for example, nitrogen trioxide. Strictly speaking, such compounds are hydroxides, but we never apply that term to them; it is restricted altogether to those compounds of oxides with water which have the power of neutralizing acids.

4. **Alkalies.** — A few of these compounds, which have exceedingly strong basic properties, are called *alkalies*. The four most common alkalies are the three hydroxides of sodium, potassium and calcium, and ammonia. If we study the formulæ of the hydroxides, we shall see that water may be taken as the type upon which all the others are built. Thus: —

Water	HOH
Caustic Potash	KOH
Caustic Soda	NaOH
Lime Water	$Ca(OH)_2$
Ammonium Hydroxide . .	NH_4OH

The only difference is that one atom of hydrogen in the water has been replaced by some metal or group of elements.

5. As most of the metals themselves have all the characteristic properties of bases, they are, by many, regarded as bases, and always spoken of as such. Probably there is no serious objection to this, but it should be remembered that, strictly speaking, all bases are compound bodies.

6. **Acids.** — It is a difficult matter to define acids. They are substances which have properties exactly the opposite of bases. They possess the power, not only of turning

blue litmus red, but of similarly affecting various other vegetable colors, all of which are restored again by the use of an alkali. They also have a sour taste, though this is not a distinctive feature, as many bodies not acids also have the same property.

7. **Their Composition.** — If we recall the formulæ of the few acids we have already used, nitric, hydrochloric, and sulphuric, we see that they all contain hydrogen; it is true also that most contain oxygen, together with some third element which seems to give the distinctive properties to the acid. It was at one time supposed that all acids contained oxygen, and in accordance with this idea oxygen received its name. Later, however, were discovered hydrochloric and other acids, which contained no oxygen whatever. A distinctive property of acids is that they all have the power of giving up the whole or a part of their hydrogen, and of combining instead with some metal or base. Thus we have seen that when zinc was treated with hydrochloric or sulphuric acid, the metal replaced the hydrogen in the acid, setting the former free. (See p. 40.)

8. **Salts.** — A salt is a compound formed by the union of an acid with a base or metal, possessing properties different from those of either of its constituents. We have been accustomed to think of *salt* as a particular substance used in seasoning food, but we must now remember that it is a term applied to a large number of compounds, called salts because they resemble common salt in appearance or properties. They are all produced in the same way. We saw above that when we neutralized hydrochloric acid with caustic soda and boiled to dryness, we obtained a white solid, resembling and tasting like common salt, which it really was.

Experiment 85.—In the same way as in Experiment 84, neutralize about 10 cc. of hydrochloric acid with caustic potash and boil to dryness as before. Compare the salt produced, in taste and appearance, with that obtained before.

9. Normal or Neutral Salts.—There are two general classes of salts, *neutral* or *normal*, and *acid*. A normal salt is one in which *all* the *displaceable* hydrogen of the acid used in making the salt has been replaced by some base. For example, when caustic potash and sulphuric acid neutralize one another, the following reaction takes place:—

$$H_2SO_4 + 2\ KOH = K_2SO_4 + 2\ H_2O.$$

We see here that all the hydrogen in the sulphuric acid, two atoms, has been replaced by an equivalent amount of the metal, potassium, and the salt produced, potassium sulphate, K_2SO_4, is a normal salt.

10. Again, if lead is treated with vinegar (acetic acid), which is represented by the formula $HC_2H_3O_2$, we have this reaction:—

$$Pb + 2\ HC_2H_3O_2 = Pb(C_2H_3O_2)_2 + H_2.$$

It will be noticed that in the salt resulting, $Pb(C_2H_3O_2)_2$, a quantity of hydrogen remains. Lead acetate is, notwithstanding, a neutral salt, because only one atom of hydrogen, the first, in each molecule of acid can be displaced.

11. Acid Salts.—If, however, we use only half the amount of caustic potash shown by the first reaction above with the sulphuric acid, we shall replace only half of the hydrogen in the acid, and the salt resulting will be an *acid* salt, thus:—

$$H_2SO_4 + KOH = KHSO_4 + H_2O.$$

12. Reading the Formulæ of Salts. — The compound, K_2SO_4, is read, *normal potassium sulphate*, or usually, simply *potassium sulphate*. The acid salt, $KHSO_4$, is read, *acid potassium sulphate*, or *potassium hydrogen sulphate*. Sometimes the prefix *mono* is applied, but usually only in the case of salts of acids having three or more replaceable hydrogen atoms, as phosphoric, H_3PO_4, or silicic, H_4SiO_4. With these acids we may form the following salts: —

Phosphoric Acid, H_3PO_4

Mono-sodium Phosphate	NaH_2PO_4
Di-sodium Phosphate	Na_2HPO_4
Normal sodium Phosphate	Na_3PO_4

Silicic Acid, H_4SiO_4

Mono-sodium Silicate	NaH_3SiO_4
Di-sodium Silicate	$Na_2H_2SiO_4$
Tri-sodium Silicate	Na_3HSiO_4
Normal sodium Silicate	Na_4SiO_4

Exercises. — In the following formulæ, state which represent acids, which bases, and which salts, giving reasons therefor. Give also the name of the substance represented. If salt, state whether acid or normal: —

Na_2SO_4, KOH, H_2SO_4, H_3PO_3, $ZnSO_4$, KNO_3, $Ca(OH)_2$, $BaSO_4$, K_3PO_4, K_2HPO_4, KH_2PO_4, HCl, NaOH, $NaHSO_4$, $NaNO_3$.

13. Nomenclature of Acids. — It will be noticed that with one exception the acids we have met with so far all have names ending in *ic;* thus: —

Sulphuric	H_2SO_4
Nitric	HNO_3
Phosphoric	H_3PO_4
Silicic	H_4SiO_4, etc.

The greater number of acids with which we shall have to deal, as already stated, contain three elements, the first of which is hydrogen, the third oxygen, and a *second* which gives the name to the acid. Thus the middle symbols in the above formulæ are: —

S	Sulphur	acid,	H_2SO_4	Sulphuric
N	Nitrogen	"	HNO_3	Nitric
P	Phosphorus	"	H_3PO_4	Phosphoric
Si	Silicon	"	H_4SiO_4	Silicic

14. Sometimes, however, this second element forms more than one acid with hydrogen and oxygen. In such cases the most common, and hence the earliest known, received the name with the termination *ic*. Then the acid having a smaller amount of oxygen is given the termination *ous*. This we have seen in the two nitrogen acids: —

Nitric	HNO_3	Oxygen, 3 atoms.
Nitrous	HNO_2	" 2 "

15. Sometimes even three or four acids are formed from the same three elements, the amount of oxygen only varying. In such cases, the one with the least quantity of oxygen is given the prefix *hypo*, meaning *under* or *lesser*, and the one with the most oxygen has the prefix *per*, *beyond* or *above*. These may be illustrated by the following series: —

Sulphur*ic*	$H_2 \mid S \mid O_4$	Oxygen, 4 atoms
Sulphur*ous*	$H_2 \mid S \mid O_3$	" 3 "
Hypo-sulphurous	$H_2 \mid S \mid O_2$	" 2 "

CHLORINE ACIDS

*Per*chloric	H	Cl	O_4	Oxygen, 4 atoms.
Chloric	H	Cl	O_3	“ 3 “
Chlorous	H	Cl	O_2	“ 2 “
Hypo-chlorous	H	Cl	O	“ 1 “

16. Nomenclature of Salts. — All of the acids named above have the power of combining with various metals, or their hydroxides, to form salts. All such as result from the union of a base with an *ic* acid are given names with the termination *ate*. Thus, all salts of sulphur*ic* acid are sulph*ates*; of nitr*ic* acid, nitr*ates*; phosphor*ic* acid, phosph*ates*, etc. To illustrate: —

H_2SO_4, sulphuric acid, gives —

with zinc, $ZnSO_4$, zinc sulphate;
with potassium, K_2SO_4, potassium sulphate;
with calcium, $CaSO_4$, calcium sulphate.

HNO_3, nitric acid, gives —

with potassium, KNO_3, potassium nitrate;
with sodium, $NaNO_3$, sodium nitrate;
with ammonia, NH_4NO_3, ammonium nitrate.

17. Salts formed from the *ous* acids receive names ending in *ite*. (It may aid the memory in associating the pronouns singular, *I*, plural objective *us*, with the *ous* acids and *ite* salts.) Thus, from

H_2SO_3, sulphur*ous* acid, we have
K_2SO_3, potassium sulph*ite*;
Na_2SO_3, sodium sulph*ite*, etc.

In the case of salts formed from the *hypo* and *per* acids, the corresponding prefix is simply given to the salt. Thus: —

$NaClO$, sodium *hypo*chlor*ite*, from
$HClO$, acid, *hypo*chlorous, and
$NaClO_4$, sodium *per*chlor*ate*, from
$HClO_4$, acid, *per*chlor*ic*.

18. Binary Compounds. — All of the above salts are formed from what are sometimes called *ternary* acids; that is, those consisting of three (or more) terms. In like manner, a *binary* compound would be one which consists of only two elements. The following are examples: —

Common Salt	$NaCl$
Calcium Chloride . . .	$CaCl_2$
Water	H_2O
Turpentine	$C_{10}H_{16}$

It will be noticed from these formulæ that though in a binary compound there are but two elements, the number of atoms of each of these elements is quite variable.

19. As already stated, there are a few acids which contain no oxygen. Salts obtained from them would, therefore, all be binaries. Thus: —

from Hydrochloric	acid,	HCl,	we obtain the	*chlorides;*
Hydrobromic	"	HBr,	"	*bromides;*
Hydriodic	"	HI,	"	*iodides;*
Hydrofluoric	"	HF,	"	*fluorides;*
Hydrosulphuric	"	H_2S,	"	*sulphides.*

20. Compounds with Oxygen Alone. — Oxides. — It will be noticed that all binary salts are given names ending in *ide*. Furthermore, it is seen that it is the second element in every case which gives the *name* to the substance; thus: —

$$\left.\begin{array}{l}NaCl\\ KCl\\ MnCl_2\\ CaCl_2\end{array}\right\}\text{ are all } \textit{chlorides}\text{, while the first}$$

element indicated in the formula is simply descriptive in character, or the *adjective* that tells what kind of a chloride. Thus the above are

$$\left.\begin{array}{l}\text{Sodium}\\ \text{Potassium}\\ \text{Manganese}\\ \text{Calcium}\end{array}\right\}\text{ Chloride;}$$

just as we might say

$$\left.\begin{array}{l}\text{Stone}\\ \text{Brick}\\ \text{Frame}\\ \text{Log}\end{array}\right\}\text{ House.}$$

21. It frequently happens that two elements, just as in the case of the ternary acids, may unite in different proportions to form two or more compounds. We have already seen this in studying the oxides of nitrogen, p. 81. When two such exist, as for example the two oxides of mercury, HgO and Hg_2O, the one having the smaller proportion of the *second* element, as indicated by the formula, is the *ous* compound, just as in the case of the acids already studied, while the one having the greater proportion of the same element is the *ic* compound.

22. Again, we noticed in studying the oxides of nitrogen: —

N_2O, ratio of oxygen to nitrogen, 1 : 2
N_2O_2, " " " 2 : 2 = 1 : 1.

In the first we found one-half as many atoms of oxygen as of nitrogen; in the second the same number; they were therefore called nitr*ous* and nitr*ic* oxides. In a few instances, instead of using the English name with the terminations *ous* and *ic*, for the sake of euphony, the Latin forms are taken. Thus: —

Cu_2O, Cuprous Oxide
CuO, Cupric "
$FeCl_2$, Ferrous Chloride
Fe_2Cl_6, Ferric "

23. Returning to the series of nitrogen compounds, it will be noticed that they were given two names. This is very often done, one of them using a prefix to indicate the exact number of atoms of the last element in the formula of the compound. Thus we have

N_2O, Nitrogen Monoxide.
N_2O_4, " Tetroxide
P_2O_5, Phosphorus Pentoxide, etc.

24. Old Forms. — Occasionally we use the old terms, *pro*, *per*, and *sesqui*. The first is a prefix, meaning *before*, and is given to some uncommon or unstable compounds which in the case of a series would be the first or lowest. Thus, FeO is sometimes spoken of as iron *pro*toxide. Nitrogen tetroxide, N_2O_4, is also called *per*oxide, as is hydrogen dioxide as well, it being the compound coming in the series *beyond* the others. *Sesqui* is applied to binary compounds in which the two elements unite in the ratio of 2 to 3, as in Fe_2O_3, iron sesquioxide.

SUMMARY OF CHAPTER

Neutralization — Meaning of the term.
                Experiments to illustrate.
Three classes of compounds.
    Compare bases and acids.
        a. In composition.
        b. In properties.
    Alkalies — What are they?
                Examples.
    Salts — What are they?
            Two classes.
                How formed.
                How distinguished by name.
                Examples to illustrate.
    Nomenclature.
        a. Of acids.
        b. Of salts.
    Examples to illustrate both.
Binary compounds.
    Meaning of term — Illustrations.
    Six important classes — Examples.
    Nomenclature — Compare with acids.

CHAPTER XI

CARBON AND A FEW COMPOUNDS. $C = 12$

1. **Abundance.** — With the exception of oxygen, carbon is the most widely distributed and most abundant of all the elements. In the form of compounds it is found in the air as carbon dioxide, resulting from combustion and respiration, and in limestone, $CaCO_3$, which constitutes a large portion of the rocky crust of the earth. It also occurs in almost all food products, such as sugar, flour, starch, vegetables, and fruits, and forms a large part of the woody structure of plants and trees.

2. **Forms.** — In the free state carbon may be considered under two divisions : —

a. Crystallized, including
  1. The Diamond.
  2. Graphite or Plumbago.

b. Amorphous (without crystalline form),
  1. Coal.
  2. Lampblack.
  3. Gas Carbon, etc.

3. **Diamonds.** — The diamond occurs in octahedral crystals. It is found in South America, Africa, Australia, and India. By some the stones are thought to be of meteoric origin and not native to the earth, but the theory seems not well founded. Moissan, the French chemist, has succeeded in making a few diamonds in the electrical furnace,

but they have all been exceedingly small, and black in color, so as to have no value except in a scientific way. In nature they occur rough and covered with a layer of partially decomposed rock. The most highly prized are perfectly transparent, but many of various colors have been found. The diamond has strong refractive power, is the hardest of known substances, and can be cut and polished only by its own dust.

4. **Their Practical Uses.** — Diamonds are used, not only as ornaments, but also in cutting glass; and the cheaper, imperfect varieties are employed as tips on drills for cutting through hard rocks. That the diamond consists of carbon may be proved by burning it between electric terminals in an atmosphere of oxygen; the diamond and oxygen disappear, and carbon dioxide, CO_2, remains.

5. **Graphite.** — Next to the diamond, graphite or plumbago is the purest form of carbon. It is sometimes called *black lead*, but it contains no lead whatever. It is often found in hexagonal prisms, is steel-gray in color, has a greasy feeling, and as a mass is comparatively soft, though the particles themselves are very hard.

6. That it consists of carbon may be proved by testing it in the electric furnace, as in the case of the diamond, similar results being obtained.

7. **Uses.** — The most common use of graphite is in making what are known as *lead pencils*, so named because plumbago was at first supposed to be a compound of lead. In making pencils the graphite is thoroughly pulverized and mixed, according to the grade of pencil, with different proportions of fine clay, also well ground. The whole is then made up with water into a dough and pressed into moulds and dried, or while still soft is forced through plates with apertures the size of the *lead* in the pencil.

Graphite is also used as a lubricant, as a stove polish, and in making crucibles.

8. Amorphous Carbon. — The most important uncrystallized forms of carbon are the various coals, — anthracite, semi-anthracite, bituminous, lignite, peat, jet, cannel, and the artificial form, charcoal. Of great importance also are gas carbon, lampblack, and coke.

9. Coal. — Coal is supposed to be the result of pressure and heat applied to a luxuriant vegetable growth in the presence of moisture. Peat is the newest of the coals, being in process of formation in swamp-lands to-day. It consists almost entirely of a mass of roots. Next in age is lignite, in which the woody structure is still apparent.

10. Anthracite and Bituminous Coals. — Anthracite differs from bituminous coal in that the former, being subjected to greater heat and pressure, has been deprived of its volatile products. These furnish in part, at least, the petroleum and natural gas of the present time. Petroleum is really a mixture of a number of different oils, with boiling points differing greatly. These, in the process of refining the crude oil, distill over at different temperatures. Such light oils as naphtha and benzine are obtained at a low temperature, a somewhat higher temperature producing kerosene, and higher still paraffine. This method of separating substances through differences in their boiling points is called *fractional* distillation, while that in which the substance heated is decomposed is called *destructive* distillation.

11. Charcoal. — Charcoal, because of the abundance of timber, has usually been prepared in a simple, but very wasteful, manner. Large piles of wood are covered with earth and set on fire. Most of the air is excluded in this way, and only enough heat is produced to expel the volatile products from the wood. At present, however, in some sections the wood is heated in iron retorts, and the volatile products are condensed and refined, much in the same way as with petroleum.

12. Coke. — Coke bears the same relation to soft or bituminous coal that charcoal does to wood. It is an artificial product obtained by expelling all the volatile products from the coal. Most of the supply comes from the gas factories as a by-product, but where the local supply is insufficient, it is prepared specially for smelters in large brick ovens. See the figure below.

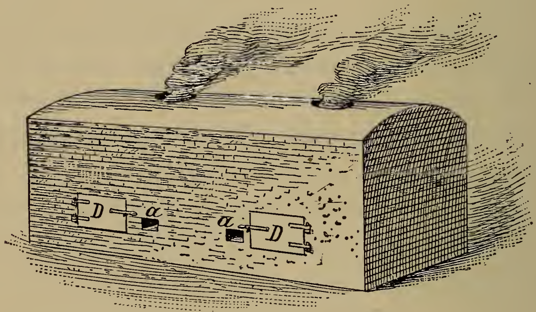

FIG. 37. — Coke Oven.

aa, openings for slight draught at first. *DD*, doors for removing coke.

The coal, in car loads, is shoveled in from above; it is then ignited, and the openings on the side almost entirely closed. In the course of several hours the combustion of the lower layer of coal has converted the remainder into coke, the doors are opened, and the coke drawn out.

13. Gas Carbon. — Gas carbon is another by-product of coal-gas manufacture. Just as soot collects in stove-pipes and flues, so on the inside of the retorts there is gradually deposited a very hard, black substance, known as gas carbon. This is occasionally removed, ground up fine, and moulded into the familiar carbon rods in our electric arc lights, and into plates for electric batteries.

14. Lampblack. — Lampblack is the result of the imperfect combustion of any substance rich in carbon. It is usually prepared by burning some hydrocarbon, such as turpentine, $C_{10}H_{16}$, in a limited supply of air. The dense black smoke resulting is allowed to deposit upon canvas in a cool room, from which it is shaken, and is then ready for commerce. It is used in making black paint, printers' ink, etc.

SOME USES OF CARBON

15. As a Reducing Agent. — In the form of charcoal or coke, at a high temperature, carbon is a great *reducing* or *deoxidizing* agent. By this we mean that when it is heated with the oxides of various metals, it has the power of combining with the oxygen and *reducing* the oxide to the metallic condition. This will be made clear by the following experiment.

EXPERIMENT 86. — Make a small cavity near one end of a stick of charcoal, and put therein a little litharge, PbO, or red lead, Pb_3O_4, and heat strongly with the *reducing* flame. Notice that in a few minutes a bead of lead appears instead of the oxide that we had. The carbon has combined with the oxygen in the lead oxide to form carbon dioxide, and the lead has been reduced to the metallic form.

16. As an Absorbent. — Carbon in the form of charcoal is an excellent absorbent, not only of gases, but of certain other substances as well.

EXPERIMENT 87. — Thrust a piece of charcoal under water and hold it there a minute or so. What is seen escaping from the charcoal? Heat another piece red-hot and plunge under water. Are the results different? Why?*

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* In this connection refer to Exp. 47, under ammonia.

Experiment 88. — Soak some vegetable matter in a vessel of water until it has become very offensive, on account of decomposition. Put a little of this water into a flask and add some bone-black or powdered charcoal, and shake well. Notice that the disagreeable odor disappears.

17. As a Purifier. — Application is made of this fact in purifying cisterns which have become foul with decomposing organic matter. The charcoal should be removed after a time and heated to redness to destroy thoroughly the organic matter which may have been absorbed. It is believed that partial oxidation takes place within the pores, but unless the charcoal is heated they eventually become clogged.

Experiment 89. — Fit a filter paper smoothly to a funnel as described in Appendix C, page 365, and partly fill it with bone-black. Now pour upon it, slowly at first, a few cubic centimeters of logwood or some other colored vegetable solution. How is it affected? Try also in the same way a solution of copper nitrate. Are the results the same?

18. In Refining. — An application of the power of charcoal to absorb vegetable colors is made in refining sugars. At first they are brown, not very different from maple sugar in appearance. This raw sugar, as it is called, is dissolved in water and passed through filters of bone-black which absorb the coloring matter and leave the solution clear. This may be shown by filtering a solution of molasses in water.

Experiment 90. — In like manner, charcoal has the power of absorbing various organic flavors. Pass through a powdered charcoal filter an infusion of tea or coffee, and taste it after it has gone through. How is it changed?

19. It would be impossible to enumerate the various uses of carbon in its different forms. Many of these are familiar to the student, and others will be learned from time to time. Many of them have already been named in the sections immediately preceding this.

Compounds of Carbon. The Oxides

20. Carbon Monoxide, CO. — This is a gas obtained when carbon is burned in a limited supply of air. It may be prepared by passing steam over red-hot coke or charcoal, whereby the steam is decomposed, thus: —

$$H_2O + C = CO + H_2.$$

It is also produced in grates and base-burners. At the lower portions of the fire where the heat is most intense the carbon is completely burned, producing carbon dioxide; as this passes up through the red-hot coal, it unites with another portion of carbon and forms the monoxide. Again, on reaching the upper surface, the monoxide unites with the oxygen of the air and is burned into carbon dioxide.

21. Carbon monoxide may be prepared in an impure form by heating oxalic acid or potassium ferrocyanide with sulphuric acid, or by passing a current of carbon dioxide slowly through a tube containing red-hot charcoal or coke.

22. Characteristics of Carbon Monoxide. — Carbon monoxide is a colorless gas, having a faint, peculiar, but somewhat unpleasant and stifling odor; it is a little lighter than air and burns with a pale blue flame. It is not soluble in water, is only slightly explosive when mixed with air or oxygen, and is poisonous when inhaled. It has the power of decomposing the blood, and thus of rendering it incapable of carrying oxygen and removing the waste of the body. On this account serious results sometimes follow its escape into rooms from coal stoves when the drafts are closed at night. Open charcoal fires also produce the same gas, and have sometimes been the means of causing death.

23. As a Reducing Agent. — It has been seen that carbon is a strong reducing agent. Carbon monoxide has the same properties, owing to the fact that it has strong affinity for more oxygen, to form carbon dioxide. The reduction of metallic ores in blast furnaces is, to a considerable extent, due to this property of carbon monoxide. It may be seen by passing a current of carbon monoxide over lead oxide, PbO, heated red hot in a tube. The monoxide abstracts the oxygen from the lead oxide, forming carbon dioxide and metallic lead. The reaction is as follows: —

$$PbO + CO = Pb + CO_2$$

24. Carbon Dioxide, CO_2. — Where found. — This gas is always found in the air, being produced by the combustion of organic bodies and by respiration. The proportion varies somewhat, but seldom exceeds four parts in 10,000 parts of air. Another source of this gas as found in the atmosphere is fermentation and decay.

25. Produced in Decomposition. — As already mentioned in considering ammonia, organic substances are very unstable and readily break up to form simpler compounds. The molecules of most so-called organic compounds consist of carbon, hydrogen, oxygen, and often nitrogen, and are usually very complicated. In the processes of decay the atoms rearrange themselves, and carbon dioxide is one of the new products. The process is the same when fermentation is induced by bacteria or germs, such as those of ordinary yeast. If into a flask containing some water sweetened with sugar or molasses a little yeast be introduced, fermentation very soon begins, and the bubbles of gas which pass off may be collected and proved to be carbon dioxide.

26. How prepared. — For laboratory purposes carbon dioxide is usually prepared by treating some carbonate, as marble, $CaCO_3$, with dilute acid.

Experiment 91. — Put into a small flask some marble, coarsely powdered, and add some dilute hydrochloric or nitric acid. Notice the rapid effervescence and evolution of colorless gas.

Experiment 92. — Collect by downward displacement a bottle of the gas, generated as above. Lower into it a burning match or candle; what are the results? Ignite a piece of magnesium ribbon and hold it in a bottle of carbon dioxide; what are the results? What two products are formed? Why does the ribbon continue to burn? Mention some other gas that supports the combustion of phosphorus, but not that of ordinary substances.

Experiment 93. — To show the density of the gas. Put into a good-sized bottle or beaker a small candle and pour in upon it another bottle of carbon dioxide. You cannot see anything being turned out, but the results are apparent. This is sometimes made more effective by fastening at short intervals upon the bottom of a trough several candles. Lift one end of the trough and pour down it a large bottle of carbon dioxide. The candles will be extinguished, one after another, as the gas reaches them.

Fig. 38.

Experiment 94. — Purpose same as preceding. Put into an evaporating dish a little gasoline and ignite it. Take a large bottle of carbon dioxide and pour suddenly upon the burning oil. The flame will be instantly extinguished.

Experiment 95. — To show effect of carbon dioxide on limestone. Pass a current of carbon dioxide through a few cubic centimeters of lime water. Notice the formation of a white precipitate, which is calcium carbonate, $CaCO_3$, of the same composition as limestone. Continue passing the gas through the milky solution; what change takes place? Can you explain?

27. Characteristics of Carbon Dioxide. — From the above experiments we learn that carbon dioxide is a colorless, odorless gas, considerably heavier than air. It is non-combustible and a non-supporter of ordinary combustion, though such substances as magnesium, which burns with great intensity, are able to decompose the gas and make use of the oxygen. It is slightly soluble in water and gives to the latter a faint acid taste and reaction. The presence of carbon dioxide may always be determined by its effect upon lime-water. It forms in the water a white precipitate which dissolves slowly again in excess of the dioxide. Limestone caves are a manifestation on a large scale of the principle shown in the simple experiment above. Water under pressure absorbs considerable quantities of carbon dioxide, which gradually dissolves the limestone and forms caverns.

28. Liquid Carbon Dioxide. — Carbon dioxide may be liquefied in strong cylinders by pressure; if the pressure is suddenly withdrawn, a portion of the liquid is rapidly vaporized, producing such cold as to convert the remainder into a white crystalline solid like snow. The temperature of this carbonic acid snow is sufficiently low to freeze mercury. The solid carbon dioxide vaporizes without first melting.

29. Choke Damp. — Because of its density, carbon dioxide frequently collects in deserted mines and deep wells, and is called by miners "choke damp." Its presence in such places, however, may always be detected by lowering to the bottom a burning candle or lantern. Carbonic anhydride is another name for the same gas, it being the anhydride of the unstable acid, H_2CO_3. It is still popularly called carbonic acid gas.

30. Uses of Carbon Dioxide. — Carbon dioxide is used extensively in making "soda water." It is confined in strong cylinders under great pressure, and allowed to flow into cold water in strong tanks also under pressure. The water is thus thoroughly charged. When the stopcock is turned and the water flows into the glass, the pressure being removed, the carbon dioxide rapidly bubbles out. It is this gas which gives the sharp biting taste to soda water and also to the water of many mineral springs. It is the same gas that causes the effervescence in beer and the sparkling appearance of some wines.

31. In some of our cities carbon dioxide is now being put upon the market in small oval-shaped steel vessels into which the gas is forced under great pressure. When ready for use, a valve is opened, the gas rushes into a glass of water flavored and sweetened, and the soda water is ready. These *sparklets*, as the steel vessels are called, are very small, and a large number may be carried without great inconvenience. In Germany the same article is sold under the name of *Sodors*. Certain fire extinguishers owe their value to the large quantities of carbon dioxide contained; and instances are on record in which fires in coal mines which have defied all other means have been extinguished by passing in carbon dioxide.

32. Though this gas cannot be inhaled in any considerable quantities, it is not poisonous, but like water causes death by shutting out the oxygen. Hence a person might *drown* in a well or vat of carbon dioxide just as readily as in one of water. To plant life, however, the gas is indispensable; it is inhaled by plants as oxygen is by animals, and in the presence of light the life forces of the plant are sufficient to decompose the compound into its constituents. The carbon is stored up in the woody structure of the tree or plant, and the oxygen is given off again to the air. Thus a considerable portion of the carbon in all our forests and coal beds was once in the form of gaseous carbon dioxide in the atmosphere.

The Hydrocarbons

33. Definition. — By this term we mean those compounds consisting of carbon and hydrogen, of which there are many. The most important are the three following: —

Marsh Gas	CH_4
Olefiant Gas	C_2H_4
Acetylene	C_2H_2

34. Marsh Gas. — This is also known as *methane*, and by miners as *fire damp*. It is often found in coal mines as the result of the decomposition of organic matter, and in swamps from the same source. By stirring the leaves and similar matter that collect upon the bottoms of ponds, bubbles of gas, consisting largely of marsh gas, are seen to rise. It is always produced in the destructive distillation of any organic matter, such as the preparation of charcoal in retorts or that of illuminating gas from coal.

35. Characteristics of Marsh Gas. — Marsh gas is a colorless, odorless gas, the lightest of all except hydrogen, having a specific gravity compared with air of less than 0.6. It is highly inflammable, burning with a pale blue flame, and with air or oxygen forms a dangerous explosive mixture. It is by this gas that most explosions in coal mines are caused, and on this account it is called *fire damp*, the word *damp* with miners being a generic term meaning *gas*. Marsh gas is somewhat soluble in water, and is neutral to test paper, affecting neither red nor blue. It is an important constituent of ordinary coal gas, and when burned produces much heat.

36. Protection against Fire Damp. — If you hold a wire screen over the flame of a Bunsen burner, you will see that the flame does not pass through it, although if you bring a lighted match above the screen, you will find there a combustible gas. This is because the wire cloth, being a good conductor of heat, withdraws it from the burning gas and so lowers the temperature that what has passed through no longer burns. Now hold the screen in the flame until it becomes red hot; the gas above will be ignited and continue to burn.

An observation of these facts led Sir Humphry Davy to design the "safety lamp" which now bears his name. It is little more than an ordinary miner's lamp surrounded by a wire screen. If the miner enters a chamber filled with fire damp, though the gas may burn on the inside of the screen, there is no danger unless he remains until the wire becomes hot enough to ignite the gas outside.

37. Olefiant Gas, C_2H_4. — This also is a constituent of common illuminating gas, and is formed in the destructive distillation of wood and coal. It may be prepared by heating ethyl alcohol with sulphuric acid. The latter has strong affinity for water and has the power of abstracting it from the alcohol, C_2H_5OH or C_2H_4, H_2O, thus: —

$$C_2H_5OH + H_2SO_4 = C_2H_4 + H_2SO_4, H_2O.$$

38. Characteristics of Olefiant Gas. — *Ethane*, as this gas is also called, is of about the same density as air, is colorless, has a faint odor, and burns with a yellowish white light, such as is seen in the ordinary gas jet. It is somewhat explosive when mixed with air or oxygen; at 40 atmospheres' pressure it is reduced to a liquid.

ACETYLENE, C_2H_2

39. How prepared. — This gas is formed in small quantities together with other hydrocarbons in the distillation of wood and coal. It is prepared now in large quantities by treating calcium carbide, CaC_2, with water, as follows: —

$$CaC_2 + H_2O = CaO + C_2H_2.$$

The lime, CaO, thus formed immediately reacts with another molecule of water, forming slaked lime, or calcium hydroxide, $Ca(OH)_2$, thus: —

$$CaO + H_2O = Ca(OH)_2.$$

The final reaction then would be indicated by —

$$CaC_2 + 2\ H_2O = C_2H_2 + Ca(OH)_2.$$

40. Calcium Carbide. — Calcium carbide is a dark gray solid, more or less crystalline in appearance, always giving off the odor of acetylene, owing to its decomposition by the moisture in the air. In America the greater portion of the commercial supply comes from Niagara Falls, where it is prepared by fusing at intense heat in electrical furnaces pure lime intimately mixed with charcoal finely pulverized. When taken from the furnace, it is packed in metallic drums, sealed air-tight, and is then ready for shipment.

EXPERIMENT 96. — Into a test-tube put a small lump of calcium carbide, cover with water, and quickly insert a cork with delivery tube and jet attached. Notice the violent chemical action and the odor of the gas. Light the jet and notice with what kind of a flame it burns.

41. Another Method. — Sometimes this method is varied slightly by using a flask fitted with a two-hole cork. Through one hole passes the delivery tube, through the other a funnel with a stop-cock. In this way the flow of water can be regulated and the rapid evolution of gas prevented. Precaution must be taken in this case not to light the jet *too soon*, as acetylene mixed with air is dangerously explosive.

42. Acetylene Generators. — This illustrates one class of acetylene generators now offered upon the market, in which the water is allowed to drip on the carbide. The objection to this is that with the small supply of water the carbide becomes so warm as to bring about a partial decomposition of the acetylene into other undesirable hydrocarbons.

Experiment 97. — For class-room work an excellent generator may be prepared thus: procure a tin can, holding a quart or two, and having a screw top. (A can in which some varieties of coffee are sold will do.) To the inside of the screw top solder a hook. Upon this suspend a small bucket or basket made from a tin can, and having a wire-cloth or perforated bottom. Cut out the bottom of the larger can as shown in the cross-sectional view *b* of the accompanying figure; then solder two strong bent wires, *W*, *W*, upon opposite sides of it.

Now obtain another can just large enough to allow the first to move up and down easily within it. Melt or cut out the top; then cut down two flaps about three-fourths of an inch deep, and bend them to a horizontal position, as at *F*. Through each flap punch a hole large enough to receive the bent guide-wires soldered on to the other can. Near the bottom cut a round hole and insert a rubber cork, through which passes a bent delivery tube extending up nearly to the top of the can.

When ready for work fill this can nearly full of water, put some carbide into the basket, suspend it upon the hook and then lower the first

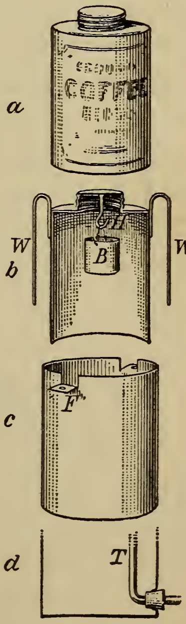

Fig. 39.

can into position, the guide-wires passing through the openings in the flaps. The screw top enables one to refill the basket without removing the entire cylinder. As soon as the carbide touches the water, acetylene will begin to form, and, mixed with air, will flow from the delivery tube *T*.

This generator, which illustrates another class now upon the market, is automatic. In case the delivery tube becomes clogged, the increasing pressure of the gas will lift the inner cylinder, and with it the basket of carbide, from the water. Or, if the guide-wires become caught and prevent this, the pressure on the water will cause it to flow out over the flaps. In either case the rapid evolution of gas will soon cease.

CAUTION. — Before beginning the generation of acetylene be sure no lights are in close proximity, and allow the first gas generated to escape. It contains too much air for good results and is too *dangerous*. With these precautions the gas may be used direct from the generator, or first passed into an ordinary gasometer, which any tinner can make cheaply.

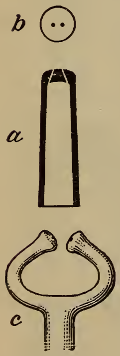

Fig. 40.

43. Acetylene Burners. — But to secure steadiness of flow and *safety*, it is always better to pass the gas through an acetylene burner or tip, which differs from the tip of an ordinary gas jet only in that instead of a slit there are two *very small* openings drilled, oblique to each other. See Fig. 40; *a* is a cross-sectional and *b* the top view. These tips are very cheap, and safe because the openings for the exit of gas are so small that the flame cannot pass back into the generator; *c* shows another form of tip frequently used. The two openings compel the issuing jets of gas to strike each other obliquely, as in *a*.

44. Characteristics of Acetylene. — Acetylene is a colorless gas, of an ethereal odor when perfectly pure, but as ordinarly obtained it is very offensive to the smell. It is soluble, volume for volume, in water and very explosive when mixed with oxygen or air. An ordinary jet of acetylene burns with a yellowish flame, and owing to the large proportion of carbon, — over 92 per cent, — it gives off considerable soot. With a burner like the one described above it furnishes an intensely white light, rivaling the calcium or Drummond light in brilliancy; so that it is now frequently used for projecting lantern slides upon screens and for bicycle lamps.

45. Intense Heat. — Fine iron wires held in the flame are quickly consumed, throwing off sparks as if burning in oxygen.

When used in a blast lamp instead of common gas, acetylene burns with a bluish-white flame. The intensity of this is sufficient to melt copper wires readily, and ordinary platinum wires in two or three minutes; furthermore, it will even soften porcelain. Iron wires a sixteenth of an inch in diameter are quickly fused and burn with a most brilliant shower of sparks, especially when a molten globule of iron upon the end of the wire is suddenly oxidized, and being thrown out into the air breaks into a shower of stars. Watch-springs and knife-blades may be as easily burned away. In a darkened room the display is very beautiful.

46. Blowpipe for Experiments. — The blowpipe best suited to this work may be made by almost any student. See Fig. 41. The outer part, *B*, is the ordinary black japanned blowpipe, costing only a few cents. A hole is cut through at the point *E*, for the insertion of an inner

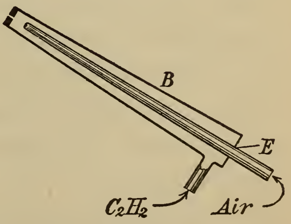

FIG. 41.

tube, which may be made by carefully straightening an ordinary eight-inch brass blowpipe. Solder this firmly in place, plug the mouth end of the outer pipe with a piece of brass through which a small hole has been drilled, and the acetylene blowpipe is complete. Connect the inner tube with the foot-bellows furnishing the air, and the outer tube with the acetylene tank, through the acetylene tip. Regulate by means of a stop-cock the flow of gas, so that when in operation the acetylene is completely burned, with the flame almost entirely blue.

47. From these experiments it will be seen that the heat of this flame is intense, reaching probably 2000° C.

Experiment 98. — To show the explosiveness of acetylene. In the center of the bottom of a pound baking-powder can punch a small hole. Place the can, bottom upward, for a minute or so over a tube delivering acetylene, then set upon the table in the same position. Bring a flame to the touch-hole, when, if the proportions are suitable, a violent explosion will ensue, and the can will be thrown several feet into the air. If too much acetylene has been introduced, it may burn quietly a moment at the opening, until, as more air enters at the bottom to take the place of the gas burned, an explosive mixture is formed and a report follows.

Illuminating Gases

48. One of the most important of these has just been considered. It is new as an illuminant, and some problems in connection with it have not been entirely solved, but it is already being extensively applied in many of the smaller towns where no gas plant exists, for railway lighting, bicycle lamps, etc. The fact that thus far no appliance has been invented for using it in cooking, for the reason that the excess of carbon covers the utensils with a deposit of soot, has prevented a much more extensive use.

Other Illuminants

49. Besides acetylene, ordinary or coal gas, "water" gas, and Pintsch gas deserve notice.

50. Coal Gas. — This is obtained by the destructive distillation of coal in iron retorts. The following diagram illustrates the essential features of a gas plant.

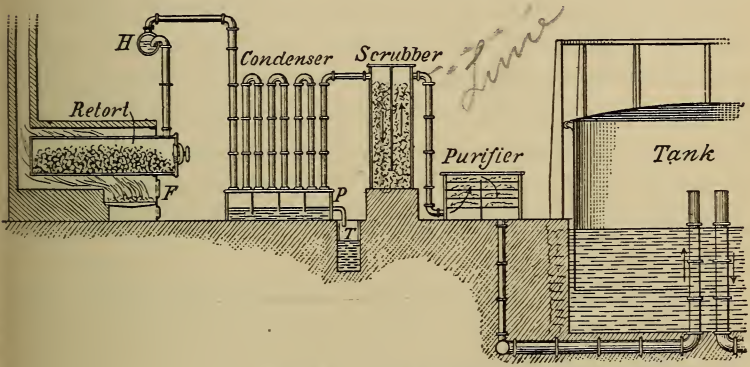

Fig. 42. A Gas Plant.

51. Preparation. — Soft coal is shoveled into the retort, beneath which is the furnace, *F*. When the retort is filled, the door is luted on air-tight. The heat from the furnace drives out the gaseous products from the coal in the retorts, and they are carried up to the hydraulic main, *H*. From here the gas is forced by means of pumps, not shown in the diagram, through the condensers, a series of pipes several hundred feet in length, where it is cooled and the tar condensed. This by-product is drawn off by pipes, *P*, to the tar-well, *T*, from which it is pumped into barrels.

52. From the condensers the gas goes through the scrubber, a large cylindrical tank filled with coke or lattice work, over which water slowly trickles. The partition through the center causes the gas to flow down one side and up the other; the coke breaks up the gas into bubbles, so as to secure a thorough washing. Here the ammonia is mostly removed, and the impure aqua ammonia thus obtained is drawn off at intervals, neutralized with acids, and treated with lime for the preparation of the ammonia of commerce, as already described.

53. The gas next passes through the lime purifiers, a number of low cylindrical tanks, containing lime spread upon horizontal shelves. The lime dries the gas and at the same time removes the sulphureted hydrogen and the carbon dioxide. In some works, ferric oxide, Fe_2O_3, is used for the same purpose. From the purifier the gas passes to the gas-holder, a very large tank, where it is stored for use.

On the inside of the retorts, as previously stated, there gradually collects a fine, hard deposit, known as gas carbon, which is now a very useful by-product.

54. Water Gas. — This gas receives its name from the fact that steam is used in one part of the process of manufacture. From the boilers steam is passed into chambers, or pipes, containing charcoal or coke, heated red hot. Here the vapor and coke react upon each other, the former being decomposed, thus: —

$$C + H_2O = CO + H_2.$$

Two gases, carbon monoxide and hydrogen, mixed together, are thus obtained. Both are combustible, and in burning produce great heat, but neither gives any light. This mixture, therefore, is next allowed to pass into retorts, kept at a high temperature, into which kerosene, or some similar oil, is sprayed. The heat vaporizes and decomposes the oil into hydrocarbons that do not liquefy again upon cooling, and which burn with a luminous flame. This last step is called "carbureting," and by it a gas is obtained not very different in composition from coal gas.

55. **Pintsch Gas.** — This is the gas so frequently used for lighting street cars and railway coaches. It received its name from its inventor, who sought to improve the old and very unsatisfactory method of lighting coaches in England by means of candles. The essential features of manufacture are similar to those of the coal gas plant. Naphtha is sprayed into retorts heated sufficiently to decompose the vaporized oil into other hydrocarbons. These are then passed through an improved form of condenser, a washer, and lime purifiers into the gasometer.

56. Next the gas is drawn through a cylinder known as the "freezer," or "dryer." Here, owing to the action of the pumps, it expands, and being cooled thereby, loses all its moisture. The same pumps force the gas into large tanks called "accumulators," from which it is drawn off into smaller tanks for shipment from place to place, or directly into the storage cylinders, so frequently seen under railway coaches. This light possesses not only the advantages of intensity and whiteness, which coal gas, as ordinarily burned, lacks, but unlike ordinary gas, its illuminating power is only slightly decreased by strong pressure such as is necessary for transportation in storage cylinders.

57. **Natural Gas.** — Natural gas is formed by the decomposition of organic matter, and the main constituents are about the same as those of the other mixed gases used for illumination.

58. **Composition of Illuminating Gases.** — With the exception of acetylene, the illuminating gases noticed are all

mixtures. The most important constituents of coal and "water" gas are given below: —

COAL GAS

Hydrogen	H,	about 46 per cent.
Marsh Gas	CH_4	" 38 "
Olefiant Gas	C_2H_4,	" 2 "
Carbon Monoxide . .	CO,	" 11 "

Small amounts of higher hydrocarbons, and such impurities as hydrogen sulphide, ammonia, and carbon dioxide.

WATER GAS *

Marsh Gas	CH_4
Carbon Monoxide . . .	CO
Hydrogen	H

Small amounts of higher hydrocarbons.

SUMMARY OF CHAPTER

Classification of free forms of carbon.
Description, preparation, and uses of.
- *a.* Diamonds.
- *b.* Graphite.
- *c.* Coals.
  - Origin of natural coal.
  - Varieties of and differences.
  - Petroleum and products from it.
- *d.* Charcoal.
- *e.* Coke.
- *f.* Gas carbon.
- *g.* Lampblack.

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* Water gas contains a larger proportion of carbon monoxide than ordinary coal gas; otherwise the two are not very different.

- Reducing power of carbon.
  - Meaning of term.
  - Experiment.
- Absorbing power.
  - For various substances.
  - Practical applications of this power.
- Compounds of carbon.
  - The oxides — Names and formulæ.
    - Preparation of CO.
    - Characteristics.
    - Sources of CO_2 in the air.
    - Laboratory method of preparing.
    - Characteristics of CO_2.
    - Experiments to illustrate same.
    - Practical uses of CO_2.
      - Soda water, sparklets, sodors, etc.
  - Hydrocarbons — Meaning of term.
    - Three important hydrocarbons.
  - Marsh gas — Sources of, in the air.
    - Characteristics.
    - Protection against explosions.
  - Olefiant gas — Where found.
    - Characteristics of.
    - Compare with marsh gas.
    - Value of each in coal gas.
  - Acetylene — How prepared for use.
    - Manufacture of carbide.
    - Description of acetylene generators.
    - Description of acetylene tips.
    - Characteristics of acetylene.
    - Experiments to show its lighting, heating, and explosive properties.
  - Other illuminating gases.
    - Coal gas.
      - Method of preparing — Apparatus.
      - Plans for purifying.
      - Different forms of gas-burners.
      - Valuable by-products — How secured — Use.

Water gas.
    How prepared.
    Characteristics of.
    Comparison with coal gas in composition.
Pintsch gas.
    Method of preparing and purifying.
    Used where.
    Comparison with coal gas.

CHAPTER XII

FUNDAMENTAL LAWS OF CHEMISTRY

1. Quantitative Work. — It may have seemed to the student that the quantity of a reagent used in any experiment makes little difference. While definite amounts are usually specified, care is not often taken to use exactly that quantity. Generally the result will be the same, but if more than the necessary amount of a substance is used, the excess remains and is simply wasted. This fact is usually stated in what is known as —

2. The Law of Definite Proportions. — Briefly, it is this: *Two or more elements, in uniting to form a compound, always do so in the same proportion by weight.* This has been illustrated somewhat in the earlier part of the book in discussing compound bodies. It is a very important law, and upon it much of the science of chemistry depends. To illustrate it more fully the student should make the following experiments, using the utmost care to insure accuracy. Let him not draw his conclusions beforehand and then endeavor to make his results conform to these.

Experiment 99. — Fill two burettes, one with a solution of caustic soda and the other with dilute hydrochloric acid, and support them upon a stand. Carefully take the reading of each, using the lowest part of the meniscus in doing this, as shown in the figure. Here the lowest part of the curve coincides with 38.4, and this would be the reading.

FIG. 43.

Now find the weight, as accurately as possible, of a small evaporating dish. Much time can be saved here if each student will provide himself with a small pasteboard box and cover, such as blank labels are packed in. Put the box and cover upon the scale pan opposite to the dish, and pour in fine shot or sand until it is exactly counterpoised. This represents the weight of the dish. Put the box with its contents away where it will be safe from accident.

Now, from the caustic soda burette allow 10 cc. to flow into the evaporating dish, and add one drop of phenolphthalein solution, or, if more convenient, enough litmus solution to give a decided blue color. From the other burette, with constant stirring, let the acid flow in slowly until the color given by the phthalein *barely* disappears, or until the blue litmus *just* shows pink. Take the reading of the acid burette, and by subtracting the previous reading determine how much hydrochloric has been used. The change in the color noted above indicates that sufficient acid has been added to neutralize the alkali and form therewith a salt.

Now place the evaporating dish upon a ring-stand, or better upon a sand-bath, and evaporate *slowly* to dryness. Do not let the liquid *boil*, as some will be lost by spurting out, and be careful toward the close to withdraw the heat before the solution is entirely dry, lest the dish become so warm as to decompose some of the salt. If the heat of the dish does not complete the evaporation, warm it *very gently* for another moment. When perfectly dry let the dish cool, and weigh it. In doing this put the small box and shot upon the opposite pan as before, then whatever weights are necessary to add will represent the weight of the salt obtained. If the shot are not used, subtract the first weight from the second. Tabulate results as below:—

Wt. of dish + salt . .	17.103	Caustic soda used . .	10.0 cc.
Wt. of dish	15.217	HCl used	6.4 cc.
Wt. of salt	1.886		

EXPERIMENT 100. — Purpose, a continuation of the preceding. Repeat the preceding experiment, using the same amount of caustic

soda, but twice as much acid. The litmus or phthalein need not be added. Use the same precautions as before. Tabulate results.

Wt. of dish + salt . .	——	Caustic soda used . .	10.0 cc.
Wt. of dish	15.217	HCl used	12.8 cc.
Salt	——		

Experiment 101. — Purpose, same as above. Repeat, using 5 cc. of caustic soda solution, a few drops of litmus or one of phthalein, and then enough hydrochloric to neutralize, as in Experiment 98. Cool and weigh as before.

3. Comparison of Results. — Comparing the results obtained, we may formulate them as below: —

Exp. 99.	$NaOH$ used . .	10.0 cc.	Salt ($NaCl$) obtained . .	—
	HCl " . .	6.4 cc.		
Exp. 100.	$NaOH$ used . .	10.0 cc.	$NaCl$ obtained	—
	HCl " . .	12.8 cc.		
Exp. 101.	$NaOH$ used . .	5.0 cc.	$NaCl$ obtained	—
	HCl " . .	——		

4. What evidence in the above experiments do you find in proof of the law of definite proportions? Is there any agreement between the first and second of the above? Between the second and third? Why?

Experiment 102. — Further proof of the law. Carefully weigh an evaporating dish or find its equivalent in shot as before, then add a half-gram weight to the pan on which the shot is, and put into the evaporating dish sodium carbonate crystals to balance. Add a few centimeters of pure water to the carbonate, and then add dilute hydrochloric acid, a little at a time. Keep the dish covered with a sheet of glass or watch crystal so as not to lose any by its spattering out. In this way cautiously add the acid until the carbonate is all dissolved, or until it no longer effervesces. Now rinse off the cover-glass into the evaporating dish, and evaporate to dryness with the same precautions used before. Cool, weigh, and determine the amount of salt obtained.

Sod. Carb.:	Na_2CO_3 + dish . .	—	$NaCl$ + dish . .	—
	Wt. of dish . . .	—	Dish	—
	Na_2CO_3	—	$NaCl$	—

Experiment 103. — Same as preceding. Pursue the same method as above, using 1 g. of the carbonate instead of a half gram.

Used: Na_2CO_3 + dish . .	—	Obtained: NaCl + dish . .	—
Wt. of dish	—	Dish	—
Na_2CO_3	—	NaCl	—

Experiment 104. — Purpose, same as before. Repeat the preceding, using this time $1\frac{1}{2}$ g. of sodium carbonate crystals. Results: —

Used: Na_2CO_3 + dish . .	—	Obtained: NaCl + dish . .	—
Dish	—	Dish	—
Na_2CO_3	1.500	NaCl	—

5. **Summary.** — In each of the last three experiments find the ratio existing between the carbonate used and the salt obtained.

1. $Na_2CO_3 : NaCl :: 1 : x =$
2. $Na_2CO_3 : NaCl :: 1 : y =$
3. $Na_2CO_3 : NaCl :: 1 : z =$

Is there any uniformity in the value of these ratios? Do your results afford further evidence of the law of definite proportions? If so, in what way?

6. **The Law of Multiple Proportions.** — We have learned that when two or more elements unite to form a compound they do so in a constant ratio. We have seen, however, that the same two or three elements may unite to form several compounds, and at first this may seem contrary to the statement of the preceding law. It is a modification, but not a contradiction. If a new and different compound is formed when other proportions are used, in this the quantity of the elements that enter into combination is always some multiple of the lowest. An illustration will make this plain. Thus, we are familiar with the series of nitrogen oxides: —

Nitrogen	Monoxide . .	N_2O	$N_2 : O :: 28 : 16$
"	Dioxide . . .	N_2O_2	$N_2 : O_2 :: 28 : 32$
"	Trioxide . .	N_2O_3	$N_2 : O_3 :: 28 : 48$
"	Tetroxide . .	N_2O_4	$N_2 : O_4 :: 28 : 64$
"	Pentoxide .	N_2O_5	$N_2 : O_5 :: 28 : 80$

It is seen that while the weight of the nitrogen entering into combination remains constant, the oxygen is in the ratio of 2, 3, 4, and 5 times what it is in the lowest of the series.

7. This law may be proved experimentally by estimating the amount of oxygen that a given weight of potassium chlorate, $KClO_3$, will yield, by the method previously suggested. Then, determine the amount in potassium perchlorate, $KClO_4$. In these two compounds we should find the ratio to agree with that expressed in the formulæ, that is, 3 and 4 times what would be contained in a molecule like mercuric oxide, HgO.

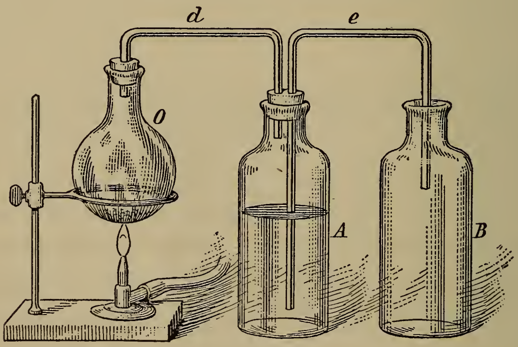


FIG. 44.

EXPERIMENT 105. — To prove the law, the work may be conveniently done as shown in the accompanying figure. Instead of the flask, *O*, a hard-glass test-tube may be used. Put into the flask about 1 g. of manganese dioxide, MnO_2, and weigh carefully the flask and contents. Then add to it about 1¼ g. of potassium chlorate, $KClO_3$, and weigh accurately. The difference between the two weights will be the exact amount of the chlorate used. *A* is a two or three liter bottle with narrow neck, and fitted with a two-hole rubber cork. The delivery tube, *d*, just passes through the corks of *O* and *A*; the connecting tube, *e*, reaches nearly to the bottom of *A*.

The bottle, *B*, is similar to *A*, but is not provided with a cork, and the tube, *e*, need not extend far into the bottle. When the connections are made air-tight, gradually heat the flask, *O*, thus driving the oxygen over into *A*, and the water from *A* into *B*. Continue the operation until no more gas is given off, then allow the whole to cool to the temperature of the room. Now measure the water in the bottle, *B*; this will give the volume of oxygen at the temperature of the room and the prevailing barometric pressure. According to methods already given on page 96, reduce this volume to what it would be under standard conditions. Knowing the weight of a liter of oxygen, 1.43 g., find the weight of the determined volume. As a check, weigh also the cooled flask, *O*, and determine its loss; this should be practically the same as the weight found by calculation.

Next, arrange the apparatus as at the beginning. Into the hard-glass tube put about 1.4 g. of potassium perchlorate, $KClO_4$, and, after making connections, heat strongly as before until no more gas is produced. Cool and weigh the flask or tube; the loss will represent the oxygen, which may be checked up by determining the volume of the gas given off as before and reducing to standard conditions. Let the student now compare results. The two reactions are as follows: —

$$KClO_3 + \text{heat} = KCl + 3\,O,$$

and

$$KClO_4 + \text{heat} = KCl + 4\,O.$$

From other experiments we know that the oxygen is entirely removed and that potassium chloride, KCl, remains. Then we should have the proportion

$$\text{Mol. wt. } KClO_3 : \text{wt. of O in 1 mol. } KClO_3 :: 1.25 \text{ g.} : m \text{ g.},$$

in which m = no. grams found by experiment above. Substituting,

$$122.5 : x :: 1.25 \text{ g.} : m \text{ g.},$$

$$x = \frac{m \times 122.5}{1.25}.$$

Then, as 16 is the weight of one atom of oxygen, there would be as many atoms of oxygen in the molecule as 16 is contained times in x; the result should agree very closely with the assumed number.

In the same way,

$$\text{Mol. wt. } KClO_4 : \text{wt. of O in 1 mol. } KClO_4 :: 1.40 \text{ g.} : n \text{ g.},$$

in which n = no. grams found in second instance above. Or,

$$138.5 : y :: 1.40 \text{ g.} : n \text{ g.},$$

$$y = \frac{n \times 138.5}{1.40}.$$

How does the value of y agree with the known value?

8. Combining Weights. — We have previously learned that when elements or compounds react with each other in the formation of new substances, they always do so in a fixed or definite proportion. We have seen also that when several compounds are formed from the same two elements, there is one smallest quantity of which all the others are multiples. This smallest amount in the case of the nitrogen oxides was found to be 16 for the oxygen, and all the others were multiples of this. Therefore, 16 is regarded as the atomic weight of oxygen, and in all chemical reactions into which it enters, this, or some multiple of it, is its combining weight.

Experiment 106. — To find the combining weight of copper. Put into a beaker $2\frac{1}{2}$ g. of clean, bright copper, accurately weighed, and dissolve slowly in nitric acid somewhat diluted. Use every precaution to prevent loss by spurting, just as in other similar work, and when the copper is all dissolved, transfer the solution to a weighed evaporating dish, as small as will conveniently hold the solution; carefully rinse off the cover-glass and the beaker into the evaporating dish, and evaporate to dryness. We now have a blue salt, copper nitrate. Be sure it is perfectly dry, and then remove the sand-bath, or any other protection used for the dish, and gradually increase the heat until all particles of the blue salt have been changed to a black compound. A dull red heat is generally necessary for this. We now have copper oxide, CuO. Cool and weigh carefully. Determine how much oxygen has combined with the copper by subtracting the amount of copper used from the weight of oxide obtained.

Dish + CuO . — $m + x$; m = wt. of dish; x, of CuO.
Dish + Cu . — $m + n$; n = wt. of $Cu = 2\frac{1}{2}$ g.
O . . . . . — $m + x - (m + n) = y$.

Numerous experiments have shown that the combining weight of oxygen is 16; using this as a basis, we can determine what it is for copper: —

Wt. of O found : wt. of Cu used : : comb. wt. of O : comb. wt. of Cu.

or, Wt. of O : $2\frac{1}{2}$ g. Cu : : 16 : z.

From this proportion the combining weight of copper should be found to be approximately what is given in the table on page 9. The sources of error are liable to make the difference comparatively great, but the result should not vary too much.

Experiment 107. — Purpose, same as above. Use 3 or 4 g. of finely powdered copper nitrate which has not been exposed to the air any length of time. Be sure the exact weight is known, then heat in a small evaporating dish, or better, in a porcelain crucible, cautiously at first; when the nitrate is converted into the black oxide as before, cool and find the weight. Experiment has shown that 1 g. of crystallized copper nitrate contains 0.2619 g. of metallic copper. From this determine the amount of copper represented by the 3 g. (or 4 g.) of nitrate used.

Wt. of dish + CuO . . . . —
Wt. of dish . . . . —
CuO . . . . —
Cu . . . . —
O . . . . —

Wt. of O : wt. of Cu : : 16 : x.

Does this give practically the same combining weight for copper that the preceding did? If the results do not correspond fairly well with each other and with the table, the experiments should be repeated.

Experiment 108. — To find the combining weight of tin. For this use granulated tin. If not at hand, procure a quantity of pure tin foil, melt it in an iron ladle, and pour into cool water. Remove from the water and dry it, when it will be ready for use. Weigh out carefully 2 g. of the granulated tin, and treat with nitric acid in an evaporating dish. Take care always to avoid loss by spurting. Evaporate slowly to dryness, and then gradually heat the white residue to dull redness.

Wt. of dish + SnO_2 . . . . —
Wt. of dish . . . . —
SnO_2 . . . . —
Wt. of Sn . . . . —
O_2 . . . . —

It has been found by analysis that the amount of oxygen in this compound indicates two atoms to the molecule, hence in making our calculations that amount must be used. Then we have —

$$\text{wt. of O found} : \text{wt. of Sn used} :: 32\ (2 \times 16) : x.$$

Experiment 109. — Repeat the above experiment, using $2\frac{1}{2}$ or 3 g. of tin, and make calculations as before.

How do the results in the two experiments agree? If they do not correspond fairly well with the atomic weight given in the table, allowing for errors in weighing, the experiment should be repeated.

9. Such experiments as the above might be endlessly multiplied. We have found in these, as has been the case in an indefinite number of instances in which chemists have done the work with the utmost care, that every element combines with others in some exact proportion by weight, and whether we use much or little of the element, in the same compound the ratio never changes. This fact is of the utmost importance, for upon it depends much of the science of chemistry. It is this that enters into the application of chemistry to the arts and manufactures, and renders its results so sure and unchanging.

10. Some Application of the Laws of Combination. — Knowing that the laws of combination are true, we may make use of the principles in determining the strength of acid or alkaline solutions. The following work will illustrate this.

Experiment 110. — To determine the strength of any hydrochloric acid solution in the laboratory. Put the acid to be tested into a burette and take the reading. From this allow 10 cc. to flow into an evaporating dish, add a drop or two of litmus or phthalein, and then, from another burette, after taking the reading, run in a solution of caustic soda until the solution in the evaporating dish is neutralized, as in previous work. Evaporate slowly to dryness, cool, and weigh. Subtract the weight of the dish to determine the salt obtained. Suppose this is 0.585 g. Now we know that caustic soda and hydrochloric acid react with each other according to the following equation: —

$$NaOH + HCl = NaCl + H_2O.$$

From this we see that one molecule of pure hydrochloric acid yields one of sodium chloride, or 36.5 parts by weight of acid give 58.5 of salt. The 0.585 g. of salt would thus correspond to 0.365 g. of acid, the amount in 10 cc. of the solution used. Then in a liter, 1000 cc., there would be 100 times this amount, or 36.5 g. of pure acid. The liter of acid then ought to weigh 1000 g. + 36.5 g. = 1036.5 g. The question simply is this: 36.5 g., the amount of pure acid, is what per cent of 1036.5 g., the weight of the acid solution? This is found to be about $3\frac{1}{2}$ per cent.

Experiment 111. — Repeat the preceding experiment, neutralizing 10 cc. of the hydrochloric acid with caustic potash. Make your calculations from the following equation: —

$$KOH + HCl = KCl + H_2O.$$

Do your results agree with the preceding as to the per cent strength of acid?

11. To determine the Amount of Caustic Soda or Potash in the Solutions used above. — We know that when an acid and an alkali are put together, they neutralize each other to form a salt. If then we know how much acid is contained in a solution, and measure the amount of the latter used, having some means of knowing when the alkali is exactly neutralized, we can easily calculate the amount of alkali contained in a given volume of solution.

Experiment 112. — Suppose we are required to determine the number of grams of sodium hydroxide in 1 liter of the solution. We know the reaction is

$$NaOH + HCl = NaCl + H_2O,$$

or by weight, $$40 + 36.5 = 58.5 + 18.$$

That is, 40 g. of caustic soda are necessary to neutralize 36.5 g. of hydrochloric acid. Suppose now we have a solution of acid that contains 3.65 g. of pure hydrochloric acid to the liter, then

1000 cc. HCl would neutralize 4.0 g. of NaOH.

Then, if with 100 cc. of caustic soda solution we used 20 cc. of the acid solution, we should have this proportion: —

$$1000 \text{ cc. HCl} : 4.0 \text{ g. NaOH} :: 20 \text{ cc. HCl} : x \text{ g. NaOH};$$

$$x = .08.$$

That is, in 100 cc. of the solution of caustic soda there are .08 g. of the solid alkali dissolved; then in 1 liter there would be 10 times as much, or .8 g.

For such work as this we ordinarily use oxalic acid instead of hydrochloric, because it is easier to obtain pure, and forms a more constant solution. Its formula is $H_2C_2O_4, 2\ H_2O$. With caustic soda the reaction is

$$2\ H_2O, H_2C_2O_4 + 2\ NaOH = Na_2C_2O_4 + 4\ H_2O,$$

or by weight, $$126 + 80 = 134 + 72.$$

That is, 126 g. of oxalic acid will neutralize 80 g. of caustic soda. Suppose for work we weigh out 6.3 g. of oxalic acid and dissolve in 1000 cc. of pure water. This will be our standard solution of acid.

To find how much caustic soda in 1 liter of solution. Measure out accurately into a beaker 50 cc. of the alkali solution, and add one drop of phenolphthalein, or about 1 cc. of litmus solution. Next take the reading of a burette containing the standard oxalic acid solution, and with constant stirring let the acid drop in slowly until, finally, by the addition of a single drop the red color of the phenol disappears, or the blue of the litmus changes to red. Again read the burette and determine how much acid has been used. Suppose it has been 10 cc. Then to calculate,

$$1000 \text{ cc. acid} \cdot 4.0 \text{ g. NaOH} :: 10 \text{ cc.} : x \text{ NaOH};$$

$$x = .04 \text{ g. NaOH},$$

the amount in 50 cc. of NaOH solution used. In 1000 cc. there would be 20 times as much, or .8 g.

Problem 1. — Let the teacher make up a solution of caustic potash with distilled water, and have the student determine the number of grams used to the liter.

Problem 2. — In the same way let the student determine the amount of common salt in a solution by using in the burette a solution of silver nitrate containing 17 g. per liter. To determine when sufficient silver nitrate is used, add to the common salt solution sufficient potassium chromate solution to give a yellow color. With constant stirring run in the silver nitrate until the precipitate that forms shows the faintest red tinge. The reaction is

$$NaCl + AgNO_3 = AgCl + NaNO_3,$$

or by weight, $58.5 + 170 = 143.5 + 85.$

That is, 170 g. of silver nitrate will precipitate the chlorine in 58.5 g. of salt, or if 17 g. of silver nitrate were used to make a liter of the solution, then 1000 cc. of silver nitrate would precipitate the chlorine in 5.85 g. of salt. Or,

$$1000 \text{ cc. } AgNO_3 : 5.85 \text{ g. NaCl} :: m \text{ cc. } AgNO_3 \cdot x \text{ g. NaCl},$$

in which m is the number of cubic centimeters of silver nitrate solution used with the amount of common salt solution taken. If this latter is 20 cc., or $\frac{1}{50}$ of a liter, then $50\,m$ = number cubic centimeters $AgNO_3$ necessary to precipitate the chlorine in 1 liter.

12. Displacing Power of Metals. — We have seen in preparing hydrogen that various metals have the power of reacting with certain acids to displace the hydrogen contained. Of course this displacing power is in accordance with the valence of the element (see chapter on

Valence), and the following plan may be used to determine it: —

EXPERIMENT 113. — Into a 4-ounce wide-mouth bottle, *C*, put 1 gram of finely granulated zinc. Insert a cork fitted with a safety tube, *A*, running to the bottom of the bottle, and with the delivery tube, *B*. Let the delivery tube extend over to a pneumatic trough, and place the end of the tube under the mouth of a 2-liter bottle filled with water. When everything is in readiness, by means of the funnel-tube, add to the zinc in *C* about 30 or 40 cc. of moderately strong hydrochloric acid. When the zinc is all dissolved and the apparatus cooled, measure the amount of hydrogen collected, by again filling the receiver with water, noting the amount required. Reduce this volume to standard conditions. Suppose, for example, it is found that it requires *m* cc. of water to refill the receiver, and that by reducing this volume to standard conditions, we obtain *n* cc. as a result, then as 1 liter of hydrogen weighs .0896 g., *n* cc. would weigh

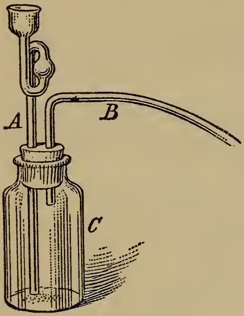


FIG. 45.

$$\frac{n \times .0896}{1000} = w \text{ g. of hydrogen.}$$

Then we should have the proportion

$$w \text{ g. of H.} : 1 \text{ g. of Zn} :: x : 65;$$

that is, the weight of the hydrogen obtained is to the weight of the zinc used in displacing it as x is to 65, the atomic weight of zinc. This should give for the value of x, approximately, 2. Then as the hydrogen atom is the standard, or 1, in this case x represents the weight of two atoms of hydrogen. In other words, the zinc atom has the power of displacing two atoms of hydrogen.

EXPERIMENT 114. — With apparatus arranged as in the preceding experiment, let the student use one gram of aluminum wire cut into small pieces. No heat will be necessary if strong hydrochloric acid be used, and the chemical action, slow at first, will soon become very rapid. Determine as before the volume and weight of the hydrogen set free. Then we have wt. of H obtained : wt. of Al used : : x : 27, atomic wt. of Al,

and $$x = ?$$

From this what can you say is the displacing power of the aluminum atom?

EXPERIMENT 115. — In exactly the same way try 1 gram of magnesium ribbon, cut into small pieces. Hydrochloric acid somewhat diluted had better be used, as the action is very rapid. Make your corrections for temperature and pressure, and calculate as before. What do you find for the displacing power of the magnesium atom?

SUMMARY OF CHAPTER

- Statement of Law of Definite Proportions.
  - Experiments illustrating it.
- Law of Multiple Proportions.
  - How illustrated.
- Combining weights.
  - Method of determining by experiment.
    - For copper.
    - For tin.
- Practical application.
  - Method of determining amount of acid or alkali in a solution.
  - Method of determining valence or displacing power of metals.

CHAPTER XIII

SULPHUR AND ITS COMPOUNDS

1. Where found. — Sulphur is an element that has been known from very early times. By some of the alchemists it, together with mercury, was regarded as forming all of the metals.

It is a native of volcanic regions, and is found in abundance in Sicily and to some extent in Iceland. There are said to be some deep deposits in the Southern States, but they have not been developed. In the form of compounds with the metals, sulphur is found abundantly and very widely distributed. Some of the more common of these compounds are *gypsum*, $CaSO_4$, *iron pyrite*, FeS_2, *galena*, PbS, and *zinc blende*, ZnS. In the form of hydrogen sulphide, it is found in many mineral springs and is often emitted from volcanoes.

2. For many years Sicily had a monopoly of the sulphur trade. It occurs there in almost unlimited quantities, mixed with earthy matter. This mixture may be partially purified by a method similar to that employed in the preparation of charcoal. Large piles of the crude sulphur are heaped up and covered with earth and sod. The mass is then ignited and a part of the sulphur in burning melts the remainder, which runs out into trenches or vats, leaving the earthy matter behind.

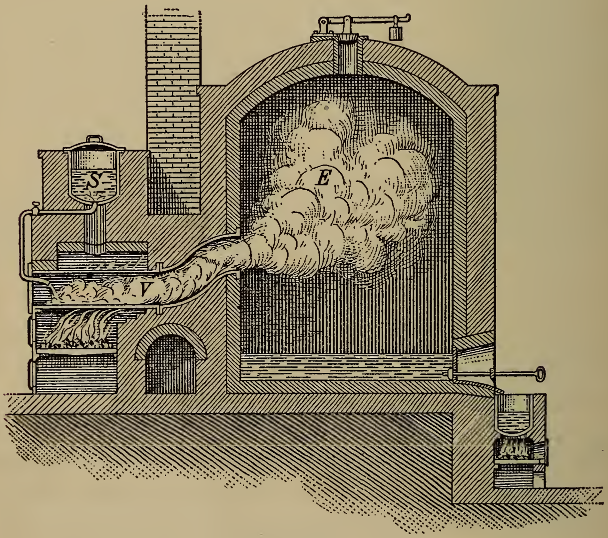


Fig. 46.

3. For many purposes the sulphur thus obtained needs further purification. It is heated and vaporized in retorts, the vapors passing over into cool chambers and condensing upon the walls in the form known as *flowers of sulphur*. If the operation continues for a length of time, however, the walls become heated enough to melt the sulphur that forms upon them. It is then allowed to run out into molds, in which form it is known as *brimstone* or *roll sulphur*. (See Fig. 46.) *S* is a cylinder in which the sulphur is melted, *V*, a retort where it is vaporized, and *E*, the condensing chamber.

4. New Source of Supply. — From the fact that Sicily controlled the sulphur trade, prices rose so high at one time that the English manufacturers were obliged to resort to some other source of supply. Sulphur was used extensively in making sulphuric acid for the manufacture of soda crystals. It was found that by roasting iron pyrite, FeS_2, a compound that had been hitherto altogether worthless, the sulphur dioxide could be obtained; or if the ore was heated in retorts sealed up to prevent access of air, the sulphur was not oxidized, and could be condensed. As the pyrite is very abundant, and the method of obtaining the sulphur cheap, this at the present time furnishes not only about all the sulphur needed in making sulphuric acid, but even more, so that the demand for Sicilian sulphur has greatly decreased. The reaction that takes place when iron pyrite is heated in sealed retorts is

$$3\,FeS_2 + \text{heat} = 2\,S + Fe_3S_4.$$

5. Characteristics of Sulphur. — Sulphur is a yellow, brittle solid, a little heavier than water. It is seen in a number of forms, of which the flowers and roll sulphur have been mentioned. It also occurs crystallized.

Experiment 116. — Into a test-tube put about a cubic centimeter of carbon disulphide, and add a little sulphur. When the latter has dissolved, pour off the clear solution upon a watch crystal, and allow it to evaporate slowly to dryness. The sulphur will form in crystals, the shape of which may be recognized if the evaporation is slow. If necessary, however, examine with a magnifying glass. What form have they?

Experiment 117. — Fill a small crucible nearly full of sulphur, and heat till it is melted. Allow it to cool, and when a crust has formed over the surface, break an opening in the top and pour out what remains molten. Let it cool a little more and break open the mass. What kind of crystals have formed?

Experiment 118. — Put 4 or 5 g. of sulphur into a test-tube and warm. Note how it changes, first melting to form a light yellow-colored liquid, then becoming quite thick again and very dark, then thin again. At this last stage, pour out the sulphur into cold water and note its condition. This is called *amorphous* sulphur, or sometimes *plastic* sulphur.

6. Sulphur is found in a large variety of crystallized forms. The octahedral and the long, needle-like crystals have been seen. Upon standing for some time these gradually change into other forms, modifications of the two. Amorphous sulphur is dark-colored and elastic, somewhat like rubber. It is regarded as an allotropic form. Sulphur is insoluble in water, hence has no taste; it is also without odor. As we have seen, it is soluble in carbon disulphide. It is combustible, burning with a pale blue flame, and forming the well-known irritating gas, sulphur dioxide. At high temperatures sulphur combines readily with most of the metals, forming sulphides. This has been shown already in preparing ferrous sulphide by heating iron filings mixed with sulphur. Copper turnings serve equally well.

7. Comparison of Ozone with Allotropic Sulphur. — In the case of ozone, we have seen that its molecule is different from that of the oxygen molecule. The same is believed to be true of sulphur and its allotropic form, as well as of all other elements which show the same variation. We cannot prove this for sulphur, but there are some facts which make this theory strongly plausible. Thus, if the vapor is weighed at 1000° temperature, it is only one-third as dense as when weighed at 500°.

8. Uses of Sulphur. — Sulphur is used largely in the manufacture of gunpowder, the other two constituents being charcoal and saltpeter. These are united in about the following proportions: —

Sulphur	12 per cent
Charcoal	13 "
Saltpeter	75 "

"Greek fire," which played so important a part in the early centuries, and the composition of which was kept a secret for several hundred years, differed very little from the gunpowder of the present time. Sulphur is employed to some extent in the manufacture of rubber goods, especially vulcanite, and considerably in fumigating buildings; it is used largely in making sulphuric acid. Because of its low kindling-point sulphur has been used very extensively in the manufacture of matches, but the irritating gas produced, and the slowness with which such matches burn, have led to the substitution of other substances.

Compounds of Sulphur

9. Hydrogen Sulphide, H_2S. — This gas, known also as sulphureted hydrogen, occurs in many mineral springs, which give it off abundantly; it is sometimes emitted from volcanoes, and is noticed in the decay of eggs and other similar substances.

10. How prepared. — For laboratory purposes hydrogen sulphide is always prepared by treating ferrous sulphide, FeS, with sulphuric acid.

Experiment 119. — Owing to the offensive odor of the gas, it should be prepared in very small quantities, and kept from access to the room as much as possible. Put into a test-tube a small bit of ferrous sulphide, cover it with water, and add a few drops of strong sulphuric acid. Action will begin at once. Notice the odor of the gas. Has it any color? Attach a jet and ignite it. With what kind of a flame does it burn? Notice the odor given off by the burning gas. Hold a cold beaker over the flame. What do you see depositing upon it? What are the two products formed when hydrogen sulphide burns? Write the reaction.

The reaction that takes place when hydrogen sulphide is prepared is seen below: —

$$FeS + H_2SO_4 = FeSO_4 + H_2S,$$
$$FeS + 2\,HCl = FeCl_2 + H_2S.$$

Hydrochloric acid may be used instead of sulphuric acid with good results.

11. Characteristics of Sulphureted Hydrogen. — It is a colorless gas, having a very disagreeable, nauseating odor; is somewhat poisonous, and should not be inhaled. It is inflammable, burning with a bluish flame, is a little heavier than air, and somewhat soluble in water. It has the power of forming precipitates with solutions of many metallic salts.

Experiment 120. — Into a test-tube put a little of a mercuric chloride solution, into another a solution of antimony tartrate, into a third arsenic trioxide dissolved in hydrochloric acid and water. Attach a delivery tube to a hydrogen sulphide generator, and pass the gas through each of the solutions. Notice the color of the precipitates obtained. Lead salts are very sensitive to the action of hydrogen sulphide, and are used in testing for its presence.

12. Use of Hydrogen Sulphide. — Mineral waters containing this gas in solution are supposed to be beneficial to health. With this exception, about the only use for hydrogen sulphide is in the laboratory, as a reagent, especially in making analyses of unknown solutions. Many of the metals in the form of salts are converted by hydrogen sulphide into insoluble sulphides. Such metals, therefore, when treated with the gas, may be separated from others which are not so precipitated.

Experiment 121. — The above statements will be made plain by this experiment. Into a beaker put a few cubic centimeters of a solution of mercuric nitrate and as much of zinc sulphate; add a few drops of hydrochloric acid, and pass through it a current of sulphureted hydrogen until the odor of the gas is still perceptible after shaking the solution. Then filter out the black precipitate and test the clear filtrate for zinc with ammonia, as you have done in Chapter VII, Section 12. Have you succeeded in separating the two metals?

13. Oxides of Sulphur. — There are two of these compounds, the dioxide and the trioxide, SO_2 and SO_3. It is only the first that is of special importance or interest to us.

14. Sulphur Dioxide, SO_2. — This is also known as sulphurous anhydride, because by passing it into water sulphurous acid is formed. It is the familiar, irritating gas always produced when sulphur is burned in the air.

15. How prepared. — For laboratory purposes sulphur dioxide is prepared by treating copper turnings with strong sulphuric acid. The reaction is usually indicated as follows: —

$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$

If this is compared with the reaction of zinc and sulphuric acid upon each other, it will be seen to be very different. Zinc is acted upon by cold, dilute acid, while copper requires the acid hot and concentrated. It is probable that, as with zinc, hydrogen is first formed, thus: —

$$Cu + H_2SO_4 = H_2 + CuSO_4,$$

and that this nascent hydrogen immediately attacks another molecule of sulphuric acid, decomposing it, thus: —

$$H_2SO_4 + H_2 = 2\,H_2O + SO_2.$$

Putting these two reactions together, we have the one given above.

Experiment 122. — Put into a test-tube a few copper turnings and nearly cover with strong sulphuric acid. Heat moderately until the fumes begin to come off, and collect two or three bottles of the gas as you have carbon dioxide, by downward displacement. What is the odor of the gas? Test it to learn whether it will support combustion or will burn. What can you say of its density? Try its effect upon moistened red and blue litmus paper; state results. Pour into one bottle of the gas a few cubic centimeters of litmus, cochineal, or some other vegetable solution, and shake it. What happens? Suspend in another bottle some colored paper, or silk or straw goods, moistened, and allow to remain some time. State results.

Invert another bottle or test-tube filled with sulphur dioxide, over a small evaporating dish of water. Does the water rise in the tube? Why? Test the water with blue litmus paper; what effects? What has been formed with the water?

16. Characteristics of Sulphur Dioxide. — It is a very irritating, colorless gas, considerably heavier than air. It is soluble in water, forming an acid solution, which, however, is very unstable. It will neither burn nor support combustion, though magnesium ribbon will burn in it with difficulty as it does in carbon dioxide. It is readily liquefied by passing the gas through a spiral tube, surrounded by ice and salt. In the liquid condition it is limpid, transparent, and very slightly yellow in color.

17. Sulphur dioxide is a great reducing agent, like charcoal, but more active. That is, it has the power of abstracting oxygen from other substances. If sulphur dioxide is passed into a bottle containing nitrogen tetroxide, N_2O_4, the red fumes will soon disappear because the tetroxide has been deprived of a portion of its oxygen and converted into the dioxide, thus: —

$$2\,SO_2 + N_2O_4 = 2\,SO_3 + N_2O_2.$$

Likewise a current of sulphur dioxide passed into a solution of potassium dichromate, or permanganate, will deprive them of a portion of their oxygen, changing the first to a compound, green in color, and rendering the second colorless. It will be important to remember this property on account of its relation to the manufacture of sulphuric acid, to be shown later.

18. Uses of Sulphur Dioxide. — These have already been mentioned. It is used frequently as a disinfectant or fumigant, and for bleaching silk and straw goods. Evaporated fruits, especially apples and peaches, owe their white, almost natural, color to the bleaching effects of sulphur dioxide, which is allowed to flow over the fruit as it is put into the evaporator. Its most extensive use is for making sulphuric acid.

19. Sulphur Acids. — Sulphur forms several acids with hydrogen and oxygen, not all of which are important. The best known is sulphuric, H_2SO_4, also called *oil of vitriol.*

Experiment 123.* — Arrange three flasks as shown in Fig. 47, one for the generation of sulphur dioxide by the treatment of copper with

---

* If it is found necessary to use simpler apparatus, fill a flask with sulphur dioxide, and introduce into it a swab of cloth upon the end of a glass rod, moistened with nitric acid. Soon, brown fumes will begin to appear,

sulphuric acid, another containing nitric acid and copper turnings for the preparation of nitrogen dioxide, and a third containing water to be converted into steam. Connect with a large flask, *D*, which has a fourth tube to allow the entrance of air.

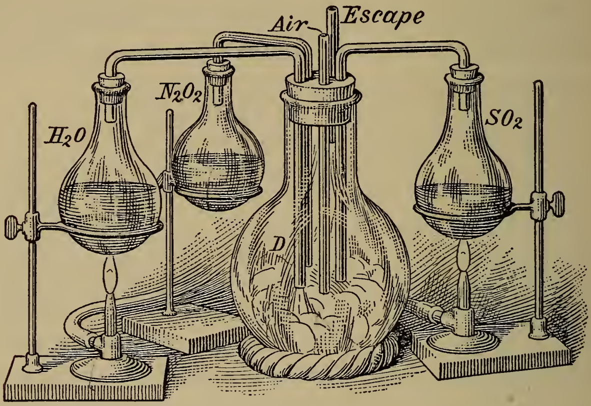


FIG. 47.

When the nitrogen dioxide enters the flask, *D*, containing air, it combines with the oxygen, forming the tetroxide, thus: —

$$N_2O_2 + O_2 = N_2O_4.$$

Immediately the sulphur dioxide attacks this compound of nitrogen, taking away two atoms, reducing it to the dioxide again, thus: —

$$N_2O_4 + 2\,SO_2 = N_2O_2 + 2\,SO_3.$$

The dioxide thus formed, with the oxygen of the air, again combines to form the tetroxide, and so serves as a *carrier* of oxygen from the air to the sulphur dioxide.

Next, the sulphur trioxide combines with the water introduced in the form of steam, producing sulphuric acid, thus: —

$$SO_3 + H_2O = H_2SO_4.$$

---

showing that the nitric acid is being decomposed and the sulphur dioxide converted into the trioxide. Now add a few cubic centimeters of water, and shake. The flask will contain a dilute solution of sulphuric acid.

20. To test the Acid prepared. — Put a little of the acid into a test-tube and add 1 or 2 cc. of a solution of barium chloride. If a white precipitate forms, which is not soluble in nitric or hydrochloric acid, or both together, sulphuric acid is indicated.

21. The Manufacture of Sulphuric Acid. — This acid is now prepared in immense quantities. The United States and Great Britain each produce annually about one million tons, and Germany is not far behind. Formerly, sulphur was used to prepare the sulphur dioxide for the manufacture of this acid, but, as stated above, the attempt to control the entire output of the Sicilian mines raised the price to such an extent that sulphuric acid manufacturers sought other sources, and finally discovered the present method. The pyrite is roasted in the presence of plenty of air, and the following reaction takes place: —

$$2\,FeS_2 + 11\,O = Fe_2O_3 + 4\,SO_2.$$

22. These fumes are conducted into large chambers lined with sheet lead, into which jets of steam are constantly sprayed, together with nitric acid vapors, obtained by treating sodium nitrate with sulphuric acid. The reactions that take place in these lead chambers are the same as already described. The amount of nitric acid necessary is very small, and theoretically might be used indefinitely, but practically it is gradually carried by the draughts of air into the flues and must be replaced.

The sulphuric acid thus prepared collects upon the floors of the rooms, — which are so large that a dancing party of a hundred couples could easily be held in them, — and is called *chamber acid*. It is only moderately strong, and is next evaporated in leaden vessels until a specific gravity of a little over 1.7 is reached, when it begins to attack the lead. It is next transferred either to glass or platinum retorts, and concentrated until it reaches a density of

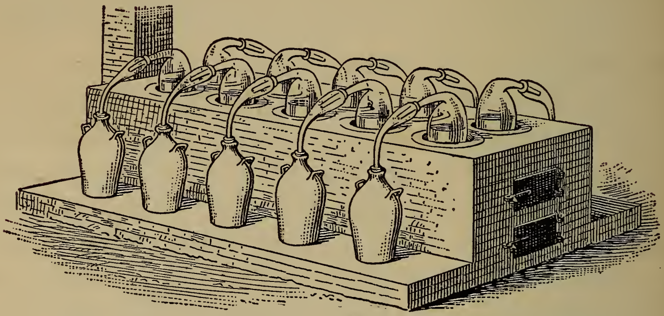


Fig. 48. — Apparatus for condensing Sulphuric Acid.

about 1.85. Fig. 48 shows the method of concentrating by glass retorts. The jars outside receive the nitric acid and other impurities contained in the sulphuric acid.

23. Characteristics of Sulphuric Acid. — It is a colorless, sirupy liquid; it received the name *oil of vitriol* on this account, and because it was made from *green vitriol*, ferrous sulphate. It is not a volatile acid, and, unlike nitric or hydrochloric, gives off no odor. It is very heavy and very corrosive. Organic matter exposed to it is charred black, as already noticed. It has great affinity for water, so much so that a beaker two-thirds filled with strong acid will in a few weeks, if left exposed to the air, absorb enough moisture to cause the beaker to overflow. Likewise when strong acid is added to water, or *vice versa*, the mixture becomes very hot, reaching nearly 100° C., owing to the strong affinity of the two for each other.

24. It is upon this principle that sugar, $C_{12}H_{22}O_{11}$, is charred. The hydrogen and oxygen, being sufficient to form eleven molecules of water, are abstracted, and the carbon remains behind as a black mass. Upon the same principle depends its use as a drying agent for various gases. They are made to bubble up through a bottle of strong sulphuric acid, and by this means lose their moisture.

25. Uses for Sulphuric Acid. — It will be concluded from the vast quantities manufactured that sulphuric acid is a very important article of commerce. It is the most useful of acids, and almost all the others are dependent upon it for their preparation. In the manufacture of soda crystals, Na_2CO_3, by the Leblanc process (see page 211), sulphuric acid is indispensable. This salt, Na_2CO_3, is the basis for all soap manufacture as well as for glass, baking powders, etc. We can thus see the commercial importance of sulphuric acid.

26. Another very extensive use is in the manufacture of artificial fertilizers from bones. When they have had the bone oil and gelatine removed, and as bone-black are no longer valuable for clarifying sugar, the bones are treated with sulphuric acid. This converts the phosphates present into a soluble form that may be used by plants. Sulphuric acid is also used in the manufacture of such explosives as nitroglycerine and gun-cotton, for making glucose, and in some of the processes of electroplating and electrotyping.

27. Other Acids of Sulphur. — Sulphurous Acid, H_2SO_3. — This acid has already been mentioned, as well as its method of formation and its instability.

We also have

Hyposulphurous, H_2SO_2.
Fuming Sulphuric, $H_2S_2O_7$,

which is really ordinary sulphuric acid, charged with sulphur trioxide, SO_3.

28. Thiosulphuric Acid, $H_2S_2O_3$. — This last is of some interest because it is the basis of the salts known as thiosulphates, the best known of which is sodium thiosulphate, $Na_2S_2O_3$. From a mistaken idea of its composition sodium thiosulphate was first named *hyposulphite*, and is still commonly sold under that name. This is the photographer's "hypo."

SUMMARY OF CHAPTER

Sulphur — Where found.
  Forms in which it occurs.
  Sources of commercial supply.
  Methods of purification.
  Characteristics of sulphur.
    Various forms — How prepared.
      How different.
  Uses of sulphur.
  Compounds.
    With hydrogen — Two names for the gas.
      Occurrence.
      Method of preparing.
      Characteristics of, and proof by experiment.
      Use of.
    With oxygen — Names and formulæ.
      Preparation of the more important.
      Comparison of method with that of making hydrogen.
      Characteristics of SO_2.
      Uses.
    With hydrogen and oxygen.
      Most important — Commercial name.
      How manufactured — Explanation of the chemical changes involved.
      Characteristics of H_2SO_4.
      Uses.

CHAPTER XIV

SILICON AND ITS COMPOUNDS — GLASS

SILICON: Si = 28

1. Abundance. — Silicon is never found free, but in the form of compounds is the most widely distributed and most abundant of the non-metallic elements except oxygen and carbon. Sand, an oxide of silicon, SiO_2, is familiar to all; quartz, crystallized or massive, including the agate, amethyst, opal, and other stones, is another variety of the same substance. All soils contain it to a greater or less extent, and it is taken up by plants and enters into their structure. Combined with sodium, calcium, magnesium, aluminum, and other metals it forms silicates which are very abundant. In this class may be placed granite, mica, and many other substances.

2. Character of Silicon. — Silicon has been prepared in such limited quantities that not a great deal is known about it. It occurs in three forms, the amorphous and the crystallized or transparent being the two most important. At high temperatures it combines readily with oxygen or with carbon dioxide, forming the dioxide.

COMPOUNDS OF SILICON

3. As already stated, *silica* or *silicon dioxide*, SiO_2, is the most abundant compound. In the crystallized form it is often called *rock crystal*, and is found in hexagonal prisms, often more or less modified. Owing to the presence of foreign substances, silica often assumes a variety of colors, and is known as *rose quartz*, *smoky quartz*, etc. It is very hard, being seven in the scale, is brilliant, highly refractive when cut, and is often used for ornaments in imitation of diamonds. It melts at about 2000° C., and is soluble in alkalies as well as in hydrofluoric acid.

4. It is from the fact above mentioned that siliceous incrustations occur about many geysers. These springs are alkaline in character, and at the high temperature present beneath the surface dissolve considerable quantities of silica; when the water becomes cold and exposed to the action of the air, it is not able to hold the silica, and this is deposited upon any bodies on which the water may fall. The power of alkalies to dissolve silica may often be observed in the laboratory, where bottles containing ammonia, caustic soda and potash, sodium carbonate solutions, etc., become etched or rough on the inside, and the glass stoppers so tight as to render their removal an impossibility.

5. The Silicates. — Theoretically, silica is the anhydride of silicic acid; that is,

$$SiO_2 + 2\,H_2O = H_4SiO_4.$$

But water added to the oxide in this case produces no reaction. The silicates, however, are based upon this acid. They are abundant, and many of them are very complicated in composition. As silicic acid is *tetrabasic*, the hydrogen may be replaced by a variety of elements, even in the same molecule; thus, we might have

$NaAlSiO_4$: Sodium Aluminum Silicate.
$CaMgSiO_4$: Calcium Magnesium Silicate.

$NaKCaSiO_4$: Sodium, Potassium Calcium Silicate.
$H_8Mg_5Fe_7Al_2Si_3O_{18}$: Mica, etc.

6. **Preparation of Silicic Acid.** — Silicic acid may be prepared from "water glass," that is, silica dissolved in boiling caustic soda, or potash, by adding a little strong hydrochloric acid till the solution is no longer alkaline. Then a jellylike mass will be precipitated, which is silicic acid. By filtering this out and igniting when dry we again obtain the oxide.

EXPERIMENT 124. — Let the student thus prepare some soluble "water glass" and the silicic acid from it.

7. Though silica is insoluble in water and has such a high melting point that only such temperatures as that secured by the oxyhydrogen blowpipe or the electric furnace will fuse it, still, if mixed with sodium carbonate and strongly heated in a blast lamp for a few minutes, it is converted into a soluble form, sodium silicate, and may then be readily taken up by water.

8. **Glass.** — This is an artificial silicate that has been manufactured in some form or other for probably 4000 years. Several of the nations of antiquity were famous for their wonderful glasswork; in beauty of coloring, their achievements have probably not been surpassed in modern times. But the applications of glass are now so varied and so adapted to the necessities of life, as well as to the luxuries, that it would seem impossible to do without it. Every year sees the manufacture of hundreds of millions of bottles, and tons of other kinds of glassware; and the art of glass blowing and working has reached such a high state of perfection that glass objects, from their nature almost inconceivable, are now of frequent manufacture.

We have seen above that if silica is fused with sodium carbonate, a new compound is formed which is quite soluble. If, however, we mix calcium carbonate, or chalk, with the silica, together with the sodium carbonate, and fuse the mixture, we then obtain a double silicate of sodium and calcium that is quite insoluble in water and in all acids, except hydrofluoric.

9. Varieties of Glass.—There are many varieties of glass. As potassium salts are so closely related to those of sodium, it is obvious that potash could be used instead of soda. In fact, glass was first made entirely in this way. Nearly all the best chemical and physical apparatus is still made from potash salts, and this variety is known as *Bohemian glass.* It is much harder to melt than glass made from sodium carbonate.

10. If an oxide of lead is used with the silica and potash, we obtain a glass that is very soft and easily worked, known as *flint glass.* It has a very high refractive power, and on this account is used for telescopes and all kinds of optical instruments. In the purest form it is known as *strass* or *paste*, and from this are made the so-called *paste diamonds.* These are so lustrous and highly refractive that, except in hardness, it is difficult for any but experts to distinguish them from the genuine article.

11. Ordinary glass, known as *crown glass*, from which windows and the great majority of glass utensils are made, is a silicate of lime and sodium, as already described. Ordinary sand contains a considerable amount of iron in the form of an oxide. This gives to the glass used for ordinary bottles and for all the cheaper grades the well-known greenish color, which, however, may be removed by the addition of a small quantity of manganese dioxide.

12. Much of the plain glassware used at present is molded just as any casting would be in an iron foundry. Window glass is first blown into a long cylinder; this is cut open and flattened while still hot by means of heavy rollers. Plate glass for large windows and heavy mirrors is cast. The molten glass is poured upon a table of the desired size, allowed to cool, and the surface afterwards ground and polished.

13. All glass articles must be carefully annealed, otherwise they would be so brittle as to have little value. The glass, as soon as shaped, is placed in an oven, and during several days is cooled so slowly that the molecules have time to adjust themselves to stable positions. Indeed, so well is this annealing done that glass vessels are made for use in chemical work that may be heated strongly and plunged into cold water immediately without danger of breaking.

SUMMARY OF CHAPTER

- Silicon.
  - Abundance of it in nature.
    - Some familiar forms.
  - Compounds of silicon.
    - The oxide — Some common forms.
      - Characteristics of.
  - Glass — Importance of.
    - What glass is.
    - Kinds of glass.
    - How different in properties.
    - Making of window glass and other forms.
    - Annealing of glass articles.

CHAPTER XV

PHOSPHORUS AND ITS COMPOUNDS

PHOSPHORUS: P = 31

1. Occurrence. — Phosphorus has been known for about two and a quarter centuries, but it is only since 1833 that it has had any real practical value. Owing to its strong affinity for oxygen it is never found free, but in the form of compounds it is very widely distributed. It is a constituent of many rocks, and, from their decomposition, also of soils. From this source plants take it up and store it away in the seeds and fruits; plants, being used as foods, transfer it to animals, where it is found in the nerve centers and bones.

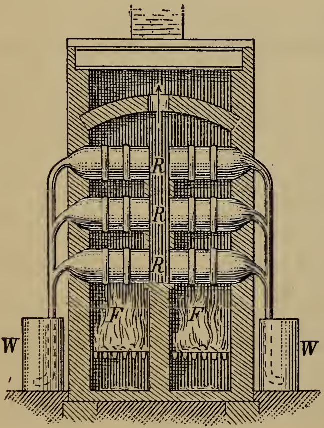


FIG. 49. — Manufacture of Phosphorus.

2. Manufacture of Phosphorus. — It is obtained almost altogether from bones. These are put into retorts and heated, much as coal is for the preparation of illuminating gas. The volatile products are thus driven off and their valuable portions condensed. The bones are reduced to what is known as bone-black, or, if not desired for clarifying sugar, to bone-ash. To this sulphuric acid is added, which converts the calcium phosphate in the bones into a salt that is soluble in water. This is dissolved out and the solution evaporated to dryness, then mixed with carbon and strongly heated. The phosphorus is thus set free; it distills out and is condensed under water and molded into sticks. (See Fig. 49.) *R*, *R*, are the retorts into which the mixture of charcoal and phosphorus compounds are put; *F* is the furnace, and *W*, *W*, the water tanks where the phosphorus is condensed. The process is very deleterious to health, the fumes from the retorts often producing dangerous ulcerations of the jawbones, a disease which is practically incurable.

3. Characteristics of Phosphorus. — Phosphorus is a very pale, amber-colored, translucent solid, somewhat waxy in appearance. When exposed to the air it almost immediately begins to give off luminous fumes having a faint garlic odor, and in the course of a short time takes fire. A little friction will readily ignite it, hence it should be cut under water. Burns from it are very serious and require weeks to heal. If heated to 240° out of contact with the air, it changes to an allotropic form, known as *red* or *amorphous* phosphorus. Unlike the ordinary phosphorus, this is not poisonous, does not readily take fire, is not soluble in carbon disulphide, and does not glow in the dark.

EXPERIMENT 125. — To show the ready combustibility of phosphorus when finely divided. Dissolve a small piece of phosphorus, half as large as a pea, in a little carbon disulphide. Pour the solution upon a piece of filter or blotting paper, and let it dry. Notice how quickly it ignites.

EXPERIMENT 126. — To show that phosphorus will burn under water. Put into a small bottle about 1 g. of potassium chlorate, add a few small pieces of phosphorus, and cover with water. By means of a pipette or funnel tube introduce beneath the water into contact with the potassium chlorate a little sulphuric acid. Notice that the phosphorus begins to burn. Explain.

Experiment 127. — To show the affinity of phosphorus for chlorine, bromine, and iodine. Put a small piece of phosphorus into a deflagrating spoon and introduce it into a jar of chlorine. What happens in a few moments? Cut a thin slice of phosphorus, and upon it place a crystal of iodine. Notice that the phosphorus is soon ignited. Try a drop of bromine in the same way.

4. **Uses for Phosphorus.** — About 3000 tons of phosphorus are manufactured annually, most of which is used in preparing matches. Small quantities also are employed in making poisons. Matches were first made in Austria by tipping small pine sticks with sulphur to which a little phosphorus had been added. This method was employed for a good many years, but the sulphur has now been largely replaced by other substances rich in oxygen, such as potassium chlorate, saltpeter, etc., together with paraffine.

5. Matches are now made entirely by machinery, and with wonderful rapidity. The wood, being sawed into convenient lengths, is pressed against knives, which split it up into the proper size for matches. These are dipped into paraffine, then tipped with a paste made of a little glue containing phosphorus and the other ingredients already mentioned, together with some coloring matter. After drying they are packed in boxes. In this way a single machine will make and pack several million matches in a day. In the case of safety matches the phosphorus is placed in the prepared surface upon the box, and the matches can be ignited only by friction on this surface.

6. **Compounds of Phosphorus.** — One of the most interesting of these is hydrogen phosphide, PH_3. It is also called *phosphine* and *phosphoreted hydrogen.* It is readily evolved when phosphorus is heated in a solution of any strong alkali, such as caustic soda or potash.

Experiment 128. — Suitable for class-room. Into a small flask put about 50 cc. of strong caustic soda or potash solution, and add several small pieces of phosphorus. Pour in about a cubic centimeter of ether, and close the flask quickly with a cork and long delivery tube. Support the flask upon a ring-stand, as shown in the figure, and heat moderately. Presently smoky-looking fumes will fill the flask, and then the bubbles issuing from the mouth of the delivery tube will take fire spontaneously. If the room is free from draughts of air, beautiful rings of smoke, growing gradually larger, will float upward. Notice the vortex motion of the rings. The ether is introduced to expel the air before any phosphine is generated; the heat should be regulated so as not to allow too rapid an evolution of gas, otherwise the rings will follow in such rapid succession as to break one another. What is the odor of the gas? Color?

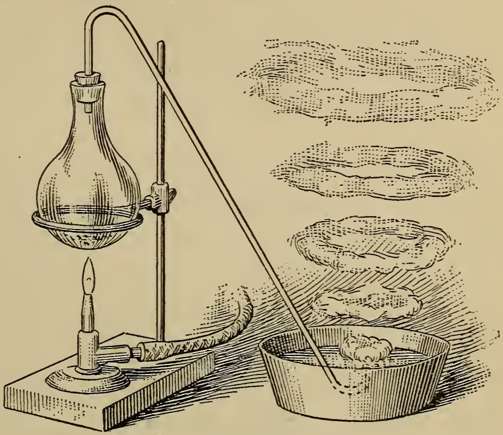


Fig. 50.

7. Oxides of Phosphorus. — Pentoxide, P_2O_5, and Trioxide, P_2O_3. The first of these has been seen on various occasions: when phosphorus was burned in oxygen, in preparing nitrogen, etc. The dense white fumes noticed consisted mainly of phosphorus pentoxide. This compound is always obtained when phosphorus is burned in a plentiful supply of oxygen. When the amount is limited, or when the combustion is slow, phosphorus trioxide is obtained. The pentoxide is a white solid which has great affinity for moisture, and if dropped into water combines with it with a hissing sound as of a hot iron in cold water.

8. Acids of Phosphorus. — The two oxides named above, like the corresponding oxides of nitrogen, are the anhydrides of certain acids, thus: —

$P_2O_3 + 3\,H_2O = 2\,H_3PO_3$ . . . Phosphorous Acid

$P_2O_5 + 3\,H_2O = 2\,H_3PO_4$ . . . Phosphoric "

The latter is the more important. It will be noticed that its molecule contains three atoms of hydrogen, all of which may be replaced by a metal. Such acids are called *tribasic.* Phosphoric acid is a white crystalline substance, which may be prepared by treating bone-ash with sulphuric acid. At high temperatures it will give up a part of the water that was taken in its formation and yield *metaphosphoric* acid, HPO_3, which is *monobasic.* The reaction may be shown thus: —

$$H_3PO_4 + \text{heat} = HPO_3 + H_2O.$$

This is frequently sold under the name *glacial phosphoric acid.*

9. Compounds with Phosphoric Acid. Phosphates.—The most common of these is calcium phosphate, $Ca_3(PO_4)_2$, found in the bones. Immense deposits of this are found in Florida, where it is mined and used as a fertilizer in various parts of the world. From the fact that all grain plants absorb the soluble phosphates from the soils, unless these salts are replaced in some way the land rapidly loses its productive power. A considerable portion of the phosphates in the grain fed to animals is thrown off in the excrement and is returned to the soil in this way.

10. Immense quantities of bones are reduced to animal charcoal, and then, by treatment with sulphuric acid, converted into soluble phosphates and returned to the soil in this way as artificial fertilizers. Another source of considerable supply is from the reduction of phosphorus-bearing iron ores by the Thomas-Gilchrist process; and a matter of interest in this connection is that the calcium phosphate thus obtained is already in the soluble form and needs no further treatment.

SUMMARY OF CHAPTER

- Phosphorus — Occurrence.
  - Source of supply.
  - Method of preparing phosphorus.
    - By-products and their uses.
  - Characteristics.
    - Two forms of phosphorus.
      - Compare with forms of sulphur.
    - Experiments to illustrate characteristics.
  - Uses.
    - Method of making matches.
    - Chemicals used.
  - Compounds.
    - With hydrogen.
      - How prepared.
    - With oxygen.
      - Names and formulæ.
      - How prepared.
    - With hydrogen and oxygen.
      - How related to the oxides.
      - Salts formed from these acids.
        - Uses.

CHAPTER XVI

AVOGADRO'S LAW — ATOMIC WEIGHTS — PROBLEMS

1. Avogadro's Law. — This law, or hypothesis, was formulated by the Italian physicist and chemist, Avogadro, and afterward, independently, by the Frenchman, Ampère. It may be stated thus: —

Equal volumes of all substances in the gaseous condition under the same pressure and temperature contain the same number of molecules. To illustrate, suppose a liter of hydrochloric acid gas contains a billion molecules, then a liter of nitrous oxide, or of any other gas, would also contain a billion molecules.

2. Proof of this Theory. — No absolute proof of this law has ever been given, but many facts seem to favor such a theory. For example, we have seen that all gases expand and contract in the same ratio under the influence of heat and pressure. As expansion and contraction mean simply a change in the distance which separates the molecules from each other, this being greater when the body is heated, and less when cooled, it would seem that bodies could expand alike only if composed of the same number of molecules, or if containing what means the same thing, the same number of intermolecular spaces.

3. Ratio of Molecular Weight to Specific Gravity. — It has been found also that there is a constant ratio existing between the molecular weight of a gaseous body and its specific gravity; that is, if we divide the molecular weight of any gas by its specific gravity, we always obtain practically the same quotient. This ratio is about 28.88. Thus, the molecular weight of carbon dioxide is 44, its specific gravity is 1.524, the ratio of 44 to 1.524 is 28.87; carbon monoxide has a molecular weight of 28, specific gravity of 0.967, the ratio is 28.94.

Exercise. — To apply this fact, suppose a given volume of nitrous oxide, N_2O, weighs 1.52 grams, and the same volume of hydrochloric acid gas weighs 1.27 grams. It is evident that the weight of any volume of gas divided by the weight of one molecule would give the number of molecules in that volume. Thus: —

$$\frac{\text{wt. of 1 l. } N_2O}{\text{wt. of 1 mol.}} = \text{no. mol. } N_2O \text{ in 1 liter.}$$

and

$$\frac{\text{wt. of 1 l. HCl}}{\text{wt. of 1 mol. HCl}} = \text{no. mol. HCl in 1 liter.}$$

We can readily find the weight of a liter of each of these gases, and also the *molecular* weight of each, but the first is in grams and the second in *microcriths*, that is, so many times as heavy as a hydrogen atom; but unfortunately we have no means of knowing how many microcriths in a gram, hence we cannot perform the division indicated above nor assign to the quotient any concrete name. If we make the division, however, we find that the quotient is always practically the same; that is,

$$\frac{\text{wt. of 1 vol. } N_2O}{\text{wt. of 1 mol. } N_2O} = 28.88 = \text{no. mol. } N_2O \text{ in 1 vol.}$$

$$\frac{\text{wt. of 1 vol. HCl}}{\text{wt. of 1 mol. HCl}} = 28.88 = \text{no. mol. HCl in 1 vol.}$$

Hence, as the ratio in each case is the same, in accordance with the axioms of geometry,

$$\text{no. mol. } N_2O \text{ in 1 vol.} = \text{no. mol. HCl in 1 vol.}$$

Putting this law into the form of a proportion, it would read: —

$$\frac{mw}{s} = \frac{m'w'}{s'}, \text{ or } mw : m'w' :: s : s',$$

in which mw and $m'w'$ represent the molecular weights of any two gases, and s and s' their specific gravities.

4. Application of this Law. — The truth of Avogadro's Law having been accepted long ago, it is now made use of in determining the molecular weights of new compounds. Having found by actual work the weight of 1 liter of the gas, and knowing the weight of 1 liter of air, the specific gravity is found. Then, substituting in the formula,

$$\frac{mw}{s} = 28.88,$$

we can easily find the value of *mw*.

5. Finding Atomic Weights. — This law is further used in determining the atomic weight of a newly discovered element.

Let *m* represent this element, and suppose we are attempting to find the atomic weight by studying some compound of it with oxygen. We should find the weight of a molecule of the oxide as shown above. Suppose this is found to be 28. Next, by chemical analysis we should determine what per cent of the compound is the new element, *m*. Suppose the analysis shows this to be 42.86 per cent, then we should have this proportion: —

$$\text{mol. wt.} : \text{wt. of } m \text{ in the mol.} :: 100 \text{ per cent} : \text{per cent of } m;$$

or,

$$28 : x :: 100 : 42.86.$$

$$100\,x = 42.86 \times 28.$$

$$x = 12.$$

In the same way we should determine the weight of the element, *m*, in a molecule of a number of other compounds containing it; then, the one having the least amount would be taken as a compound containing but one atom of the element, and the value of *x* in that compound would represent the atomic weight. To illustrate, suppose in this way we find in our analyses, and subsequent determinations, that *m* or *x* is equal to 24, 12, 36, 120. The second, 12, being the smallest amount found in any compound, would be accepted as the atomic weight. This would not be absolute proof, however, as later another compound might be discovered which contained a smaller amount of *m*, in which case that smaller amount would be taken as the atomic weight.

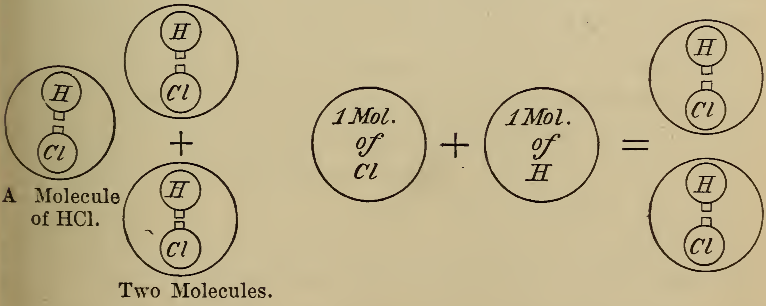
6. Constitution of the Molecules of Elements. — How many atoms are there in a molecule of an elementary substance, like oxygen, hydrogen, etc.? In writing some of the reactions in the earlier part of this book the molecules were shown as having two atoms. With some exceptions, this is true; that is, a molecule of hydrogen, oxygen, chlorine, and of many other elements contains two atoms. How do we know this? A proof in the case of one or two elements will illustrate for the others.

We have seen that when hydrogen and chlorine are caused to unite, they form hydrochloric acid. It is found also by further experiment that in uniting thus the volume is not decreased; that is, if we put together a liter of chlorine and one of hydrogen, after causing them to combine, we have 2 liters of hydrochloric acid. Perhaps it will be clearer, stated in the form of an equation, thus: —

$$1000 \text{ cc. of Cl} + 1000 \text{ cc. of H} = 2000 \text{ cc. of HCl.}$$

Now, according to Avogadro's Law, there would be the same number of molecules in a liter of chlorine as of hydrogen or of hydrochloric acid. Dividing the entire equation through by this common factor, the number of molecules of chlorine in 1 liter, or 1000 cc., we should have

$$1 \text{ mol. of Cl.} + 1 \text{ mol. of H} = 2 \text{ mol. of HCl.}$$



Chemical analysis shows that in hydrochloric acid the hydrogen and chlorine are united in the ratio of 1 to 35.5, or one atom of each, as represented by the formula HCl, or by the figure.

It is evident, therefore, that two molecules of hydrochloric acid contain two atoms of hydrogen and two of chlorine, and as we only had one molecule of each of these elementary gases, each of those molecules must have contained two atoms. In a similar way we would prove for bromine, fluorine, oxygen, and others.

7. Most Molecules Diatomic. — Such molecules as these are called *diatomic*. There are a few, sodium, potassium, cadmium, mercury, and zinc, whose molecules contain only one atom, and such are called *monatomic*. Their molecule is, therefore, identical with the atom. Only one *triatomic* elementary molecule is known, and that is the allotropic form, ozone. A few, like phosphorus and arsenic, are *tetratomic;* that is, the molecule is made up of four atoms.

8. Application of this Fact. — It often becomes necessary in chemical problems to know the weight of a liter of a gas. This may very easily be found, but we must first know its *vapor density;* that is, its density compared to hydrogen. With the elementary substances this is, as a rule, the same as the atomic weight; for example, the atomic weight of hydrogen is 1, the molecular weight is 2; the atomic weight of nitrogen is 14; the molecular weight 28. Hence, whether we take the atomic weight of nitrogen, or its molecular weight and divide by the molecular weight of hydrogen, we obtain the same results. Then, as the hydrogen molecule weighs two, we find the vapor density of any other substance by dividing its molecular weight by 2. Thus: —

1 mol. N_2O weighs $2 \times 14 + 16 = 44$

1 “ H “ $2 \times 1 = 2$

1 “ N_2O “ $44 \div 2$ times as much as 1 mol. H

Again, —

1 mol. CO weighs $12 + 16 = 28$
1 " H " $2 \times 1 = 2$
1 " CO " $28 \div 2$ times as much as 1 mol. H

Therefore, *vapor density* of CO is $28 \div 2 = 14$.

Thus find the vapor density of CO_2, N_2O_3, O, HCl, SO_2, Cl, N.

9. To find Weight of One Liter of Any Gas. — Having found the weight of a gas compared to hydrogen (its vapor density), it is only necessary to multiply the weight of 1 liter of hydrogen by this figure. A liter of hydrogen has been found to weigh .0896 g., a number which should be remembered. Suppose now we desire to find the weight of a liter of carbon monoxide, CO. Above we found its vapor density to be 14. Then, as a liter of hydrogen weighs .0896 g., one of carbon monoxide will weigh $14 \times .0896$, or 1.2544.

Thus find the weight of 1 liter of the gases whose densities were found above. Also of N_2O, NH_3, H_2S.

10. The Formulæ of Compound Bodies. — We have learned that the formula of a compound is a short method of expressing its composition. It may be of interest to know how to determine the formula of a compound. The substance is first carefully analyzed, and the percentage composition determined.

Suppose we have in mind a compound which analysis shows consists of carbon and oxygen, 27.27 per cent of the former, and 72.73 per cent of the latter. We should next weigh a liter of it; suppose we find this to be 1.9712 g. As a liter of hydrogen weighs .0896 g., the unknown gas is $1.9712 \div .0896$, or 22 times as heavy.

We have seen that the molecular weight is twice the vapor density, then the weight of the molecule would be 2×22, or 44. Now, as the carbon is 27.27 per cent of this, it equals .2727 of 44 = 11.9988, and the oxygen, 72.73 per cent, or its weight in the molecule is 72.73 per cent of 44 = 32 +. Previous experiments have shown that the atomic weight of carbon is 12, hence the weight found above, 11.9988, practically corresponds to one atom, and that would be the amount of carbon in the compound. In the same way as the atomic weight of oxygen is known to be 16, the amount found in the compound, 32, would indicate two atoms. The substance in question, therefore, would contain carbon, 1 atom, oxygen, 2 atoms, and would be carbon dioxide, formula CO_2.

PROBLEMS. — 1. A liter of a certain gas weighs 0.8064. It consists of hydrogen $\frac{1}{9}$ and oxygen $\frac{8}{9}$. Find its vapor density, molecular weight, and the formula.

2. A gas consisting of carbon and oxygen has 42.86 – per cent of the former, and 57.14 + per cent of the latter. If 1 liter of it weighs 1.2544, what is its formula?

3. What per cent of turpentine, $C_{10}H_{16}$, is carbon? Hydrogen?

4. The vapor density of a body is found to be 50.5. If analysis shows that 2.359 g. of it contain 1.12 g. of oxygen, how many atoms of oxygen are there in the formula representing the substance?

5. What is the molecular weight of a certain substance if 50 g. of it contain 32.65 g. of oxygen, knowing that there are four atoms of oxygen in the molecule of the substance?

6. Find the percentage composition of nitric acid.

SUMMARY OF CHAPTER

Avogadro's Law — Statement of the law.
    Illustration.
    Proof of the law.
        a. As seen in effects of heat.
        b. Ratio of molecular weight to specific gravity.
    Value of the law.
        a. Finding atomic weights — Illustration.
        b. Constitution of molecules — Proof.
    Meaning of terms *monatomic*, etc.
Problems.
    Method of finding weight of a liter of any gas.
    How to determine the formula of a compound.

CHAPTER XVII

THE METALS — PERIODIC LAW

1. Metals and Non-metals. — It has been customary to divide the elements into two great classes, the *metals* and *non-metals*, of which the former includes by far the greater number. This classification, however, is based largely upon the external characteristics or appearance rather than upon the chemical deportment. In appearance the metals have a peculiar luster, known as the *metallic* luster, considerable density, with few exceptions have high melting points, and are electro-positive in character. As a rule, their oxides are not *anhydrides*, and yet there are many exceptions to this statement, for we find various compounds of *tin*, *arsenic*, *antimony*, *chromium*, *aluminum*, etc., in which these metals seem to serve as the acid-forming element. And some even possess more chemical char-

NON-METALS	METALS
Their oxides form acids, as for example:	Their oxides form bases as:
N_2O_3 . . . HNO_2, SO_2 . . . H_2SO_3, P_2O_5 . . . HPO_3, etc.	CaO . . . $Ca(OH)_2$, Na_2O . . . NaOH, K_2O . . . KOH, etc.
Many are gaseous.	Most are solids.
Many are transparent.	All are opaque.
Poor conductors of heat and electricity.	Good conductors of heat and electricity.

acteristics in common with the non-metals than with the metals. It must be concluded, therefore, that there is no clearly dividing line between the two classes. Nevertheless, some distinctions in addition to those mentioned above may be noted.

2. Tabular Classification. — It will be seen that the above division is almost purely an arbitrary one. At the present time it is customary to classify the elements into a number of groups in accord with what is known as the *periodic law.*

TABLE OF ELEMENTS

		I	II	III	IV	V	VI	VII	VIII
Period I		H=1 Li=7	Gl=9	B=11	C=12	N=14	O=16	F=19	
“ II		Na	Mg	Al	Si	P	S	Cl	
“ III	*A*	K	Ca	Sc	Ti	V	Cr	Mn	Fe, Co, Ni
	B	Cu	Zn	Ga	Ge	As	Se	Br	
“ IV	*A*	Rb	Sr	Y	Zr	Nb	Mo		Ru, Rh, Pd
	B	Ag	Cd	In	Sn	Sb	Te	I	
“ V	*A*	Cs	Ba	La	Ce				
	B								
“ VI	*A*			Yb			W		Os, Ir, Pt
	B	Au	Hg	Tl	Pb	Bi			
“ VII	*A*			Th			U		
	B								

3. Recurrent Characteristics in the Table. — If the above table is studied in connection with the atomic weights of the elements, it will be seen that, reading from left to right, they are arranged with reference to their weights. Thus, in the first period, we have

Li = 7, Gl = 9, B = 11, C = 12, N = 14, O = 16, F = 19;

in the second,

Na = 23, Mg = 24, Al = 27, Si = 28, P = 31, S = 32, Cl = 35.5.

4. In thus arranging them it was noticed that, starting with lithium, not until we reach the eighth element beyond, do we come to another, sodium, similar to lithium in characteristics; and from sodium there are seven more before another is reached similar to this. From these observations the above table was arranged, and though it is far from complete, wonderful results have come from it. We notice that in group VII, we have fluorine, chlorine, bromine, and iodine, four elements that we have found to have very similar properties. We shall hereafter find the same to be true of lithium, sodium, and potassium of the first group; magnesium, calcium, strontium, and barium of the second, and so on. If we take these vertical columns or groups and compare their atomic weights, we notice some interesting facts.

$$\left.\begin{array}{lcr}\text{Li} & = & 7\\ \text{Na} & = & 23\\ \text{K} & = & 39\end{array}\right\}\text{The atomic weight of sodium is exactly halfway between the other two.}$$

$$\left.\begin{array}{lcr}\text{Ca} & = & 40\\ \text{Sr} & = & 87\\ \text{Ba} & = & 136\end{array}\right\}\text{The weight of strontium is practically the mean of the other two.}$$

$$\left.\begin{array}{lcr}\text{P} & = & 31\\ \text{As} & = & 75\\ \text{Sb} & = & 120\end{array}\right\}\text{The same is true of the middle element.}$$

$$\left.\begin{array}{l} S = 32 \\ Se = 79 \\ Te = 125 \end{array}\right\}$$ The same is true of the middle element.

5. If we study the compounds that the elements form, we shall find that those falling in the same group are strikingly similar in their chemical behavior. Thus, lithium, sodium, potassium, rubidium, and cæsium in the first group are all univalent and form oxides with the general formula, M_2O, in which M represents any metal of the group. Furthermore, they form no compounds with hydrogen. If we take the second group, they are all bivalent, forming oxides with the general formula, MO, as MgO, CaO, etc. They form no hydrogen compounds. The members of the third group are trivalent, as seen in their oxides, Al_2O_3, general formula M_2O_3. And so we might go on through the table.

6. Vacancies in the Table. — It will be noticed that there are many vacant places, but it is an interesting fact that when the table was first worked out there were many others that have since been filled. And strange to say, from this table the author of the plan not only predicted that these very elements would be found, but even gave in a general way their characteristics, and in accordance therewith suggested names for them. In the same way, it is possible that many of the places now vacant will sometime be filled by elements as yet undiscovered.

Note. — Some teachers may prefer to defer a close study of the Periodic Law until after the completion of the work with metals.

SUMMARY OF CHAPTER

Classes of the elements.
Characteristics of the two classes.
    Wherein different.
    Wherein alike.

The Periodic Law.
  Recurrence of certain characteristics.
  Relation of atomic weights.
  Similarity of chemical behavior.
  Value of the law and table.

CHAPTER XVIII

THE ALKALI METALS

SODIUM : NA = 23

1. **Its Discovery.** — Up to the year 1807 caustic soda and caustic potash had been regarded as elementary substances; by electrolysis, however, Sir Humphry Davy in 1807 proved both of these substances to be compounds, and hydroxides of the metals sodium and potassium.

2. **Where found.** — Sodium is very widely distributed, traces of it being found everywhere. On account of the strong affinity existing between it and water, it never occurs in the metallic state. Its most abundant compound is common salt, NaCl, which constitutes a large per cent of the solid matter found in sea water, salt lakes, and springs; vast deposits of it, more or less pure, occur in many parts of the West as well as in other portions of the world. Sodium nitrate, $NaNO_3$, is found in immense quantities in Chile and elsewhere. Other compounds occur in smaller proportions, but in some form or other sodium can be detected in every particle of dust that may be seen floating in the sunbeams.

3. **Reduction of Sodium from its Compounds.** — Since the isolation of the metal by Davy, various other plans have been tried, but they are all modifications of the

original. What is known as the *Castner* process is the one generally used at present. See Figure 51.

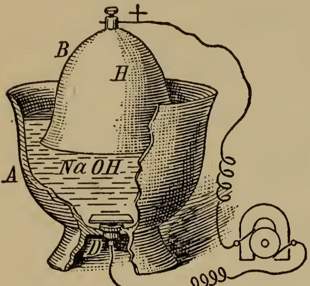


Fig. 51.

A in the figure is a large iron vessel, *B* another, similar but smaller, inverted over *A* and dipping into the fused caustic soda in the lower vessel. It is held in position by insulated supports not shown. Through the bottom at *D* is inserted the negative electrode, and *B* serves as the positive. When the current from the dynamo is passed through, the caustic soda is electrolyzed, *B* gradually fills with hydrogen which bubbles out underneath, while the metallic sodium collects upon the surface of the fused mass. In this way it is prepared for about two dollars a pound.

4. **Characteristics of Sodium.** — It is a silvery white metal, so soft at ordinary temperatures that it may be molded with the fingers, about like stiff putty. At – 20° C., however, it becomes hard. It tarnishes so rapidly in the air that only for an instant after being cut can its true color be seen. It takes up moisture and carbon dioxide from the air, forming first caustic soda, and afterward sodium carbonate. In course of time a piece of sodium left more or less exposed is entirely converted into amorphous sodium carbonate. It is usually preserved in naphtha or some similar light oil containing no oxygen.

5. Sodium is soluble in liquid ammonia and forms with it a blue solution. Its properties are strongly alkaline. If heated and plunged into a jar of chlorine it burns vigorously, forming common salt. Thrown upon water it is immediately melted, owing to the heat generated by the

strong chemical action, and the water is decomposed, as already shown in our study of hydrogen. If a burning match is touched to the sodium as it spins about on the water, the hydrogen will burn with a yellow flame, due to the vaporization of a small portion of the sodium. Upon moderately warm water the gas will take fire spontaneously. If a small piece of sodium is dropped upon a moistened blotting paper, it is quickly ignited. If, when it begins to burn, the molten sodium is allowed to roll off and drop upon the floor, it will burst into many particles which will spin about, burning with the characteristic yellow flame.

Experiment 129. — Moisten a piece of blotting paper with water, to which a little phenolphthalein has been added. Drop a small piece of sodium upon the blotter. Notice the red track it leaves as it slowly moves about from place to place. You have seen similar results in previous work. Let the molten globule of sodium roll off upon the floor and notice what happens.

Compounds of Sodium

6. Caustic Soda, Sodium Hydroxide, NaOH. — This compound is prepared by treating sodium carbonate, Na_2CO_3, in solution with lime-water. The reaction is

$$Na_2CO_3 + Ca(OH)_2 = 2\,NaOH + CaCO_3.$$

The calcium carbonate, thus formed, is insoluble in water, hence is precipitated. The sodium hydroxide is drawn off, evaporated to dryness, purified, then fused and molded into sticks; in this form it is put upon the market. It is a white solid, deliquescent, with strongly alkaline properties.

7. Sodium Chloride, NaCl. — As already stated, this compound occurs very abundantly. In some places it is mined much as rock or metallic ores are mined. In other places, where the deposits are upon the surface, mingled with considerable quantities of sand and earthy matters, it is dissolved out and the strong solution evaporated. In some of our states wells are sunk into the deposits, and water pumped in to dissolve the salt. This is again drawn out and evaporated. In some places along the Mediterranean the sea water is pumped up and allowed to trickle down over brush or lattice work, whereby it is much concentrated in strength, then this solution is evaporated to dryness in large shallow pans. It crystallizes in cubes, as may be seen if a strong solution is allowed to evaporate slowly.

Sodium chloride, if chemically pure, is not deliquescent, but owing to impurities present that which is generally put upon the market soon becomes damp when exposed to the air. It is used very extensively in the manufacture of other important compounds of sodium ; also largely in our food. A part of it is said to be decomposed by the digestive fluids of the stomach and to form hydrochloric acid.

8. **Sodium Carbonate, Na_2CO_3.** — This is a very important compound used in the manufacture of soap, glass, and for a variety of other purposes. In the early part of this century soda crystals, as this compound is often known in commerce, sold for over $300 a ton, while now the same quantity is worth scarcely $20. There are two general processes of manufacture. The simplest and the one most in favor at the present time is the —

Solvay Process. — This consists of passing a current of ammonia into a strong solution of sodium chloride until it is saturated; carbon dioxide is next forced in and with the ammonia forms ammonium bicarbonate. This reacts with the common salt, forming sodium bicarbonate. These processes may be shown thus: —

$$NH_4OH + CO_2 = NH_4HCO_3,$$

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

The sodium bicarbonate crystallizes out much more quickly than the ammonium chloride, and in this way the two compounds are separated. The bicarbonate of soda is then heated to expel a portion of the carbon dioxide, and sodium carbonate results, thus:—

$$2\ NaHCO_3 + \text{heat} = Na_2CO_3 + CO_2 + H_2O.$$

This process is very cheap because the salt can be had for a few cents per hundred pounds, the ammonia is obtained abundantly from all gas factories, and the carbon dioxide can be had by calcining limestone in making lime. Or, as seen by the last reaction above, the carbon dioxide driven off from the bicarbonate of soda may be utilized for this purpose, and from the ammonium chloride obtained in the second step ammonia may be evolved by treating it with lime. It will be seen, therefore, that the result of one part of the process may serve in another part and thus reduce the final cost of manufacture.

The Leblanc Process.—This is more complicated than Solvay's, and more expensive; hence, were it not for the value of some by-products which are obtained, it would no longer be used. It really consists of three steps. First, common salt is treated with sulphuric acid and heated, at first moderately and then more strongly. In the beginning the salt is converted into acid sodium sulphate, thus:—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Next, this acid salt reacts with another part of sodium chloride, forming normal sodium sulphate, thus:—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl;$$

or, putting the two together, we have—

$$2\ NaCl + H_2SO_4 = Na_2SO_4 + 2\ HCl.$$

The sodium sulphate thus obtained is called *salt cake.* The hydrochloric acid vapors are passed into flues, down which water constantly trickles and absorbs the acid. This is a valuable by-product, and serves in some places to keep alive the Leblanc industry.

Second, this salt cake is mixed with powdered coal and limestone, and heated, when sodium carbonate, mixed with several other substances, is obtained. The mixture is black in color and is known as *black ash.* The reaction shows the chemical changes that take place:—

$$Na_2SO_4 + CaCO_3 + 2\ C = Na_2CO_3 + CaS + 2\ CO_2.$$

This black ash is treated with water to dissolve out the sodium carbonate, and the solution is concentrated and purified by calcining, dissolving, and recrystallizing.

In connection with almost every Leblanc factory is also one for the manufacture of bleaching powder on a large scale, by using the hydrochloric acid obtained as a by-product, with native manganese dioxide.

9. Sodium Nitrate, $NaNO_3$. — This is known as Chile saltpeter on account of the locality from which it is obtained and its close resemblance to potassium nitrate. The crude salt found native in Chile is dissolved in water and concentrated, whereupon the pure crystals separate. From the fact that it absorbs moisture from the air, it cannot be used in making gunpowder to any great extent. It is used largely, however, in the manufacture of nitric acid and also for artificial fertilizers.

10. Sodium Sulphate, Na_2SO_4. — This is frequently called *Glauber's salt.* It is a white crystalline salt obtained in the preparation of sodium carbonate as described above.

11. Sodium Bicarbonate, $NaHCO_3$. — This is common cooking soda, and is usually prepared by the Solvay process of making soda crystals, hence is very inexpensive. In making bread the "soda" is put with some such acid as sour milk. The acetic or lactic acid, or whatever it may be, reacts with the soda, setting free carbon dioxide, which raises the dough by struggling to escape through it. At the same time the acid disappears in the formation of a neutral salt. This may be seen by the following reaction of "soda" with acetic acid : —

$$NaHCO_3 + HC_2H_3O_2 = NaC_2H_3O_2 + H_2O + CO_2.$$

12. Soap. — This is a substance which has been made in greater or less quantities for probably two thousand years. At first, however, it was used simply as an ointment in a medicinal way, and not till about 200 A.D. was it applied as it is to-day, and even then only to a limited extent. Soap is made by combining some alkali, as caustic soda or potash, with some fatty substance or oil. The fat contains an acid which combines with the alkali, hence we see that soap is really a salt. It retains some alkaline properties, however, just as many other salts do, simply because both sodium and potassium are strong alkalies, while the fatty acids are comparatively weak; hence the alkaline properties really overbalance the acid properties. It has been said that soda crystals, Na_2CO_3, are used in making soap. They must first be converted into caustic soda, however, and this is done by treating the solution with milk of lime, $Ca(OH)_2$, as described.

13. **Hard and Soft Soap.** — We have two kinds of soap, *hard* and *soft;* the former is made from sodium compounds, the latter from potassium. Wood ashes contain considerable quantities of potassium carbonate; formerly, these were saved by farmers, placed in large "hoppers," lime added, and then leached. A dark-colored, strongly alkaline solution filtered out, containing a considerable percentage of caustic potash. This was treated with waste fat, and boiled, when in the course of a few hours a strongly alkaline *soft soap* was obtained, which always remained pasty. By adding common salt to this, it could be converted into a dark-colored solid mass; for many years this was the only hard soap known. Sodium compounds yield hard soap directly on combination with fats, hence they are most used at the present time in the manufacture of ordinary hard soap.

14. The practical value of soap lies in the fact that on account of its slightly alkaline properties it has the power of uniting with the oil secreted by the glands of the skin, and which holds the particles of foreign matter; this "dirt," therefore, may be removed by the mechanical action of the water. This also explains why frequent bathing with the application of strong soap will tend to cause the skin to chap, by the removal of the oil which keeps it soft and pliable.

15. Test for Sodium. — Sodium may always be detected by what is known as the flame test.

Experiment 130. — Heat a platinum wire in the Bunsen flame until it no longer imparts any color to the flame. Then dip it into the sodium solution and again hold in the flame. The bright yellow color is distinctive.

POTASSIUM: K = 39

16. Where found. — Because of its great affinity for other substances, potassium never occurs free. It is very widely distributed, however, in the form of compounds; it is a constituent of many rocks, and by their decomposition becomes a part of various soils. Being stored up by plants it enters into the animal economy, and by some animals, especially sheep, it is exuded from the skin and collects in considerable quantities upon the wool in an oily substance called *suint*.

17. How obtained in Metallic Form. — Potassium, like sodium, may be obtained by electrolysis, but is usually reduced by treating caustic potash with charcoal. The reaction shows the chemical changes: —

$$6\,KOH + 2\,C = 2\,K_2CO_3 + 3\,H_2 + K_2.$$

The potassium distills out and is collected under oil.

18. Characteristics of Potassium. — It is a metal somewhat softer than sodium; has a bright luster and white color, but it tarnishes instantly when cut in the air, so great is its affinity for oxygen and moisture. At zero it becomes crystalline in structure, hard, and brittle. When thrown upon water it immediately begins to decompose the water, and with such energy that it is melted and the hydrogen given off is ignited, burning with a violet color. This is due to the vaporization of a small portion of the potassium. As hydrogen is set free from the water caustic potash is formed, according to a reaction previously seen: —

$$H_2O + K = KOH + H.$$

With the halogens, chlorine and bromine, potassium ignites spontaneously, and with liquid ammonia it forms a blue solution. It possesses all the strong alkaline characteristics of sodium in a degree even more marked.

19. In the metallic form potassium has no uses in the arts. Its compounds, however, are very valuable. Any potassium salt may be tested in the same way as are the sodium compounds, with a platinum wire. The violet flame is characteristic. If both sodium and potassium are present it will be necessary to observe the flame through a blue glass. This transmits the potassium rays, but absorbs those of the sodium.

Compounds of Potassium

20. Potassium Hydroxide or Hydrate, KOH. — In earlier days the most common source of potassium compounds was wood *ashes*, which were boiled with water in iron pots. The potassium salts were dissolved out in this manner, and from them was prepared *caustic potash*, KOH. This is now obtained by a method similar to that used in the preparation of caustic soda, viz. by treating potassium carbonate with milk of lime, $Ca(OH)_2$, when this reaction takes place: —

$$K_2CO_3 + Ca(OH)_2 = 2\,KOH + CaCO_3.$$

The latter compound is insoluble and is precipitated; the former is drawn off, concentrated, purified by redissolving in alcohol, again dried, fused and molded in the familiar round sticks. It is very deliquescent, and quickly dissolves in the moisture it obtains from the air. It is used largely as a reagent in the laboratory.

21. Potassium Carbonate, K_2CO_3.—As already indicated, this was at one time obtained almost exclusively from the ashes of wood. These were treated with water, by which the potassium carbonate was dissolved out; the solution was boiled dry, forming a white salt known as *pearl ash.* Now large quantities are obtained by washing sheep's wool in hot water, then drawing off the greasy products obtained and heating them very strongly to expel the oil. The potash salts remain and are dissolved out by water.

Another source of considerable quantities is the beet-sugar industry. The beet sap is boiled down to a sirup, and from this sirup is extracted the sugar, leaving a sort of molasses, in which still remain the potassium compounds that the beets had obtained from the soil. This is generally first fermented and distilled; the residue is boiled to dryness and calcined. Then from the ashes the potash salts are obtained by lixiviation.

Potassium carbonate may be prepared from the chloride by the Leblanc process.

22. Potassium Chlorate, $KClO_3$. — This is a white, crystalline salt, often sold under the misleading name *potash.* It has a not unpleasant, cooling taste, and is used somewhat for throat affections. In the laboratory it has numberless applications, many of which are familiar to the student. In the arts it is used in making matches, for fireworks, etc. It is prepared by passing a current of chlorine into a solution of caustic potash, by which both potassium chloride and potassium chlorate are formed. The former is much more soluble, hence in concentrating the solution the potassium chlorate will crystallize out first, leaving the chloride still in solution.

23. **Potassium Nitrate, KNO_3.**—This is commonly known as saltpeter. It is a white, crystalline salt, found native in various parts of the world. As we have seen, it is produced by the decomposition of organic matter, especially the refuse from stables. This decomposition is supposed to be brought about by the presence of certain bacteria, and in some countries the process is now carried on artificially to a considerable extent.

24. The refuse is mixed with ashes and lime, and frequently stirred to increase the rapidity of decomposition. After a time the whole is leached with water to dissolve out the nitrate. The solution thus obtained is concentrated and the salt allowed to crystallize.

Considerable quantities are now made by treating sodium nitrate, which occurs in almost inexhaustible quantities in Chile, with potassium chloride, whereby this double reaction takes place: —

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

Potassium nitrate is used extensively in making gunpowder.

25. **Potassium Iodide, KI.** — This is a white crystalline salt. It is used frequently in the laboratory as a reagent, and to some extent in medicine.

26. **Potassium Bromide, KBr.** — This is a white salt, very similar in general appearance to the iodide. It is used frequently in medicine as a sedative.

Experiment 131. — Take any potassium solution and make the flame test just as you did for sodium in Experiment 130. Notice color of the flame. Now mix with it a solution of some sodium compound, and again test. Can you see the potassium flame? Next observe the flame through a sheet of blue glass. State results.

COMPARATIVE REVIEW OF THE ALKALI METALS

Sodium and Potassium.
    As found in nature — Two important native compounds of each — Where found.
        Which the more important.
Comparison of the two metals.
    Color.
    Tendency to oxidize.
    Hardness.
    Affinity for water.
    Melting point.
    Affinity for the halogens.
Experiments that illustrate most of these properties.
    Proof that hydrogen is set free from water by these metals.
    Proof of the hydroxide formed.
Compounds.
    The Hydroxides — Method of preparing — Reactions.
        Usual form — Appearance — Properties — Uses.
    The Carbonates — Source of supply.
        Former method of obtaining K_2CO_3.
        Present sources.
        Two methods of preparing Na_2CO_3.
        Uses of the carbonates.
            Review work in glass.
            Kinds of glass — Differences.
            Soap making — Chemistry of.
                Kinds of soap.
    Common salt.
        Preparation for market.
    Cooking soda — Chemical name and formula.
        Chemistry of in bread making.
    Saltpeter — Chemical name and Formula.
        Preparation — Appearance — Uses.
    Potassium chlorate — Formula,
        Appearance — Uses.

CHAPTER XIX

THE ALKALINE EARTHS

MAGNESIUM: $Mg = 24$

1. Occurrence. — Magnesium in the form of certain compounds is widely distributed. Among the most important of its compounds may be named the familiar minerals, *asbestos* and *meerschaum.* The first is a silicate of magnesium and aluminum, and the second a silicate of magnesium. Magnesium limestone, or *dolomite*, $CaMg(CO_3)_2$, occurs in considerable quantities.

2. Peculiarities of the Metal. — Magnesium is silvery white in color, and melts at a red heat. In dry air it does not tarnish, but moisture quickly affects it. While at ordinary temperatures it is slightly brittle, as it nears the melting point it becomes malleable and may be drawn into wires. These, flattened into ribbons, are the usual commercial form, though the powder is also frequently seen. The metal is easily ignited and burns with a dazzling white light, rich in actinic properties. This combustion is so vigorous that it will decompose even carbon dioxide and certain other similar oxides. (See carbon dioxide, page 143.)

3. Uses. — On account of the light furnished by burning magnesium, it is frequently used in taking flash-light pictures of caverns, and other interior views. It is likewise used to a limited extent in making fireworks. In the form of a powder it is often used like zinc in the reduction of ferric to ferrous salts (see page 307), on account of the rapidity with which, in the presence of sulphuric or hydrochloric acid, it yields hydrogen. It is also used by chemists in cases of supposed arsenic poisoning, in making Marsh's test. Zinc nearly always contains traces of arsenic, whereas magnesium is obtained practically pure; for this reason it is substituted for the zinc.

Compounds of Magnesium

4. Magnesium Sulphate, $MgSO_4$. — One of the most common compounds is *epsom salts*, *magnesium sulphate*, $MgSO_4, 7\ H_2O$. This is a salt found in the water of many mineral springs. It has a very bitter taste and is used largely in medicine, also extensively in finishing cotton goods.

5. Magnesia, Magnesium Oxide, MgO. — This is a white solid obtained when magnesium is burned in the air or in oxygen. It is often prepared by heating magnesium carbonate to expel the carbon dioxide, just as lime is prepared from limestone (see lime, page 221). The reaction is seen below: —

$$MgCO_3 + \text{heat} = MgO + CO_2.$$

It is used as a face powder, and, because of its high melting point, sometimes for making or lining crucibles.

CALCIUM: Ca = 40

6. Occurrence. — In the form of compounds, calcium is one of the most abundant and most widely distributed elements known. Because of its strong affinity for water, however, it never occurs free. The carbonate of calcium, $CaCO_3$, is the most abundant form and includes many well-known substances, such as marble, limestone, and chalk. Some of the more highly crystallized forms are Iceland spar, calcite, and dog-tooth spar, while stalactites, corals, and shells have the same composition. The next most abundant natural compound of calcium is gypsum, calcium sulphate, $CaSO_4$, 2 H_2O.

7. Production of the Metal. — Calcium has seldom been prepared, and then only for the purpose of studying its properties. Sir Humphry Davy, who first isolated potassium and sodium from their hydroxides by means of an electric current, in the same way decomposed calcium chloride and obtained calcium in the metallic form.

8. Characteristics. — Calcium is of a brassy yellow color, and somewhat malleable and ductile. It has a density of about 1.6, and like sodium readily decomposes water, forming the hydroxide, $Ca(OH)_2$. It is readily soluble in dilute acids, and at a temperature a little above its melting point it burns with a reddish yellow light. The cost of its production, $5.00 a pound, precludes its practical use.

Compounds of Calcium

9. Although as a metal calcium is of so little value, it would be difficult to estimate the worth of the compounds.

10. Lime, Calcium Oxide, CaO. — This is one of the most important compounds known. It is easily prepared from limestone by heating it to a red heat, at which temperature carbon dioxide is expelled, thus: —

$$CaCO_3 + \text{heat} = CaO + CO_2.$$

Lime is prepared in kilns, which are simply square rooms or ovens 15 to 20 feet high, and 10 to 15 feet each way. See Fig. 52. The limestone is thrown in from above and strongly heated with dry cordwood or coke in alternate layers. In a few hours the limestone is converted into lime, then the fire is removed, the mass is allowed to cool and the lime withdrawn, and if intended for shipment packed in barrels. Some kilns are arranged below so as to enable the workmen to remove the lime without putting out the fire. Such are continuously fed from above, and the operation goes on without ceasing.

FIG. 52.

11. Properties of Lime. — Prepared as above it is in the form of white lumps, but if left exposed to the air it begins at once to take up moisture and in a short time crumbles to a fine powder. It is then said to be "air-slaked," although it is really the water in the air that has caused the change. The reaction is as follows : —

$$CaO + H_2O = Ca(OH)_2.$$

12. If a lump of freshly prepared lime be treated with water, the change indicated above takes place rapidly, accompanied by the evolution of considerable heat. The hydroxide, $Ca(OH)_2$, thus obtained is soluble in water, though very much less so than ordinary caustic soda or potash. The solution of caustic lime is known as lime-water.

13. Uses of Lime. — Lime is indispensable in the erection of almost all structures. Mixed with sand it forms the mortar for nearly all stone and brick work — except such as is laid under water — and much of the plaster for indoor work. Unmixed with sand it is frequently used to give the white or finishing coat in plastering, though various plasters are now beginning to take the place of ordinary lime in this respect.

14. It is also used extensively in the lime purifiers of illuminating gas works, in the manufacture of bleaching powder, of ammonia, in removing the hair from hides in the process of tanning, and for numerous other purposes where a cheap and easily prepared alkali is demanded.

15. Calcium hydroxide, exposed to the air, absorbs carbon dioxide and forms calcium carbonate, thus: —

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

The same reaction takes place in mortar, hence that which has been properly prepared should grow gradually harder, in time being converted back again into a siliceous limestone. If a beaker containing lime-water be left exposed to the air, in a little while a white film will be seen to cover the surface of the liquid. This is really a precipitate of calcium carbonate, resulting from the absorption of the carbon dioxide of the air by the lime-water. If the breath from the lungs be blown through a clear solution of lime-water, it quickly becomes clouded from the same cause.

16. Calcium Carbonate, $CaCO_3$. — In the natural form this is known in the several varieties mentioned above. Artificially, it may be prepared as a white precipitate by adding some alkaline carbonate, as sodium or ammonium carbonate, to a solution of calcium. The following reaction takes place: —

$$CaCl_2 + (NH_4)_2CO_3 = 2\ NH_4Cl + CaCO_3.$$

It is insoluble in pure water, but when an excess of carbon dioxide is present, it slowly dissolves.

Experiment 132. — Through a few cubic centimeters of lime-water in a flask or beaker, pass a current of carbon dioxide, or blow the breath for some time. What finally becomes of the white precipitate which forms at first? Preserve the water.

In this way water charged with carbon dioxide percolating through limestone rocks gradually dissolves them, and has formed many of the great caves known in this country. This same water, dripping from the roof of caverns, being no longer under pressure, gives up its carbon dioxide, and the calcium carbonate, no longer held in solution by the gas, is deposited in the form of stalactites and stalagmites.

17. Calcium Chloride, $CaCl_2$. — This is a white salt which may be prepared from any form of the carbonate by treating with hydrochloric acid. It is a by-product formed in the preparation of carbon dioxide from limestone: —

$$CaCO_3 + 2\ HCl = CaCl_2 + CO_2 + H_2O.$$

It is strongly deliquescent, and is often used in drying gases, damp cellars, etc.

18. Calcium Sulphate, $CaSO_4$, 2 H_2O. — In the natural form this is the gypsum already mentioned. It occurs in vast quantities in many of our states, notably Kansas, New York, Illinois, etc., both in the form of rich, heavy deposits, and mixed with various impurities upon the surface. It is used extensively in making plaster of Paris. This is manufactured simply by strongly calcining the powdered gypsum until the water of crystallization is expelled. During this time, as the water escapes from the powdered mass, the whole seems to boil vigorously. After two or three hours the process is complete, and the plaster is ready to be mixed with the "retarder," if necessary. This plaster has the property of "setting" or hardening quickly when water is added to it. This is due to the fact that the anhydrous salt again takes up the water of crystallization expelled in the previous calcination. If the plaster which has been used once be again calcined, it acquires again its property of "setting."

19. Uses of Plaster of Paris. — It is employed extensively in making molds for many of the finer castings, in dental work and surgery, for statuettes, as a finishing coat in plastering, and for stucco and other ornamental work on the interior of buildings. For most purposes, a plaster that does not harden so rapidly is desirable, hence it is customary to mix with it some kind of clay, or other substance, which causes it to "set" more slowly. This clay has already been spoken of as the "retarder."

20. Cements. — Cements are a species of lime which have the power of hardening or setting rapidly, like plaster of Paris. They are prepared by calcining limestone, which contains a large percentage of silica and alumina, SiO_2 and Al_2O_3. Dolomitic or magnesium limestones, containing also the silica and alumina, when calcined, produce a cement that will harden under water, known as *hydraulic* cement. It has been stated that ordinary plaster hardens by the absorption of carbon dioxide from the air, forming again calcium carbonate. This is, necessarily, a slow process. Cements, as already stated, are produced by driving out the water of crystallization; hence, when they are mixed with water for use, they very rapidly take this up again, forming practically the original rock. Hydraulic cement is used in laying the piers of bridges, building jetties, and other work that is to be under water. Ordinary cements are used extensively for laying pavements, building roadbeds, for the concrete foundation for various kinds of masonry, etc. The following shows the composition of some cement rocks from various localities: —

Locality	$CaCO_3$	$MgCO_3$	SiO_2	Fe_2O_3	Al_2O_3	H_2O	Undetermined
Rosendale, N. Y.	45.91	26.14	15.37		11.38	1.20	
Utica, Ill.	42.25	31.98	21.12		1.12	1.07	2.46
Milwaukee, Wis.	45.54	32.46	17.56	3.03	1.41		
Cement, Ga.	43.50	22.00	22.10	1.80	5.45	4.95	
Siegfried, Pa.	78.90	2.66	11.62		6.25		0.55
Ft. Scott, Kan.	73.95	2.26	18.75	2.32	2.15	0.37	0.20
Ft. Scott, Kan., No. 2	65.21	10.65	15.21		4.56		4.37

21. Hard Water. — Hardness in water is due to the presence of certain salts in solution, very commonly some compounds of calcium. This hardness may be either *temporary* or *permanent*, according as it may be removed by boiling or by adding ammonia, or not at all.

Experiment 133. — Prepare a soap solution by dissolving a shaving of soap in warm distilled water. Allow it to stand a few minutes. It should be perfectly clear. To a few cubic centimeters of the lime-water, through which the breath was blown till clear again, add a little of the soap solution. What happens? Why? Take another portion of the clear lime-water and boil it for a few minutes. Has any sediment formed in the flask? The heat has expelled the carbon dioxide; why does the precipitate form? Decant a portion of it and test with the soap solution: is the water still "hard"? What effect has the boiling had?

To another portion of the same hard water (which has not been boiled) add a few drops of ammonia and again test to see whether the water is still hard. What are the results?

Add a little powdered calcium sulphate, $CaSO_4$, to some water, and after some time test a portion of it to learn whether it is hard. Now try to remove the hardness by the methods previously used. State results.

22. Water the hardness of which may be easily removed is said to be *temporarily* hard, while that which cannot be so changed is *permanently* hard. When the hands are washed with soap in hard water, the soap precipitates the salts in the water, of which a portion settles upon the skin, giving it an unpleasant feeling. Another part of the precipitate is usually seen as a scum upon the surface of the water.

23. Bleaching Powder, $Ca(ClO)_2 + CaCl_2$. — This is also called hypochlorite of lime. It is a white powder which is prepared by passing chlorine into chambers containing common lime spread loosely upon shelves. The reaction may be represented thus: —

$$2\ CaO + 4\ Cl = Ca(ClO)_2 + CaCl_2.$$

When treated with any dilute acid, chlorine is again set free; for this reason the compound is used extensively as a source of chlorine in bleaching muslin and other cotton goods.*

24. From the fact that chlorine does not bleach dry cloth, it is believed to be not the direct bleaching agent, but simply that which sets free another. It will be seen later, in studying the compounds of manganese, that logwood, litmus, and other colored vegetable solutions are rapidly bleached by the use of potassium permanganate, in the presence of some acid. Experiment shows that this is due to the oxygen that is set free from the permanganate. Similarly the chlorine, which has most wonderful affinity for hydrogen (see page 108), sets free the oxygen from the water with which the cloth is moistened, and this in the nascent state oxidizes the coloring matter and reduces it to colorless compounds.

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* See work under Chlorine, page 111.

25. When a current of carbon dioxide is passed through a solution of bleaching powder, chlorine is liberated, and can be detected by the odor, just as when treated as above with a dilute acid. Exposed to the air, bleaching powder yields up its chlorine, owing to the action of the carbon dioxide always present; but naturally the process is very slow. On account of this fact, and because chlorine is an excellent germicide and disinfectant, bleaching powder is used frequently in sick rooms and hospital wards. The generation of the chlorine is so slow as to be scarcely noticeable, and yet sufficient to keep the atmosphere in a wholesome condition.

STRONTIUM: Sr = 87

26. Its Name. — Strontium is a rare metal, which received its name from Strontian, a place in Scotland, where it was discovered. One of its chief sources is the mineral *strontianite*, $SrCO_3$.

Compounds of Strontium

27. Strontium Nitrate, $Sr(NO_3)_2$. — This is a white crystalline salt, soluble in water. It is used considerably in fireworks and in making "red fire."

EXPERIMENT 134. — Mix thoroughly about a gram each of strontium nitrate and potassium chlorate, finely pulverized, and about as much in bulk of powdered shellac. Place the mixture in an iron saucer and ignite with a match. State the results.

28. Strontium Carbonate, $SrCO_3$. — This is a white precipitate, like calcium carbonate, obtained when ammonium or sodium carbonate is added to a neutral or alkaline solution of a strontium salt.

$$Sr(NO_3)_2 + (NH_4)_2CO_3 = SrCO_3 + 2\,NH_4NO_3.$$

29. Strontium Hydroxide, $Sr(OH)_2$. — When water is added to strontium oxide, SrO, like lime, it is slaked, evolves much heat, and is converted into the hydroxide, $Sr(OH)_2$. In this form it is used considerably in the manufacture and refining of beet sugar.

BARIUM: Ba = 137

30. Its Name. — This metal, also rare, received its name from a Greek word, meaning *heavy*, and was so called because its chief natural ore, *baryta*, $BaSO_4$, has great density. It is also found as a carbonate, $BaCO_3$, known as *witherite.*

Compounds of Barium

31. Barium Chloride, $BaCl_2$. — This is a white crystalline salt, readily soluble in water. It is used in the laboratory in testing for sulphuric acid.

32. Barium Sulphate, $BaSO_4$. — This is a heavy white precipitate, insoluble in water and acids. It is easily prepared by adding sulphuric acid or any soluble sulphate to a solution of barium chloride. It is used considerably as an adulterant for white lead (see page 280), and to some extent in weighting paper.

33. Barium Carbonate, $BaCO_3$. — This is a white precipitate formed when ammonium or sodium carbonate is added to a neutral or alkaline solution of a barium salt. It is insoluble in water, but soluble in weak acids.

EXPERIMENT 135. — Let the student prepare both of the above compounds, using barium chloride for the barium solution. Note the differences between the two and test their solubility in the common acids. State results.

34. Barium Nitrate, $BaNO_3$. — This is a white crystalline salt. It is used to a considerable extent in the making of green fire for fireworks.

Experiment 136. — Repeat Experiment 134, substituting barium nitrate for the strontium nitrate, and state results. Sulphur or powdered charcoal may be used instead of the shellac, but the sulphur yields very irritating fumes of the dioxide, and the charcoal does not burn so readily.

35. Barium Hydroxide, $Ba(OH)_2$. — This is a compound obtained from barium oxide, BaO, by the addition of water, just as slaked lime is prepared. Like calcium hydroxide, it forms a precipitate of the carbonate upon the addition of carbon dioxide. It was formerly used extensively in clarifying beet sugar, but as it is very poisonous, and traces of it sometimes remain in the sugar, its use has been supplanted by that of strontium hydroxide.

36. Flame Tests. — The metals of this group, calcium, strontium, and barium, may be detected by the flame test.

Experiment 137. — Just as you tried sodium and potassium, now take some solutions of these three metals and make the flame test in the same way. State results as to color and duration of flame.

REVIEW OF WORK IN ALKALINE EARTH METALS

Magnesium, Calcium, Strontium, Barium.

1. Occurrence — Compare native compounds.
    Crystallized forms of calcium compounds.
    Uncrystallized forms.
    Special forms.
2. Artificial compounds.
    a. The Oxides of Mg, Ca, Sr, Ba.
        Wherein is their preparation similar? Why are such compounds used?
        Importance of CaO and MgO.
    b. The Hydroxides — Similarity of preparation.
        Uses of $Ca(OH)_2$ and $Sr(OH)_2$.
        Preparation of mortar; chemical change it undergoes as it hardens.
        Hydraulic cement; other cements; uses; explanation.

c. The Nitrates — Use in the arts of $Sr(NO_3)_2$; $Ba(NO_3)_2$. How used.
  Chemical action of each constituent.

d. The Sulphates — Two important ones.
  Preparation of Plaster of Paris — Compare with preparation of CaO.
  Uses of $CaSO_4$ and $BaSO_4$.
  Chemical change which takes place when Plaster of Paris hardens.
  Compare with hardening of mortar.

e. Hard Waters — Due to what compounds.
  Two classes, how different.
  Methods of softening water.
  Chemistry of these methods.

f. Some special calcium compounds.
  CaF_2 — Use, and method of using.
  Bleaching powder — Uses — Compare Cl and SO_2 as bleaching agents — Chemical action of each.
    Use of bleaching powder as a disinfectant — How is chlorine set free?

3. Flame tests — Method of making test.
  Comparison of colors imparted.
4. Comparative value of the metals in metallic form.
5. Exercise — Given some marble, HCl, H_2SO_4, H_2O, and Na_2CO_3. Tell how to prepare CaO, $Ca(OH)_2$, $CaSO_4$, $CaCl_2$, $CaCO_3$ (amorphous). Write all reactions concerned.

CHAPTER XX

THE COPPER-SILVER GROUP—COPPER, SILVER, GOLD

COPPER: $Cu = 63$

1. **History.** — Copper has been known from earliest antiquity, its use being mentioned by Jewish, Assyrian, and other ancient historians. By the Greeks it was obtained from the island of Cyprus, and from this fact probably received the name *kuprum*, and its present symbol, Cu. In England copper-mining was begun before the close of the twelfth century. It met with little success, however, till about five hundred years later. In the United States, the oldest mines are those of the Lake Superior region. The remains of prehistoric tribes about the mines indicate clearly that these deposits were known and used in very early times. The metal was obtained by stripping the rock and earth from the outcropping strata. When the rock had been broken or cracked off, the thin sheets of copper were removed and hammered into vessels of various shapes.

2. **Sources of Supply.** — Besides the mines of northern Michigan, which yield almost pure copper, large quantities are obtained from the silver ores of Montana and Colorado. Many of the mines of Michigan are exceedingly productive, some of them yielding annually about 25,000 tons, but in recent years the mines of Montana have furnished about 40 per cent of the world's supply. Among the ores found in the Western mines may be mentioned *malachite*, $CuCO_3$, $Cu(OH)_2$, green in color; *azurite*, $CuCO_3$, $2\,Cu(OH)_2$,

a beautiful blue, usually associated with the malachite; *chalcopyrite*, or copper pyrite, $CuFeS_2$, a brass-colored ore, resembling *fool's gold*, but often having a purplish cast; and *bornite*, a sulphide of iron and copper of varying proportions.

3. Reduction of the Ore. — In the case of the copper from the Lake Superior mines, scarcely any refining is necessary. It is passed through crushers to break up the rock associated with the metal, then by washing and other mechanical processes the separation is effected.

4. Methods in the West. — When the ore is a carbonate, like malachite or azurite, or the oxide, it is simply mixed with coke and reduced according to the general plan of reducing metallic ores. Thus,

$$CuO + C = Cu + CO.$$

Usually, however, there is a high per cent of sulphur present, and the process is much more complicated. There are, in reality, four stages necessary before *blister copper*, that is copper about 98.8 per cent pure, is obtained. These four are *concentration*, *calcination*, *reverberation* or *blast reduction*, and *converting*. The first consists in the separation of the silica or rock from the copper ore. This is done by mechanical washing with "jiggers." By calcination the sulphur is partially removed. After the ore has been roasted, either one of two plans may be followed. According to one method, the red-hot ore is placed in *reverberatory* furnaces and melted. The sulphide of copper, mixed with the sulphide of iron, always present, and the silver and gold, being heavy, settle to the bottom. This molten mixture is drawn off and is known as *matte*.

5. Sometimes the ore, even without concentration or calcining, is put directly into blast furnaces. In this case limestone rock is mixed with the ore; when the mass is heated the silica and limestone unite to form a glassy slag which takes up about 75 per cent of the iron. The slag, being relatively light, is drawn off above the metal. The sulphur in excess is removed by the strong draughts of air which are forced through the blast furnace. A *matte* is thus obtained similar in composition to that produced by reverberation.

6. The fourth stage consists in converting this *matte* into *blister* copper. This is done in a *converter*, which in its essentials is not unlike the Bessemer converter described in detail in the chapter on iron. The molten *matte* has fine streams of air driven through it, and in a few minutes is converted into copper about 98.5 per cent pure. This still contains small quantities of iron, arsenic, gold, and silver, which are finally separated at the refineries.

EXPERIMENT 138. — Put upon charcoal a little copper oxide, CuO, mixed with sodium carbonate, and heat strongly in the reducing flame. Note the color of the granular mass remaining. Test its malleability with a hammer. What have you obtained?

7. Characteristics of Copper. — Copper is a very tenacious, malleable, ductile metal, of a reddish color. It does not tarnish in dry air, but in the presence of moisture and carbon dioxide is slowly converted into a green carbonate of copper. With the exception of silver it is the best conductor of electricity known. Its melting point is high, being nearly 1100° C. In the oxidizing flame it is converted into the black oxide of copper, CuO. It is soluble in nitric acid and in hot concentrated sulphuric acid. From its solutions it is easily precipitated by iron, zinc, and certain other metals.

8. Applications in the Arts. — With the exception of iron, copper, probably, has more varied uses than any other metal. It is employed very extensively in alloys, among them being the following: —

Brass: consisting of copper and zinc in varying proportions.

Bronze: copper, zinc, and tin.

Bell-metal: copper and tin.

Coinage: gold and silver with copper.

Aluminum bronze: aluminum and copper.

A peculiarity of the last is that, with about 1 to 3 per cent of copper, it is of a beautiful silver-white color, much whiter even than aluminum; with 10 per cent of copper it somewhat resembles gold. In the latter proportions it is used largely for making various fancy articles and novelties.

9. Unalloyed, copper is used for roofing, for the sheathing of vessels, for making various utensils, and for wire for trolley, telegraph, and telephone systems, and for electric lighting.

Compounds of Copper

10. Two Classes of Salts. — Copper, like several other metals, forms two classes of salts, *cuprous* and *cupric*, though as a rule only the latter are of importance.

11. Cupric Sulphate, $CuSO_4$, 5 H_2O. — This is commonly known as *blue vitriol.* It forms in beautiful blue crystals, and is obtained when metallic copper is dissolved in boiling sulphuric acid. The commercial supply is obtained mostly as a by-product from the great gold and silver refineries, such as those of Kansas City and Omaha. The smelters at the former place produce monthly about eighteen hundred tons, worth between $100,000 and $200,000. The silver ores contain more or less copper in the form of cupric sulphide, which in the roasting of the ore is converted into cupric sulphate.

$$CuS + 2\,O_2 = CuSO_4.$$

This, being soluble in water, is washed out and concentrated, whereupon the crystals separate out from the solution.

12. Characteristics and Uses. — The salt is somewhat efflorescent, and when exposed to the air gradually gives up a portion of its water of crystallization. At the same time it breaks up and becomes almost white in color. By heating, the water of crystallization may be entirely removed and the blue color destroyed. This may be restored, however, by digesting for some time in water. Blue vitriol is very poisonous, and is used extensively in making Paris green and Bordeaux mixture for spraying fruit trees to destroy moths and other insects. It is employed largely in electroplating and electrotyping, also in galvanic batteries, though the dynamo is now taking the place of these batteries.

13. Cupric Nitrate, $CuNO_3, 3\,H_2O$. — This is a deep blue solid, soluble in water, obtained when copper is treated with nitric acid.

14. Cupric Chloride, $CuCl_2$. — This is a beautiful turquoise-blue, finely crystallized salt.

15. Cupric Sulphide, CuS. — This is a black precipitate obtained when a current of hydrogen sulphide is passed through a solution of a copper salt. It is soluble in hot nitric acid, and partially so in warm yellow ammonium sulphide.

16. Cupric Acetylide, CuC_2, H_2O, or CuC_2. — Cupric acetylide is a reddish brown precipitate formed when acetylene is passed through a copper solution. In drying it gives up its molecule of water and becomes very explosive, a slight jar being sufficient to touch it off. Metallic copper which has for some time been in contact with moist calcium carbide is partially converted into the acetylide, and shows the same explosive tendencies.

17. Cupric Oxide, CuO. — This is a black powder, obtained when copper is heated to redness in the air, or when cupric nitrate is treated in a similar manner. In the hydrated form, CuO, H_2O, it may be obtained by treating a copper solution with caustic soda or potash and boiling for a few minutes.

Experiment 139. — To prepare some of the above compounds. The nitrate and sulphate have already been prepared. Review the work with nitrogen dioxide and sulphur dioxide.

Add to a few cubic centimeters of copper nitrate solution a few drops of ammonium sulphide, $(NH_4)_2S$, or pass through it a current of hydrogen sulphide. Note the color of the precipitate formed. What is it?

Put into a crucible or small evaporating dish a half gram of powdered copper nitrate, and heat gradually to dull redness. How is the nitrate changed? What gas did you see expelled? What have you obtained? Save the powder.

Put into a test-tube a few cubic centimeters of a solution of copper nitrate or sulphate, and add a little caustic soda or potash. A blue precipitate of cupric hydrate is obtained, $Cu(OH)_2$. Boil it for a few minutes. Notice the change in color. What have you obtained?

Make a borax bead upon a platinum wire and fuse into it a little of the cupric oxide prepared above. What colored bead do you obtain? The oxide is thus used sometimes in preparing emerald glass.

Experiment 140. *Practical Work.* — To determine the composition of brass. Dissolve a few brass filings in warm nitric acid. Notice the color of the solution obtained. What metal is indicated by the color? Evaporate nearly to dryness, and take up with 40 to 50 cc. of water. Warm gently and pass a current of hydrogen sulphide for several minutes, or until no further precipitate will form. This may be determined by filtering out a little and passing the gas through it. If no precipitate forms, the whole may be filtered. Punch a hole in the bottom of the filter as it rests in the funnel, and wash the black precipitate through into a beaker with a little nitric acid diluted. Heat until it dissolves. What is indicated by the color of the solution? To prove, add ammonia until alkaline. Do you obtain a *deep* blue solution? If so, copper is indicated.

The filtrate obtained above from the black precipitate will contain the other metal or metals found in the brass. Add to it a few drops of ammonium hydroxide and then a little ammonium sulphide. Do you obtain a starchy white precipitate? If so, zinc is indicated.

EXERCISE. — Write reactions showing the preparation of cupric sulphate, nitrate, sulphide, acetylide, hydrate, oxide, and the reactions in the analysis of brass as far as possible.

SILVER: Ag = 108

18. Ores of Silver. — This metal has been known from remote antiquity, because of the fact that it frequently occurs free in small particles disseminated through quartz and other rock. Occasionally large masses have been found, and in the museum at Copenhagen there is to be seen one weighing about five hundred pounds. Usually, however, silver is in combination with other elements. One of the most important ores is *horn silver*, $AgCl$, named from its general resemblance in color and texture to the horns of cattle. Another important ore is *argentite*, Ag_2S. As the greater part of the lead ore smelted contains more or less silver, lead furnaces yield the largest portion of the world's output of silver.

19. Reduction of the Ores. — The following experiment will illustrate roughly one of the methods by which silver ores are reduced.

EXPERIMENT 141. — To about 10 cc. of a solution of silver nitrate, add a little hydrochloric acid. The precipitate is silver chloride, $AgCl$; shake the contents, warm slightly, and when the precipitate has settled, decant the moderately clear solution. Transfer the curdy white precipitate to a piece of charcoal, cover with sodium carbonate, and heat strongly in the reducing flame. Presently a bright globule of silver will appear. This may be preserved for tests upon the metal if desired, or dissolved in dilute nitric acid and converted again into silver nitrate.

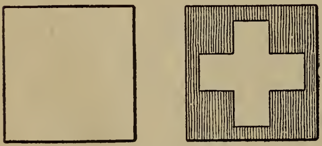
20. Other Methods. — Various processes are used in reducing silver ores, depending upon the character of the ore. But so large a proportion of the silver output results from lead reduction, that we shall confine ourselves here to only one or two of the methods employed. When these argentiferous lead ores are reduced (see Lead, page 275), the two metals, silver and lead, are formed together as an alloy, and they must then be separated. There are two methods for doing this. When the alloy is *rich in silver*, Pattison's method is employed.

21. Pattison's Method. — It has been found that when such an alloy is allowed to cool slowly the lead will crystallize before the silver. Hence, as the lead crystals begin to form they are skimmed out with perforated ladles, thus dividing the alloy into two portions, one containing the silver with a very little lead remaining in it, and the other the lead, with very small quantities of silver. The first of these is then submitted to *cupellation.* The alloy is gradually run into a *cupel*, or cup, which is placed upon a hearth within the furnace. A blast of air and flame is directed upon the surface of the alloy, and the lead is oxidized to litharge, PbO. The current of air constantly drives this film of oxide off into another vessel so placed as to receive it. In this way the lead is entirely removed, and the completion of the process is known by the brilliant appearance of the molten silver.

22. Parke's Process. — Zinc will readily alloy with silver but not with lead, and this principle is made use of in Parke's process of separating lead and silver. Zinc is added to the alloy, and the whole is melted. The alloy of zinc and silver, being lighter than the lead, rises to the surface, and as it begins to solidify is skimmed off in the form of crystals. Thus there is obtained an alloy of zinc and silver with very little lead adhering. This alloy is now very carefully heated in a furnace, the bottom of which is inclined; the lead melts and runs off before the fusing point of the alloy is reached. The zinc still remaining is next removed by heating strongly in retorts, when it is vaporized and passes off.

Experiment 142. — Making use of the bead of silver obtained above in Experiment 141, test its hardness and malleability. Try to oxidize it in the oxidizing flame. Does any coating form upon the charcoal? For just a moment put a silver coin into a solution of hydrogen sulphide or sodium sulphide. What are the results? Next immerse it in a moderately strong solution of potassium cyanide, and allow it to remain some time, if necessary. State the results. This last suggests a method of cleaning tarnished silverware, but it should be used with caution, as the cyanide is deadly poison.

Experiment 143. — Add to 2 or 3 cc. of silver nitrate a little hydrochloric acid, spread the white precipitate smoothly upon a sheet of paper, place upon it any figure cut from thick paper, and expose it to the light. In a few minutes, notice what has happened. This illustrates the method of printing from photographic negatives upon sensitized paper.



Before Exposure. Fig. 53. After Exposure.

The experiment may be varied, and with care and patience most beautiful prints may be obtained. Immerse in a solution of silver nitrate a sheet of drawing paper, and allow it to dry *in the dark*. Next immerse in a solution of common salt, and again let it dry in the dark. When ready to print, place upon this paper, thus sensitized, an old negative, or even a fern leaf or any similar object, and expose to bright sunlight, under a sheet of glass to hold in place. Notice when a deep purple is obtained, then immerse in a solution of sodium thiosulphate, the photographer's "hypo," and rinse thoroughly in water several times.

23. Characteristics of Silver. — Silver is a white, lustrous metal, malleable and ductile, an excellent conductor of electricity and heat, of medium hardness and density. It is quickly attacked by many sulphur compounds and by the members of the halogen group, although it does not tarnish in the air at any temperature. In living rooms silverware is tarnished by the action of the sulphur gases thrown off in the combustion of coal or of ordinary illuminating gas. Eggs and various other articles of food tarnish silverware for a similar reason. What is known as "oxidized" silver is really that which has been treated with some compound of sulphur, producing silver sulphide upon the surface.

24. Uses for Silver. — Owing to its brilliancy and durability, silver has long been used for jewelry and various other articles of ornament. Alloyed with some other metal to make it harder, it is employed extensively in coinage; is also used in amalgams for dentistry and for the backs of high grade mirrors, and for plating innumerable articles of use and ornament.

Compounds of Silver

25. There are only a few compounds that are of interest, and but one or two that are of any considerable value.

26. Silver Nitrate, $AgNO_3$. — This is important because most of the other silver compounds are prepared from it, and because it has numerous applications in the arts. It occurs in slab-like, almost transparent, white crystals, which are soluble in water. It is prepared by dissolving silver in nitric acid. When exposed to the light, especially if in contact with any organic matter, it turns dark. It is used for sensitizing paper for photographic work, as the principal ingredient of indelible ink, and in hair dyes.

In the form of *lunar caustic*, which is simply crystallized silver nitrate fused and molded into sticks, it is used in cauterizing wounds, such as dog bites, for ulcerated sore throat, in removing warts and other similar excrescences of the skin.

27. **Silver Chloride, AgCl.** — This is prepared from a solution of silver nitrate by adding to it hydrochloric acid or any soluble chloride, like common salt. It is a white precipitate, curd-like in appearance, especially when shaken for a moment. It is soluble in ammonium hydroxide, and in sodium thiosulphate, "hypo." It is much more sensitive to light than the silver nitrate, and hence for photographic work the latter salt is generally converted into the chloride, or bromide, which is even more sensitive. It is believed that the light gradually converts this compound back into metallic silver, which is insoluble in the "hypo," while the unchanged portions of silver chloride are dissolved out and the paper thus de-sensitized.

EXPERIMENT 144. — To about 1 cc. of a solution of silver nitrate add a few drops of hydrochloric acid. Notice the appearance of the precipitate that forms. What is it? Write the reaction. To a portion of it add a little ammonium hydroxide and shake it. What results? To another portion add a solution of "hypo" and state the results.

28. **Silver Chromate, Ag_2CrO_4.** — This is a blood-red powder obtained as a precipitate when potassium chromate is added to a solution of silver nitrate.

EXPERIMENT 145. — Prepare the chromate as indicated, and note its appearance.

29. The formation of silver chloride and the chromate, with their characteristic appearance and the ready solubility of the former in ammonia, serve to distinguish a solution of silver, and may be used as tests.

EXERCISE. — Write the reactions, showing the preparation of silver nitrate, silver chloride, and the chromate; also silver bromide and iodide, from silver nitrate with potassium bromide, and with sodium iodide.

30. Photography. — At the present time almost all young people take more or less interest in this wonderful art. The first experiments along this line were made as early as 1727, but they were nothing more than what the student has done in the first part of Experiment 143, and the print soon disappeared. From that time to this many different plans have been tried, but we can only notice briefly that used at present.

31. Preparation of the Plates. — The plates upon which the negatives are made are prepared as follows: for the most sensitive plates, potassium or ammonium bromide with gelatin and silver nitrate added is dissolved in water and heated to boiling. Thus the silver is converted into silver bromide: —

$$KBr + AgNO_3 = AgBr + KNO_3.$$

An excess of water is added, and the potassium nitrate formed is readily washed away. This gelatin emulsion, as it is known, is poured upon glass plates and allowed to harden; they are then ready for use.

32. Exposure and Developing. — As previously stated, when such plates are exposed to light, the silver salts are decomposed. In the camera the exposure is so brief that the decomposition is only partial; when, however, the plate is put into the *developer*, this solution continues the action begun by the light. Hence those portions of the plate which have received the most light have the larger amount of the silver salts decomposed, and are dark in color. If allowed to remain in the developer long enough, all the silver would be reduced, and the plate would be uniformly dark.

33. Fixing. — When it is seen by examination that the development has proceeded long enough, the plate is rinsed in water and placed in the *fixing bath*. This is a solution containing sodium thiosulphate, which is an excellent solvent for many silver compounds. The fixing bath soon removes from the gelatin film the silver bromide or chloride that remains unaffected by the light or by the developer. The plate is thus *cleared* or *fixed*, and is no longer sensitive to light. As the lights and shadows are all reversed, it is called a *negative*. After thorough washing it is allowed to dry, when it is ready to be used in making *prints*.

34. Printing. — Various kinds of paper are now used for making prints, among them being the *solio*, *velox*, *platinotype*, *carbon*, and *blue print*. The first and last of these require the least skill. Solio has a sensitized film of silver chloride ; in printing, this is placed against the film side of the negative, which causes the objects to appear in the picture in their natural position. As the dark portions of the negative transmit the fewer light rays, the picture appears as a *positive*, or like the original as to high lights and shadows. The advantage of solio is in the fact that it is only moderately sensitive, and that it readily shows when it has been exposed long enough. More sensitive papers, such as the velox, are like the gelatin plates in that they show no image until treated with a developer. Solio prints require toning, and all varieties need fixing by some method or other. In the platinotype papers, a compound of platinum is used which yields the dark appearance now so much admired.

35. Solio papers cost so little that it would be easy for a class to make some experiments along this line. Let any of the pupils who may have them bring in some of their negatives and printing frames, and do some work of this kind.

36. Blue prints* are the simplest of all, are cheap, and yet for landscapes often give most excellent effects. They possess the advantage of requiring no toning or fixing except such as is secured by thorough washing. Place the paper under the negative in direct sunlight, and allow it to remain until the high lights begin to look somewhat muddy in appearance ; then put into a basin of water with the printed side down. Allow the print to remain there until the light portions are quite clear, then wash for ten minutes in running water. The beauty of these prints will be enhanced by leaving a pure white border around the picture ; this may be secured by using a black mat between the negative and print so as to cover the portion which it is desired to have white.

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* If he desires, the instructor may prepare his own blue print paper. Make

Solution *A*

Oxalate of iron and ammonia	1 g.
Water	10 cc.

Solution *B*

Potassium ferricyanide	1 g.
Water	10 cc.

When ready for use mix *A* and *B* in a dark room, and apply to the paper with a brush ; or, the paper may be floated in the solution. This must be used within a day or two after it is prepared, as it does not keep well. A few drops of a 10 per cent solution of potassium bromide added to *A* and *B* above will render the keeping qualities of the paper much better.

GOLD : Au = 197

37. Occurrence. — From the fact that gold occurs free, it has been known from the earliest antiquity. It is widely distributed over various portions of the earth and usually occurs in fine grains and nuggets disseminated through the rocks. These are gradually disintegrated and brought down by rains and streams in the form of sand and gravel, with which the gold is associated. The best-producing gold regions are those of the western part of the United States, Australia, Southern Africa, and the Klondike. Gold also occurs in quartz veins deeply buried in the earth's strata.

38. Methods of Mining. — The original method consisted simply in *cradling* or *panning* the sand and gravel; thus the nuggets and larger grains find their way to the bottom, while the lighter stone and earthy matter is washed out. By this method only the larger particles are saved. *Placer* mining consists in washing the gold-bearing sand down through sluices, along the bottom of which are arranged pockets of mercury, or over plates of copper amalgamated with mercury. This readily amalgamates with the gold, and the other portions are carried away by the current. The gold amalgam thus obtained is heated in retorts, by which the mercury is vaporized, leaving the gold behind. The vapors of mercury are conducted into cold chambers where they are condensed, so that very little loss occurs. *Hydraulic* mining differs from the above only in that streams of water are directed with great force against the loose rock and cliffs overhanging, washing them down into the sluice-ways.

39. Vein Mining. — *Vein* mining differs from placer mining in that the latter is surface mining, while in the former the ore is taken from greater or less depths, usually from quartz veins; hence it is sometimes called *quartz* mining. Gold sometimes occurs in combination with iron in pyrites, and it is then obtained by the *wet* or *chlorination* process. The ore is roasted, then moistened and treated with chlorine, obtained usually from bleaching powder. The chlorine dissolves the gold, forming gold chloride, $AuCl_3$. This is now dissolved out and ferrous sulphate added, which precipitates gold in the metallic condition, as seen in the following reaction: —

$$6\ FeSO_4 + 2\ AuCl_3 = 2\ Au + 2\ Fe_2(SO_4)_3 + Fe_2Cl_6.$$

40. Cyanide Process. — Potassium cyanide is an excellent solvent for gold, and at the present time is used extensively in separating it from its ores. The process is valuable where the gold occurs in a finely divided form; another advantage is that the ore does not need the roasting that is necessary in the chlorination process. After the gold-bearing quartz has been finely crushed, it is treated with a solution of potassium cyanide in water. The gold is dissolved out, thus: —

$$4\ Au + 8\ KCy + O_2 + 2\ H_2O = 4\ KAuCy_2 + 4\ KOH.$$

41. The oxygen shown in the reaction is derived from the air, and it has been found that, unless the surface of the ore is left well exposed, the process is not satisfactory. The double cyanide of gold and potassium thus obtained is treated with zinc, which precipitates the gold, as shown in the reaction: —

$$2\ KAuCy_2 + Zn = K_2ZnCy_4 + 2\ Au.$$

42. There is always some zinc left in a more or less finely divided form which cannot be separated mechanically from the gold; hence, when melted down the metal is seldom over 80 per cent pure. For this reason some companies prefer to deposit the gold by electrolysis upon lead terminals. By this method, after oxidizing the lead in cupels, the gold remains in a very pure form.

43. Characteristics. — Gold is a bright yellow metal, which, seen in light reflected several times, looks red. It is so soft that for ordinary purposes it must be alloyed with some other metal; it is heavy, is not affected by the oxygen of the air at any temperature, is very ductile and malleable. Advantage is taken of this property in hammering out the metal into gold leaf, the thickness of which is not over $\frac{1}{300000}$ part of an inch, 1500 of which sheets are necessary to make one as thick as ordinary note paper. Pure gold is not affected by single acids, but is readily attacked by aqua regia, forming gold chloride, $AuCl_3$. However, if richly alloyed with several other metals, it becomes soluble in single acids.

44. Uses. — These are too well known to need specification. In the arts gold leaf has numerous uses, such as in making display signs, covering high grade moldings, for filling teeth, etc.

SUMMARY OF CHAPTER — COMPARATIVE STUDY

- Copper, Silver, Gold.
  - Histories — Wherein are they similar? — Why?
  - Occurrence — In what forms?
    - Most productive regions.
    - Some important ores.
  - Various forms of gold mining — Description.
  - Reduction of the ores.
    - Special plans for copper.
    - Special processes for gold reduction.
      - Chlorination and cyanide.
    - Special plans for separation of silver.
      - Pattison's and Parke's.

Comparison of the three metals as to
  - *a.* Color.
  - *b.* Density.
  - *c.* Melting point.
  - *d.* Permanency in the air.
  - *e.* Malleability.
  - *f.* Conductivity.
  - *g.* Solubility in acids.

Uses of the metals.
  - *a.* Important alloys.
  - *b.* Other uses — Why so used.

Compounds — Most important.
  - Of Copper — The Sulphate — Commercial name and formula.
    - How obtained.
    - Characteristics and uses.
  - Of Silver — The Nitrate — Commercial name and formula.
    - How prepared.
    - Appearance and uses — Why so used?
    - What other compounds prepared from this one? How?

Special points.
  - Meaning of the terms *blister copper*, *matte*, *concentration*, *calcination*, *converting*.
  - Describe method of determining the composition of brass.
  - Meaning of terms *cupel*, *cupellation*.
  - Describe experiment illustrating principles of photography.
  - Method of sensitizing photographic plates.
  - Chemistry of the developing and fixing of negatives.
  - Reactions showing the preparation of $CuSO_4$, CuO, $AgNO_3$, $AgCl$, $AgBr$, AgI.

CHAPTER XXI

ZINC, CADMIUM, MERCURY

ZINC: $Zn = 65$

1. History. — Brass, an alloy of copper and zinc, has been known for centuries, but it was formerly made by fusing together copper and a mineral called *calamine*, which we now know is an ore of zinc. It was not until about the close of the seventeenth century that zinc was recognized as a distinct metal and its characteristics carefully determined.

2. Ores of Zinc. — Zinc occurs abundantly in many parts of the United States and Europe. In Missouri the mines of Joplin and Webb City are the best known. There thousands of tons are produced annually. Kansas also yields a considerable quantity. The ore most generally found in these states is the *sulphide*, ZnS, known as *zinc blende*. By the miners it is called "jack," or in its purer forms "rosin jack," because of the general resemblance of a broken specimen of the ore to rosin. In New Jersey the ore *franklinite* is the most abundant. It is a mixture of zinc oxide and ferric oxide, $ZnFeO, Fe_2O_3$. Other sections yield the carbonate, $ZnCO_3$, known as *smithsonite*. It is said that the metal is sometimes found pure in Australia.

3. Reduction of the Ores. — The general method employed in the reduction of the greater number of metallic ores is used in the case of zinc. They are first ground fine and roasted. This not only drives out certain volatile impurities, such as arsenic, but converts the ore into the oxide, ZnO, the most convenient form for the next step. The reaction that takes place when the ore is roasted may be seen from the following: —

$$ZnS + 3\,O = ZnO + SO_2,$$

$$ZnCO_3 + \text{heat} = ZnO + CO_2.$$

4. The oxide thus obtained is mixed with powdered coke and heated red hot in earthen cylinders about 4½ feet long, placed horizontally over one another. The zinc is thus reduced to the metallic form, and at the temperature obtained is vaporized. The vapors pass out into conical-shaped earthen condensers attached to the outer end of the retorts, where they liquefy. Twice in twenty-four hours these condensers are "tapped" and the molten zinc drawn off and run into molds. The chemical change taking place is a familiar one: —

$$ZnO + C = Zn + CO.$$

The retort is shown by *R* in the figure and the condenser by *C*. The condensers are readily detached, and when the retorts have been charged or filled with the mixed ore and coke they are again attached and luted on nearly air-tight with clay. When in operation there is usually some escape of vaporized zinc with other gases, and these, in burning at the mouth of the condensers, give a beautiful display of colors, yellow and blue and white, which, especially at night, is exceedingly striking.

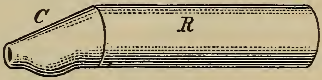

FIG. 54.

5. A single charge requires about twenty-four hours for complete reduction, and as the workmen are usually paid by the amount of metal they "draw off" they generally work twenty-four hours successively, and then are off during the next twenty-four. The zinc obtained in this way is more or less impure; it almost always contains some cadmium, and usually some arsenic, and is known as "spelter."

6. Characteristics of Zinc. — Zinc is a bluish white metal of moderately low melting point, about 420° C.; it tarnishes but slightly in the air, and then only upon the surface. At a temperature slightly above the melting point it burns with a brilliant, bluish white flame, and if a jet of oxygen be directed upon it the light is almost dazzling.

Experiment 146. — Examine a piece of zinc and note its color, malleability, hardness, and tendency to oxidize. Test also its melting point by heating a small piece on charcoal with the blowpipe. Try it also with the oxidizing flame and note the deposit upon the charcoal, both when hot and when cold. State the results.

Experiment 147. — To learn the solvents for zinc. Try a small piece of the metal in a test-tube with hydrochloric acid. How is it affected? What gas is obtained? What proof can you offer? Write the reaction.

In the same way try nitric acid, and compare results with the above.

Into each of two test-tubes put a small piece of zinc. To one add about a cubic centimeter of copper sulphate solution, and cover the other with water. After a few moments, to each add a little sulphuric acid. Is there any difference in the rapidity of the chemical action in the two cases? Why?

Experiment 148. — Sift some zinc dust through a wire sieve of fine mesh upon a Bunsen burner flame and note the results.

7. Further Characteristics of Zinc. — Ordinary commercial zinc as it comes from the smelter is brittle, but if it is heated to something over 120°, and then rolled into sheets or drawn into wires, it is found to be malleable, and will remain so. As it approaches the melting point, however, it again becomes brittle, and may be ground into a powder known as *zinc dust.* It is of medium density, being a little lighter than iron, is not magnetic, and when chemically pure is but slightly soluble in dilute acids. When impure, or if in contact with some other metal, as copper or platinum, the solution is rapid.

8. **Uses for Zinc.** — In the metallic form zinc is used extensively in many varieties of galvanic batteries, also as linings for refrigerators, bathtubs, and for various other domestic purposes. One of its most important applications is in coating or "galvanizing" iron wire and other forms of iron as a protection from moisture. Galvanized iron is prepared by thoroughly cleansing the iron to be coated, heating it, and plunging it into a bath of molten zinc until a thin covering of the latter metal adheres. There are also three important alloys: —

Brass: consisting of zinc and copper in varying proportions;
Bronze: zinc, copper, and tin;
German silver: zinc, copper, and nickel.

In the chemical laboratory zinc is frequently used: in making hydrogen; in reducing ferric compounds to the ferrous condition; and for precipitating various metals from their solutions.

Compounds of Zinc

9. **Zinc Sulphate, $ZnSO_4$, 7 H_2O. — White Vitriol.** — This is a white crystalline salt which has been obtained in the preparation of hydrogen by treating zinc with sulphuric acid. It is very soluble in water, and is used mainly for calico printing. It has a bitter, astringent taste.

10. **Zinc Chloride, $ZnCl_2$.** — This is a white solid, obtained when zinc is dissolved in hydrochloric acid. It has great affinity for water, and is, therefore, often used in

chemistry as a drying agent. It is also frequently used as a soldering solution, but as it is poisonous, serious results have sometimes followed its use in soldering tin cans containing fruits and other food products.

11. Zinc Hydroxide, $Zn(OH)_2$. — This compound of zinc may be studied in the following experiment: —

Experiment 149. — To a few cubic centimeters of a solution of any zinc salt, as the chloride or sulphate, add a few drops of ammonium hydroxide. What are the results? Add more ammonia; does the precipitate dissolve? Describe the precipitate, $Zn(OH)_2$, that formed, and write reaction. In the same way prepare a little zinc hydroxide by using a solution of caustic soda or potash instead of ammonia as above. Test a portion of the precipitate with hydrochloric acid; does it dissolve? Write the reaction.

12. Zinc Sulphide, ZnS. — Many characteristics of zinc sulphide may be discovered from the following experiment:

Experiment 150. — To a few cubic centimeters of a solution of some zinc salt add two or three drops of ammonium sulphide. Describe the precipitate that forms. It is zinc sulphide. Test its solubility in dilute hydrochloric or nitric acid.

13. Zinc Oxide, ZnO. Zinc White. — This was the white deposit formed on charcoal when the zinc was heated by the oxidizing flame. It is now used extensively as a substitute for white lead in painting, and is preferable in localities where much coal is used as fuel, because of the discoloration of lead compounds by the considerable quantities of hydrogen sulphide found in coal smoke.

* CADMIUM, Cd = 112

14. Supply. — Cadmium is a rare element, discovered about 1817. It received its name from a Greek word,

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* This is an unimportant element, and its study may be omitted, if desired.

kadmeia, an ore of zinc, now known as calamine, with which cadmium is usually associated. Our present supply is obtained mostly from zinc ores, with which it is found, in the form of a sulphide, CdS, called *greenockite*.

15. Reduction of the Ore. — In smelting cadmium-bearing zinc ores, they are first roasted in retorts, where both sulphides are converted into oxides, thus: —

$$\left.\begin{matrix} CdS \\ ZnS \end{matrix}\right\} + 3\,O_2 = \left\{\begin{matrix} CdO \\ ZnO \end{matrix}\right. + 2\,SO_2.$$

These oxides are then mixed with coke or charcoal and again heated, when the usual reduction takes place: —

$$\left.\begin{matrix} CdO \\ ZnO \end{matrix}\right\} + 2\,C = \left\{\begin{matrix} Cd \\ Zn \end{matrix}\right. + 2\,CO.$$

To separate the two metals thus obtained they are dissolved in hydrochloric acid, and the solution treated with rods of zinc, by which the cadmium is reduced to the metallic form, thus: —

$$\left.\begin{matrix} Cd \\ Zn \end{matrix}\right\} + 4\,HCl = \left\{\begin{matrix} CdCl_2 \\ ZnCl_2 \end{matrix}\right. + 2\,H_2,$$

and

$$\left.\begin{matrix} CdCl_2 \\ ZnCl_2 \end{matrix}\right\} + Zn = Cd + 2\,ZnCl_2.$$

16. Appearance and Characteristics. — Cadmium is usually marketed in the form of small rods, 8 or 10 inches in length. It is a white metal, closely resembling tin, and is of about the same hardness, but it has a melting point not very different from lead, 315°, and boils at 860°. Cadmium tarnishes slowly in the air, becoming coated with a very thin covering of yellow oxide. It is malleable and ductile, and when bent, like tin, gives a creaking sound. With mercury it forms a silvery white amalgam which soon becomes hard and brittle. It is easily soluble in nitric acid, less so in hydrochloric and sulphuric acids. It is but little used in the arts, though it has been applied somewhat as a filling for teeth; but as a cadmium amalgam gradually turns dark, it has not found favor with dentists.

Compounds of Cadmium

17. Cadmium Nitrate, $Cd(NO_3)_2$. — This is a white salt obtained when the metal is dissolved in nitric acid.

18. Cadmium Sulphide, CdS. — This is a yellow powder used in oil and water colors. Artificially, it is obtained when a current of hydrogen sulphide is passed through a solution of any cadmium salt. It resembles the sulphides of arsenic and tin, As_2S_3 and SnS_2. Unlike the arsenic, however, cadmium sulphide is not soluble in ammonium carbonate, and unlike the tin, is insoluble in yellow ammonium sulphide.

Exercise. — Write reactions showing the formation of cadmium nitrate, chloride, sulphate, and sulphide.

MERCURY: Hg = 200

19. Historical Facts. — Mercury was one of the seven elements known to ancient chemists, and by them was dedicated to the god from which it received its name. Its symbol is taken from the Greek word, *hydrargyrum*, by which name it was also known. This term means *water* (or *liquid*) *silver*. Similarly, at the present time it is spoken of as *quicksilver*. By Geber, the famous alchemist of the eighth century, mercury and sulphur were regarded as the two elements from which all metals could be made. He claimed that any one knowing the proper proportions could prepare any of the noble metals from these two.

20. The Source of Supply. — The commercial supply of mercury comes from its chief ore, cinnabar, or vermilion, HgS. This is an exceedingly heavy, brick-red mineral, found in Spain, India, Bavaria, California, Mexico, etc.

Experiment 151. — Near one end of a piece of hard glass tubing place a little vermilion, HgS, as much as will remain on the point of a knife-blade. Now, with this end down, hold in a slanting position in the Bunsen burner and heat strongly. Notice the formation on the upper, cooler portion of the tube. What gas, detected by its odor, is given off from the upper end of the tube? Name the two products resulting from the heating of mercuric sulphide. Compare with the preparation of oxygen from mercuric oxide.

21. Reduction of the Ore. — This experiment illustrates the reduction of cinnabar in the preparation of mercury for commerce. The ore is placed upon shelves in an oven over a furnace (see Fig. 55). Hot blasts of air flow up through the shelves, oxidizing the sulphur to sulphur dioxide, and at the same time vaporizing the mercury. These gases pass out together into cool chambers, where the mercury condenses, while the sulphur dioxide escapes. As thus obtained the mercury is more or less impure. It is purified first by being strained through porous leather or chamois skin, and then distilled at moderate temperatures.

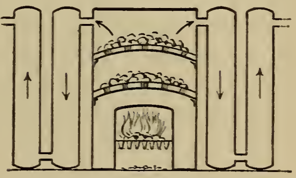


Fig. 55.

22. Characteristics. — Mercury is the only metal that is liquid at ordinary temperatures. At 39° below zero it becomes a solid, and in that condition possesses some of the properties of lead. It has about the same color, is malleable, and soft enough to be cut easily. Mercury is a silver-white metal, which does not tarnish in the air, but which slowly vaporizes at all temperatures.

23. Amalgams. — The most remarkable property of mercury is its power of dissolving many of the metals and forming with them what are known as *amalgams.* If the mercury be largely in excess, the other metal disappears as a lump of sugar does in a cup of tea; if a smaller proportion be used, the mercury simply combines with the outer portions of the other metal, changing more or less its appearance and general properties. There are two methods of forming amalgams.

24. *a.* By bringing metallic mercury into contact with a metal perfectly clean. If this is broken up into small pieces, or in the form of dust or filings, and is then heated with the mercury, the amalgamation takes place quickly.

Experiment 152. — Into a few drops of mercury in an evaporating dish, put a perfectly clean strip of zinc. After a few moments, examine it; has it changed in appearance? Bend it; has it changed in properties? Try in the same way a five-cent piece, a penny, a nail, or any other convenient metals. Be careful, however, of any gold rings, as mercury amalgamates very readily with gold.

25. *b.* The second general method is by immersing the metal to be amalgamated in a solution of some salt of mercury. Try in this way the following: —

Experiment 153. — Put into a beaker, or evaporating dish, a few cubic centimeters of a solution of mercurous nitrate, $Hg_2(NO_3)_2$. Immerse in it a brass pin, or a thimble, a copper penny, a key ring, etc. After remaining a few minutes, they may be removed and rubbed a little, if dull in appearance. State which have been amalgamated.

26. This second method is employed frequently by street fakirs as a means of "silver plating." They prepare the solution by dissolving mercury in nitric acid and then adding some coloring matter. This very rapidly "plates" certain metals, but the amalgamated articles retain their brilliancy but a short time.

27. Solvents for Mercury. — The best solvent for mercury is nitric acid, which attacks the metal even at ordinary temperatures. When heated, sulphuric acid also dissolves it, with the formation of sulphur dioxide gas. Compare this with the preparation of sulphur dioxide as given on page 177, section 15.

28. Uses for Mercury. — Mercury is employed extensively in the manufacture of thermometers and barometers; in the laboratory it is often used instead of water in the pneumatic trough for collecting such gases as are soluble in water, especially when they are desired perfectly free of air. Large quantities are also used in placer mining of gold and silver (see page 246). In the form of amalgams it is used with various other metals for filling teeth; with tin or silver for the backs of mirrors, for rendering zinc plates to be used in batteries less soluble in acids, and sometimes for amalgamating surfaces which are to be silver plated. This is done because silver seems to adhere better to a surface which has been thus treated.

Compounds of Mercury

29. Like several other metals, mercury forms two series of compounds, the mercurous and mercuric.

30. The Nitrates, Mercurous, $Hg_2 (NO_3)_2$; Mercuric, $Hg(NO_3)_2$. — These may be prepared by treating mercury with nitric acid; for the former, using dilute acid with the mercury in excess; for the latter, concentrated, with the acid in excess. Mercuric nitrate is a white salt of fine silky crystals, soluble in water. In dissolving it yields at the same time a yellowish powder, known as basic nitrate, having the formula $HgNO_3, Hg(OH)_2$. Mercurous nitrate is of a pale yellow color, almost white. It usually occurs in crystals larger than those of the mercuric nitrate and is soluble in water. Both are used in the laboratory, and occasionally for the preparation of other compounds of mercury.

31. **The Chlorides, Mercurous, Hg_2Cl_2; Mercuric, $HgCl_2$.** — The former is known as *calomel*, the latter as *corrosive sublimate*. Mercurous chloride may be prepared by adding to mercurous nitrate, hydrochloric acid, whereupon it falls as a heavy white precipitate. On a large scale it is manufactured by thoroughly mixing in the proper proportions mercuric chloride and mercury, heating them strongly to vaporize, whereupon they combine and are condensed in cold chambers. Calomel is a white, flour-like substance, insoluble in water. It is used largely in medicine.

32. Mercuric chloride is prepared by subliming, as described above in making calomel, a mixture of mercuric sulphate and common salt. It is a white, crystalline salt, somewhat soluble in water, and very poisonous. It is used in the laboratory as a reagent, is a constituent of some vermin exterminators, and has frequent use in surgery as an antiseptic.

33. **Mercuric Oxide, HgO.** — This orange-red salt, commonly known as red precipitate, is prepared by heating mercuric nitrate for a considerable length of time. It is used sometimes for preparing small quantities of oxygen, and in some quantitative determinations in the laboratory.

34. **Mercuric Sulphide, HgS.** — As an ore it is known as cinnabar, but the artificial product is sold under the name vermilion. It is of a bright scarlet color, and is used in making tube paints and in coloring sealing-wax. As ordinarily prepared in the laboratory, it is black, but under certain conditions is obtained in varying shades of red.

Experiment 154. — To prepare certain compounds of mercury. Put a drop of mercury into a test-tube and add about a cubic centimeter of dilute nitric acid, warm gently, and after a few minutes, or when the action has ceased, decant the solution and boil it nearly dry in an evaporating dish. Now add a few cubic centimeters of water and pour into three test-tubes. To the first add a little potassium iodide; to the second, hydrochloric acid; to the third, ammonia. Notice the color of the precipitate in each case. Write the reactions in the first two, and state what compound is formed. Tabulate results as follows: —

	$Hg_2(NO_3)_2$	$Hg(NO_3)_2$
KI		
HCl		
NH_4OH		

You should have prepared mercurous nitrate by the above treatment of mercury with nitric acid.

To another drop of mercury in a test-tube add some strong nitric acid, and warm until the mercury is all dissolved. Transfer to an evaporating dish and boil nearly dry, then add a few centimeters of water. You should now have a solution of mercuric nitrate. Divide into three parts and treat with the same three reagents that you used with the mercurous nitrate, and tabulate the results.

35. From the above experiments, it will be seen that the two series of mercury salts may be easily distinguished by the precipitates which they form with different reagents.

Experiment 155. — Let the student be given some mercurous and mercuric solutions, and have him determine what each is.

Exercise. — Write out the reactions that take place in preparing the two nitrates, mercurous chloride, mercurous and mercuric iodide, and mercuric sulphate. Before attempting the last, unless you know the results, put into a test-tube a small drop of mercury, add a little strong sulphuric acid, and heat until some familiar gas is produced.

COMPARATIVE STUDY

Zinc and Mercury — Early history.
  Ores of these metals — Most important of each — Localities where found.
  Plan of reduction.
    Wherein are they alike?
    How different?
    Why is carbon not necessary for the mercury?
    Reactions for each.
    Description of furnaces.
  Comparison of the two metals in
    a. Color.
    b. Melting point.
    c. Density.
    d. Ease of oxidation.
    e. Malleability.
    f. Conductivity.
    g. Solubility.
  Special properties of each.
    Brittleness of zinc at certain temperatures.
    Condition of mercury at low temperatures.
    Power of forming amalgams.
      Names of metals which will amalgamate and of those which will not.
    Two methods of making amalgams.
  Important uses of each metal.
    Alloys of zinc.
    Amalgams of mercury.
    Other uses.
  Compounds.
    The oxides — Appearance and use of each.
    The chlorides — One of zinc, two of mercury.
      Preparation of each — Use — Commercial name.
    Two classes of mercury compounds — Methods of distinguishing them.

CHAPTER XXII

ALUMINUM AND ITS COMPOUNDS

Aluminum : Al = 27

1. **Abundance.** — This metal was first isolated about 1827, being reduced by metallic sodium. For some years all that was used in the arts was prepared by strongly heating aluminum chloride, and passing the vapors into which it was converted over sodium. The reaction may be represented thus: —

$$AlCl_3 + 3\,Na = Al + 3\,NaCl.$$

By this method about three pounds of sodium were required for the preparation of a single pound of aluminum, and the cost was about one dollar an ounce.

2. No metal occurs more abundantly than aluminum, and but one or two non-metallic elements are more widely distributed. It forms a large per cent of feldspar and of various other rocks, and consequently, from their decomposition, of all clays.

3. **The Commercial Supply.** — It is evident that all that is needed to insure a large output of aluminum is a cheap process of reducing it from its natural compounds. Various methods have been patented, but none has, as yet, brought aluminum within the reach of all, although its market value now is only about $1.50 per pound. Perhaps the most satisfactory plan yet adopted is the following: *a* is a large crucible lined with some infusible substance, like

graphite; *c* is a bundle of carbon rods. The crucible and carbons are made the kathode and anode from the dynamo *d*. Into the crucible is put *cryolite*, a compound of aluminum and sodium fluoride, $Al_2Na_6F_{12}$, mixed with *bauxite*, or aluminum oxide, Al_2O_3. The former compound has a very low melting point and serves as a flux. When the mixture of the two minerals has been fused, a powerful current is passed through, and the bauxite alone is decomposed. We may represent this by the simple equation

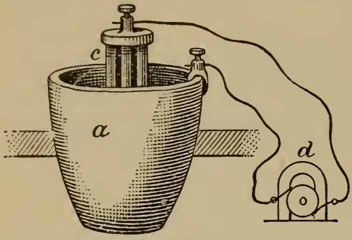


FIG. 56.

$$Al_2O_3 = Al_2 + 3\ O.$$

The metallic aluminum collects at the bottom of the crucible and may be drawn off.

4. **Characteristics.** — Aluminum is a silvery white metal, having a density of only 2.6, or about one-third that of iron. It is very tenacious, ductile, malleable, and sonorous. Its melting point is only moderately high, 700°. It is permanent in the air and a good conductor of electricity. Aluminum is strongly electropositive in its character, and may be used to reduce various other metals from their compounds, just as zinc will reduce lead, tin, and others.

5. **Uses.** — As the output of aluminum has increased and the price cheapened, its uses have rapidly multiplied.

6. The metal will take a very high polish, and as it is permanent in air it is now used extensively in the manufacture of ornaments and novelties, for which, in the past, silver alone had been employed.

7. A more valuable use of aluminum is in the place of copper in electric circuits. Because of its lightness, an aluminum wire, much larger in cross-section than any copper wire used for this purpose, may be employed without increasing the weight in a given length. This fact will nearly suffice to offset the lower coefficient of conductivity of the newer metal, and makes its carrying capacity not very different from that of copper. Another practical use of aluminum is in the manufacture of cooking utensils. It is claimed that these vessels will prevent the scorching of liquid foods, such as milk. The metal is also used in many places where iron has heretofore been employed, having the advantage of great tenacity. In time, if the cost of production is sufficiently decreased, it may find extensive use in shipbuilding. In the form of alloys, with varying proportions of copper, it is much used.

Compounds of Aluminum — Native

8. **Kaolin.** — This is one of the most valuable natural compounds of aluminum; it is the silicate, $Al_4(SiO_4)_3$, almost pure. Ordinary clays contain, in addition to this, iron compounds and other foreign materials. Kaolin, when heated with a kind of rock called feldspar, melts and forms a semi-translucent mass, used in making various kinds of porcelain wares.

9. **Emery.** — In the form of a rock or mineral, emery is known as *corundum*. It is the oxide of aluminum, Al_2O_3, and is extremely hard. It is used in the form of emery wheels, and in other ways, for polishing and for grinding and sharpening tools.

10. **Precious Stones.** — The Oriental ruby, the emerald, sapphire, and many other stones prized for their beauty are merely aluminum oxide, Al_2O_3, crystallized with some

silica, SiO_2, and differ in almost no other respect from emery or corundum, which is uncrystallized. These jewels contain in addition very small quantities of some foreign substance, such as iron, chromium, or copper, which imparts the colors for which they are valued. The true or Oriental ruby and other gems differ from the spinel or ordinary ruby and emerald in that the latter contain in addition to the aluminum oxide, certain other compounds, which render the stones much less valuable.

Compounds of Aluminum — Artificial

11. Alums. — The term *alum* is applied to a large number of salts, known as double sulphates. They all contain two metals, or an equivalent. Thus, common alum is potassium aluminum sulphate, $K_2Al_2(SO_4)_4\,24\,H_2O$. By inspection, it will be seen that this is simply potassium sulphate, K_2SO_4, crystallized with aluminum sulphate, $Al_2(SO_4)_3$. They all crystallize in octahedrons, sometimes singly, more usually piled in masses one upon another.

EXPERIMENT 156. — Put about 50 cc. of water into a beaker, warm it somewhat, and add powdered alum as long as any will dissolve. Now, pour the saturated solution into a good-sized test-tube, and suspend therein a string with a small knot at the end. Allow it to stand several hours and note the shape of the crystals that form. By adding a strong chromium solution to the alum, delicately colored violet crystals may be obtained.

12. Common alum is prepared by burning a shaly rock which contains a compound of aluminum, moistening it, and exposing it to the air. The aluminum compound is thus converted into a sulphate. A potassium salt is then added to the solution, whereupon the alum crystallizes out. If the ammonia water from gas factories be used instead of the potash salts, ammonia alum is obtained, represented by the formula $(NH_4)_2Al_2(SO_4)_4 24 H_2O$. This is used very largely instead of the potash alum.

13. The term alum is also applied to many double sulphates which contain no aluminum, as, for example, $K_2Cr_2(SO_4)_4$, potassio-chromic alum. In such cases the compound is designated by the names of both of the metals entering into the compound. By studying the formulæ for the alums mentioned above, it will be seen that the first metal is always univalent and the second usually trivalent. If, then, we represent the univalent metals by M and the trivalent by R, we may write as the general formula for the alums, $M_2R_2(SO_4)_4$, in which M is usually potassium, sodium, or ammonium, and R aluminum, iron, or chromium.

Exercise. — Write formulæ for sodium alum, ammonio-ferric alum, potassium alum, sodio-chromic alum, potassio-ferric alum, and ammonio-chromic alum.

14. Alum possesses a sweetish, astringent taste, and upon heating readily gives up its water of crystallization. In doing so it crumbles to an opaque mass, and in this form is known as *burnt alum*.

15. Uses. — In medicine, alum is used as an astringent. It checks bleeding by contracting the tissues, and in the form of burnt alum it serves as a mild caustic agent, especially for ulcerations of the mouth. In the arts alum is used largely as a mordant, that is, to fix the color in dyeing cloth.

Experiment 157. — In a solution of logwood heat two pieces of cloth for several minutes, or until both are well colored. Now, remove and allow them to dry. Then immerse one in a strong solution of alum and let it stand a few minutes; remove, and when dry wash both in water. Which retains its color the better?

16. Alum is also used frequently as an adulterant for baking powders, sometimes in very considerable quantities.

Experiment 158. — Examine a number of specimens of baking powder for alum and state results. Test them as follows: Put about a half gram of baking powder into a test-tube with 4 or 5 cc. of water and a little hydrochloric acid. Heat gently for a few moments, or until the solution is clear. If necessary, filter so as to obtain a *perfectly* clear solution; then add a few drops of ammonia, or enough to make it alkaline. If alum is present, a more or less heavy precipitate, white or nearly transparent, will form. Some idea of the amount of alum present may be obtained by the quantity of the precipitate formed. This, however, should be verified by further tests.

17. Clarifying Water. — In large cities obtaining their water supply from rivers which are muddy during certain seasons of the year, considerable quantities of alum are used for settling the sediment. Weighed amounts of lime and alum are thrown into the settling basins; the lime, on coming into contact with the water, is slaked, as you have learned, forming calcium hydroxide, thus: —

$$CaO + H_2O = Ca(OH)_2.$$

This is a strong alkali, like ammonia, and forms in the water with the alum a precipitate of aluminum hydroxide, $Al_2(OH)_6$, just as the ammonia did with the alum in the baking powders. The reaction is as follows: —

$$Al_2(SO_4)_3 + 3\,Ca(OH)_2 = Al_2(OH)_6 + 3\,CaSO_4.$$

Aluminum hydroxide is a gelatinous or starchy precipitate which in settling brings down with it practically all of the sediment, leaving the water clear. The only substance added to the water is calcium sulphate, which, as seen in the study of calcium, simply renders the water a little more "hard." No trace of alum will be found to remain in the water, since the hydroxide is insoluble.

18. Aluminum Hydroxide, $Al_2(OH)_6$. — This, as stated above, is a starchy, white, semi-translucent precipitate, formed when ammonia is added to any aluminum salt in solution. It may also be formed by adding caustic soda or potash to an aluminum solution, but in excess of these reagents it is soluble.

Experiment 159. — Prepare some aluminum hydroxide as described above, using ammonia. Notice its appearance, and test its solubility in hydrochloric acid. What results? Write the reactions.

Repeat the experiment, using caustic soda or potash instead of the ammonia. Add cautiously a drop at a time until the precipitate forms, and then an excess. State results. Write the two reactions, knowing that in the latter case potassium aluminate, K_3AlO_3, a compound soluble in water, is formed.

REVIEW OF WORK IN ALUMINUM

- Abundance of the metal.
  - Form in which it occurs.
  - Former methods of obtaining it and cost.
  - Present methods of reduction.
- Description of the metal.
  - Color, density, melting point, malleability, tenacity, conductivity, ease of oxidation, susceptibility of polish.
  - Value of the metal in a practical way.
    - Minor uses — Alloys.
    - As a substitute for copper; for iron.
- Compounds — Native.
  - Difference between kaolin and clay.
  - Uses of the former.
  - Difference between emery and certain gems.
    - Artificial compounds.
  - Alums — Meaning of the term.
    - Preparation of common alum.
    - What is burnt alum.
    - Uses of common alum.
      - Chemistry of its use in clarifying water.
      - Method of showing its presence in baking powders.
      - Mordant — Meaning of term.

CHAPTER XXIII

TIN AND LEAD

TIN: Sn = 118

1. Source of Supply. — Almost the entire commercial supply of tin is obtained from the ore, *cassiterite*, SnO_2, sometimes called *tin-stone*. The ore probably received its technical name from an early appellation of the British Isles, *Cassiterides*. Extensive mines located at Cornwall, England, have been worked for hundreds of years. Long before the Christian era the Phœnicians brought back great quantities of ore from these mines; yet even to this day they are very productive. They extend down into the earth thousands of feet, and far out, even under the bed of the ocean. The purest tin is said to be that obtained from India, known as Banca tin. Other sources of supply are Australia, Bolivia, and the Black Hills of Dakota; the last-named mines, however, have not yet been well developed.

2. Reduction of Ore. — With cassiterite there are usually found small quantities of arsenic in the form of arsenic sulphide, besides some other metals. After crushing the ore, it is strongly heated in a reverberatory furnace, where the volatile products, such as arsenic and sulphur, are expelled. At the same time the sulphides of the other metals are converted into sulphates, thus: —

$$CuS + 2\,O_2 = CuSO_4.$$

These sulphates are soluble in water, and to remove them the roasted ore is thoroughly washed; it is then mixed with coke or coal and reduced in a blast furnace, the carbon, as usual, serving to deoxidize the cassiterite. This last process may be indicated thus: —

$$SnO_2 + 2\ C = Sn + 2\ CO.$$

Experiment 160. — If granulated tin is not to be had, some foil, procured from the tobacconist, will serve. Test the melting point of tin by holding a small piece in the flame. Try the effect of nitric acid upon tin. Also hydrochloric, and state results. Try it on charcoal with the oxidizing flame. State results. Does tin oxidize readily at ordinary temperatures?

Heat a piece of "tin plate" in the burner flame a moment, and then plunge it into cold water. Now rub the surface with a cloth moistened with diluted aqua regia, and wash with water. State the appearance of the surface.

3. Characteristics of Tin. — Tin is a silvery white, lustrous metal which does not tarnish in the air. It is somewhat harder than lead, but melts at a lower temperature. By the oxidizing flame it may be converted into a white powder, SnO_2. It is highly crystalline in structure, as may be seen by removing the surface of a sheet or bar of tin with acid. The crystals may be prepared by melting some tin in a crucible, and when it is partially cooled, pouring out what is still molten. When a bar of tin is bent, these crystals rub together, and produce a distinctly audible sound, known as the "tin cry." This metal is very malleable, and may easily be beaten or rolled into thin sheets. It is soluble in aqua regia and in hydrochloric acid, but ordinary nitric acid converts it into a white powder, metastannic acid, from which we may obtain stannic oxide, SnO_2, by expelling the water.

4. Uses. — Because of its permanency in the air, tin is used in coating sheet iron, making what is known as tin plate. From this all "tin" vessels are made. In making sheet tin, the sheet iron is first thoroughly cleansed by immersion in dilute acids, then washed and dried. It is next dipped into a bath of molten tin, of which a thin coating adheres to the iron. A second and a third dipping increase the thickness of the coating. For outdoor work, such as roofing and guttering, a heavier quality of sheet iron is used, and the tin is generally alloyed with lead because the latter is much cheaper.

5. In the form of foil, tin is extensively used for wrapping purposes; at present, however, it is often adulterated with lead, especially in cases where the latter metal will be of no disadvantage. Tin foil amalgamated with mercury is also used frequently for the backs of mirrors.

6. As stated elsewhere, tin is used extensively in alloys, among them being common solder, type metal, German silver, and the fusible metals. To these it imparts the property of a low melting point, that of the fusible metals being even lower than the boiling temperature of water. Spoons made from these metals, if dipped into a cup of hot tea or coffee, would rapidly melt and disappear.

Compounds of Tin

7. Stannous and Stannic Salts. — As is the case with many other metals, tin forms two general classes of salts: the *stannous* and the *stannic*.

8. The Chlorides: Stannous, $SnCl_2$, and Stannic, $SnCl_4$. — The former is a white crystalline salt which may be prepared by dissolving tin in hydrochloric acid. It is a great reducing agent, and readily reduces mercury from certain of its salts. If a solution of stannous chloride be gradually added to one of mercuric chloride, at first a white precipitate of mercurous chloride forms, and then by the addition of more of the tin solution, the precipitate slowly turns darker from the fact that the mercury is reduced to the metallic condition, though in a very finely divided form. The following reactions express the changes that take place: —

$$2\ HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4;$$

$$Hg_2Cl_2 + SnCl_2 = Hg_2 \quad + SnCl_4.$$

Various other metallic salts are in a similar way reduced from the *ic* to the *ous* condition. The above reaction of stannous chloride and mercuric chloride upon each other may be used as a test for the presence of either metal.

9. Stannic chloride may be prepared by dissolving tin in aqua regia.

Experiment 161. — Dissolve some tin in hydrochloric acid, and boil nearly to dryness to expel the excess of acid. Take up with a few cubic centimeters of water, and gradually add it to a little of a solution of mercuric chloride in a test-tube. Do you obtain first a white precipitate, and afterward a gray one, becoming nearly black, as explained in the text above? If necessary, warm gently.

Dissolve a little tin in hydrochloric acid with a little nitric added; boil nearly dry, and after adding a few cubic centimeters of water, test with mercuric chloride, as before. State the results.

10. The Sulphides: Stannous, SnS, and Stannic, SnS_2. — These may be prepared by passing a current of hydrogen sulphide through solutions of stannous and stannic chloride, respectively. The former is a dark brown precipitate, the latter, bright yellow, closely resembling arsenic sulphide. These two, though alike in some respects, differ, however, in that the latter is soluble in ammonium carbonate, while the former is not. Stannic sulphide, more-over, is soluble in hot concentrated hydrochloric acid, while the arsenic is not.

Experiment 162. — Add a drop or two of hydrochloric acid to a solution of stannous chloride, and pass through it a current of hydrogen sulphide. Describe the precipitate which forms. Write the reaction. Treat a solution of stannic chloride in the same way; what are the results? Write the reaction. Take a part of this precipitate and add a little yellow ammonium sulphide; what happens? To the remainder add some ammonium carbonate solution. Is the sulphide dissolved?

11. Stannic Oxide, SnO_2. — This is principally of interest because it is the chief ore of tin. It is obtained when tin is strongly heated with the oxidizing flame; it is pale yellow when hot, but white when cold.

Exercise. — Write the reactions showing the preparation of all the above-named compounds.

Experiment 163. — To determine whether any specimen of tin contains lead as an adulterant. Poisoning sometimes results from the canning of fruit in tin which is alloyed with lead. Procure any specimens of tin plate, or foil, and put upon them a drop or two of nitric acid. When dry, add a little of a solution of potassium iodide to the same spots. If the tin is adulterated with lead, bright yellow spots will appear, owing to the formation of lead iodide.

LEAD : Pb = 207

12. History. — Lead has been known from very early times because of the ease with which it is reduced from its ores. It is mentioned several times by biblical writers, but seems to have been confounded with tin. The two metals are spoken of by Latin writers as *black* and *white lead*, respectively; yet tin was the more expensive, and known to be suitable for soldering.

13. Occurrence. — The principal ore of lead is *galena*, or lead sulphide, PbS. It is a dark-colored, almost black, lustrous mineral, resembling somewhat metallic lead itself, but does not tarnish in the air as the metal does. It occurs in masses which tend to split up into cubical form; it is widely distributed, but is usually found in what are called "pockets." It has very frequently associated with it ores of zinc, silver, iron, and some other metals.

EXPERIMENT 164. — Put into a small cavity in a stick of charcoal a little lead oxide, PbO, or minium, Pb_3O_4, or powdered galena, and heat with the reducing flame before the blowpipe. Do you obtain a metallic globule?

14. Reduction of the Ores. — This experiment illustrates in the main what is usually known as the "carbon reduction." The furnace used in this method is not essentially different from the blast furnace shown under iron, for the reduction of iron ores. See the illustration on page 301.

15. The Oxidation Process. — The second method may be called the "roasting" or "oxidation" process. The finely ground ore is placed upon the floor of the oven in a reverberatory furnace (see Fig. 57). The heat and flames are directed downward from the arching roof above upon the ore. In this way the upper layers are converted from the sulphide into the oxide, as seen in the reaction: —

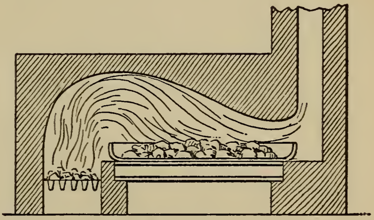


FIG. 57.

$$PbS + 3\,O = PbO + SO_2.$$

The central portion of the mass being less strongly heated is converted into the *sulphate*, thus: —

$$PbS + 2\,O_2 = PbSO_4.$$

The bottom portions of ore, not receiving sufficient heat, undergo no chemical change. When sufficient time has elapsed to secure the above results, the strong draughts of air are shut off, in order to prevent the process of oxidation from going further; thereupon the unchanged sulphide, PbS, reacts upon the oxide, PbO, and the sulphate, $PbSO_4$, already formed, whereupon metallic lead is obtained. We may represent this by the following reactions: —

$$PbS + 2\,PbO = 3\,Pb + SO_2,$$

and

$$PbS + PbSO_4 = 2\,Pb + 2\,SO_2,$$

or representing the complete change by a single reaction,

$$2\,PbS + 2\,PbO + PbSO_4 = 5\,Pb + 3\,SO_2.$$

This is the process, probably, most commonly used, because the most economical, but it is adapted only to moderately rich ores.

16. Reduction of Impure Ores. — When the lead ores are considerably mixed with the ores of other metals, the processes described above are not satisfactory.

Experiment 165. — Suspend in a test-tube or bottle, about two-thirds full of a moderately strong solution of lead acetate, a strip of zinc. Allow it to stand for several hours without shaking. Notice the flaky crystals of lead that form on the zinc, giving what is called the "lead tree." After 24 to 48 hours carefully lift out the "tree," remove the crystals of lead, and notice how soft and porous the mass seems. Notice how the zinc strip has changed. If you test the solution in the bottle, you will find that it contains zinc now instead of lead. That is, as the lead has slowly deposited upon the zinc, the zinc has likewise slowly dissolved. The chemical change is shown by the following reaction: —

$$Pb(C_2H_3O_2)_2 + Zn = Zn(C_2H_3O_2)_2 + Pb.$$

17. For impure ores a similar method is adopted. They are mixed with scrap iron, and melted in a furnace, whereupon the lead, together with any silver present, is set free, and the iron combines with the other matters present. Thus: —

$$PbS + Fe = FeS + Pb.$$

18. Characteristics of Lead. — Many of these may be learned from the following simple experiments: —

EXPERIMENT 166. — Take the globule of lead obtained in Experiment 164, and cut it with your knife. What can you say of its hardness? its color? its luster? Does it retain this luster? Test its melting point with the blowpipe and state results. What proof can you give that it oxidizes in the air? Try it on charcoal with the oxidizing flame; what is seen upon the charcoal around the metal? Compare it with silver in this respect. Put a small piece of lead into a test-tube and determine whether it is soluble in nitric acid; in hydrochloric acid.

19. Lead is a very heavy, soft, malleable, dark gray metal, with a specific gravity of 11.3 and a melting point of about 330°. It has a brilliant luster when first cut; but, owing to the fact that it so readily oxidizes in the air, the surface is soon tarnished. This coating, however, protects the metal from further oxidation, and it is very durable. Lead is very different from iron in this respect, as the layer of rust, oxide, that forms upon the latter metal on exposure does not protect it. Lead is slightly soluble in ordinary water, and as all lead salts are very poisonous, water that has stood in leaden pipes any considerable length of time should not be used. The effects of lead compounds upon the human system are often seen among painters, who suffer from what is known as "lead colic."

20. Uses for Lead. — This metal, as well as its compounds, has almost numberless uses. One of the most important is for lead pipes in plumbing, used because they may be bent with ease. It is also employed largely for underground telephone conduits in cities, as well as for casings or sheaths for bundles of overhead wires. This pipe is made by forcing lead at a temperature near the point of solidification through an annular opening in a steel plate.

21. **Shot.** — Another use of lead is in making shot and bullets. As stated elsewhere, for this purpose arsenic in small quantities is alloyed with the lead. One method is to allow the molten alloy to flow into a perforated vessel, from which the streams of metal fall long distances into water. In the descent the streams are broken into globules, which before reaching the water have solidified. The various sizes and shapes thus obtained must next be sorted. The shot are allowed to roll down over inclined screens with a mesh of different sizes. The smaller shot will drop through first into one bin, the next size into a second, and so on. The irregular-shaped pieces will not roll through, and eventually make their way off the end of the plane. The shot are next polished by rotating in cylinders containing a little powdered graphite.

22. **Type Metal.** — A third important use is in the manufacture of type for printers. This is made of an alloy of lead, tin, and antimony, or bismuth. The latter metals are used to give hardness to the alloy and to secure expansibility at the moment of cooling. Owing to this property the type has clear, sharply cut faces, whereas lead alone would produce that having a battered or worn-out appearance.

23. **Solder.** — A fourth use of lead is in solder, an alloy of tin and lead, the ordinary proportions being half and half. The tin is added to secure a low melting point, and

the proportions vary according to the use to which the solder is to be put. Lead is also used in making pewter, an alloy of lead and tin, and in storage batteries, but never for "lead" pencils.

Compounds of Lead

There are many of these, the most important among them being the following: —

24. **Lead Acetate, $Pb(C_2H_3O_2)_2$**, known also as Sugar of Lead, because of its sweet taste. It is a white crystalline salt, which may be obtained by dissolving lead in vinegar or acetic acid, $HC_2H_3O_2$. It is used frequently for dyeing, and in medicine as an external application for ivy poisoning and in acute cases of erysipelas.

25. **Lead Chloride, $PbCl_2$.** — This may be prepared by adding hydrochloric acid to a lead solution, especially the acetate. It is a white solid, somewhat soluble in cold water, completely so in hot water, from which it crystallizes out upon cooling in small crystals that rapidly settle.

EXPERIMENT 167. — To a few cubic centimeters of a solution of lead acetate, or nitrate, in a test-tube, add about 1 cc. of hydrochloric acid. Note the results. Write the reaction. Now add a little water and heat the contents of the tube to the boiling point. What happens? Allow it to cool and watch the tube meanwhile; what happens? How do the two solids differ in appearance?

26. **Lead Sulphate, $PbSO_4$.** — This may be prepared by adding sulphuric acid to a soluble lead salt, as the acetate or nitrate. It is a heavy white salt, very slightly soluble in water and almost entirely insoluble in alcohol.

27. **Lead Nitrate, $Pb(NO_3)_2$.** — This salt is obtained when lead is dissolved in nitric acid. It is a white, crystalline compound, soluble in water. It is used somewhat in the laboratory.

28. The Oxides. — There are several oxides of lead, the most important of which are PbO, *litharge*, or lead oxide ; PbO_2, lead peroxide ; and Pb_3O_4, *minium*, or red lead. This last is a deep red compound, used in plumbing to secure tight joints, and is sometimes regarded as a mixture of the other two, thus : —

$$2\ PbO + PbO_2 = Pb_3O_4.$$

It may be prepared from lead oxide, PbO, by heating. Litharge is a light brown-colored powder, obtained in large quantities when argentiferous lead ores are reduced by the cupellation process, and is always produced when lead is heated strongly in the air. It is used frequently in storage batteries, in preparing red lead, as stated above, and in making flint glass, to which it seems to impart the qualities of high refraction, almost perfect transparency, and softness.

29. Lead Carbonate, $PbCO_3$. — This is an insoluble white compound, which may be obtained by treating a solution of lead nitrate with one of ammonium carbonate. If sodium carbonate is used instead of the ammonium, a basic carbonate is obtained, or what may be represented by the formula, $2\ PbCO_3, Pb(OH)_2$, that is, two molecules of lead carbonate combined with one of lead hydroxide. In commerce this is known as *white lead*, and is used very extensively as paint.

30. White lead is prepared by several methods, the oldest and perhaps the best being that known as the "Dutch method" (see Fig. 58). Glazed earthen jars, 8 or 9 inches in height, are used. About 3 inches from the bottom on the inside are some projections, upon which a small board rests. Beneath the

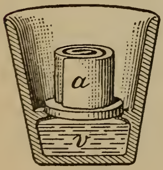


FIG. 58.

shelf is vinegar, *v*, and above it a coil of sheet lead, *a*. Hundreds of these jars so prepared are placed side by side and covered with tan bark; above them another layer of jars with a covering of bark is placed, and so on, to a considerable height. The whole is then buried under compost, which in decaying generates not a little heat. The fumes of acetic acid act upon the lead, gradually converting it into lead acetate. Then the carbon dioxide set free from the decaying tan bark combines with the acetate, slowly changing it into the basic carbonate. Several weeks are required for the completion of the process. The white lead is next removed from the jars, washed to dissolve out any lead acetate remaining, then ground in oil, and is ready for use

31. Milner's Method. — Numerous attempts have been made to devise a method whereby white lead could be made quickly. One of these, which is fairly good, is *Milner's*. Four parts of litharge, PbO, are mixed with one of common salt, $NaCl$, and sixteen of water. The whole is ground together in a mill for 4 or 5 hours, then transferred to a leaden vessel, into which is conducted a current of carbon dioxide until the whole is neutral.

32. White Lead by Electrolysis. — A current of electricity is passed through a solution of sodium nitrate in water, in which a bar of lead is suspended. By the electric current the sodium nitrate is decomposed, forming caustic soda and nitric acid, thus: —

$$NaNO_3 + H_2O = HNO_3 + NaOH.$$

The nitric acid thus produced attacks the lead, and converts it into lead nitrate, $Pb(NO_3)_2$. A second reaction follows, the lead nitrate and caustic soda combining to form lead hydroxide and sodium nitrate, thus : —

$$Pb(NO_3)_2 + 2\,NaOH = Pb(OH)_2 + 2\,NaNO_3.$$

Thus we have produced again the same solution we had in the beginning, and only the lead needs to be renewed. The lead hydroxide thus obtained is treated next with sodium carbonate, when basic lead carbonate is obtained, as follows : —

$$2\,Pb(OH)_2 + Na_2CO_3 = 2\,NaOH + PbCO_3, Pb(OH)_2.$$

This process is continuous, very rapid, and is said to produce a fairly good quality of white lead.

33. Lead Chromate, $PbCrO_4$. — This is an insoluble compound of bright yellow color, and is easily prepared by adding a solution of potassium dichromate to one of a lead salt. It is used to a considerable extent as a paint, being sold under the name *chrome yellow*.

EXPERIMENT 168. — Let the student prepare some of this pigment, and examine it. Use either potassium chromate or dichromate with a solution of lead nitrate or acetate.

34. Lead Sulphide, PbS. — This is an insoluble compound, black in color, prepared by passing a current of hydrogen sulphide through a solution of lead nitrate or acetate. It has the same composition as native galena, but lacks the metallic luster. Galena is used in glazing pottery ware, except such as is to be used for articles of food. It is ground fine, mixed with pulverized clay and water, and the mixture washed over the pottery. When the vessels are strongly heated in ovens, the silica in the clay and the lead sulphide melt and form a glass which fills the pores of the clay. As such glazes are soluble, they are not suitable for pottery of all kinds.

Exercise. — Write the reactions expressing the preparation of all the lead salts described above.

35. Identification. — Any solution of a lead salt may be identified by adding to it sulphuric acid or potassium dichromate, as in preparing the sulphate, or chromate, described above. A solution of potassium iodide is sometimes used with the lead solution, and gives a bright yellow precipitate resembling chrome yellow.

Experiment 169. — To determine the composition of common solder. Add to a small piece, not larger than a grain of wheat, about a cubic centimeter of concentrated nitric acid, and warm gently. When the alloy has disappeared, and the white powder which has formed is settled, decant the clear solution into an evaporating dish. Add some water to the white powder, and decant again. Now evaporate the solution decanted nearly to dryness, add a little water, and make two tests for lead with separate portions of it, according to method of identification suggested above. State your conclusion.

To the white powder obtained at the beginning, add a little strong hydrochloric acid, and heat until solution is secured. Boil down nearly to dryness, add 25 to 50 cc. of water, and through part of it pass hydrogen sulphide; to another portion add slowly, drop by drop, mercuric chloride. State results. From these can you determine what metal you have? See section 9, page 273, and compare results.

SUMMARY OF CHAPTER

- History of tin and lead.
- Occurrence of each — Chief ore, and its composition.
  - Principal tin mines — Description.
- Reduction of the ores.
  - Wherein similar.
  - Purpose of the roasting in each case.
  - Description of a second method of reducing lead.
    - Furnace used.
    - Chemical changes and reactions.
  - Experiment of "lead tree" — Description — Purpose.

Characteristics of lead and tin — Compare them in
  - Color.
  - Density.
  - Hardness.
  - Melting point.
  - Malleability.
  - Tendency to oxidize.
  - Tendency to crystallize.
  - Solubility in acids.

Uses.
  - Sheet tin — What is it? — Its use — How made? — Why?
  - Alloys of tin — Properties secured by the tin.
  - Foil — Purposes.
  - Lead pipes — Use — How made?
  - Shot — Manufacture of.
  - Type metal.
  - Solder.

Compounds.
  - The oxides of tin and lead — Compare them.
    - Uses and preparation.
  - Stannous chloride; lead chloride.
    - Preparation of each.
    - Interesting facts about each.
  - The Sulphides — Preparation of each.
    - Appearance of each.
    - Uses of PbS.
  - Other important lead compounds.
    - Sugar of Lead — Chemical name and formula.
      - How prepared.
      - Uses.
    - White lead — Composition.
      - Best way of preparing; give plan and chemical reactions.
      - Electrolytic method.
    - Chrome yellow.
      - How prepared in laboratory.
      - Appearance and uses.

Usual method of identification of lead and tin salts.
  - Analysis of common solder.

CHAPTER XXIV

ARSENIC, ANTIMONY, BISMUTH

Arsenic: As = 75

1. Source of Supply. — In limited quantities metallic arsenic is found free in one or two countries of Europe, especially Germany. The greater part, however, is obtained from arsenical pyrite, that is, iron pyrite, FeS_2, in which arsenic has replaced an atom of sulphur, thus, FeAsS. It also occurs in combination with other metals, such as zinc and nickel, and with sulphur, as red arsenic sulphide or *realgar*, As_2S_2, and yellow arsenic sulphide, As_2S_3, or *orpiment*.

2. Reduction of the Ores. — As already stated, arsenical pyrite is most commonly used for the production of arsenic. This ore is first roasted in ovens at a moderately strong heat, by which it is oxidized, thus: —

$$2\,FeAsS + 5\,O_2 = Fe_2O_3 + As_2O_3 + 2\,SO_2.$$

The last two of these products are volatile and are passed over into cold chambers, where the oxide of arsenic condenses in a white sublimate. This is next mixed with powdered charcoal, put into retorts, and heated. The arsenic oxide is deoxidized by the charcoal, the metallic arsenic vaporizes and is condensed in cold chambers, thus: —

$$As_2O_3 + 3\,C = 2\,As + 3\,CO.$$

Experiment 170. — Mix well a little arsenic trioxide and some powdered charcoal and put into one end of a piece of hard glass tubing. Now, heat strongly in the Bunsen flame, holding the tube in a slanting position, with the cooler end up. Notice the deposit forming. Describe it. What has been the effect of the charcoal?

This experiment illustrates the commercial method of preparing arsenic.

3. Characteristics of Arsenic. — In many respects arsenic is not unlike some of the non-metallic elements, notably phosphorus. It forms compounds with hydrogen and oxygen similar to those of phosphorus, and with several metals a variety of salts in which arsenic is the acid-forming element; for example, sodium arsenate, Na_3AsO_4, nickel arsenide, NiAs, etc. In general appearance, however, arsenic is more like the metals. Thus, it is of a dark gray color, with metallic luster when freshly broken, has a marked tendency to crystallize, and tarnishes slowly in moist air. It vaporizes without melting, and when in the form of vapor has a sickening garlic odor. It is of medium density, and, like phosphorus, has four atoms to the molecule. It is but little acted upon by nitric or hydrochloric acid, but dissolves readily in aqua regia or nascent chlorine. It has strong affinity for chlorine, and if it be finely powdered and sifted into a bottle of the gas it burns readily.

Experiment 171. — Examine some crystals of metallic arsenic and notice their color and general appearance. Are they malleable? Heat a small piece on charcoal with the blowpipe. Notice the odor. Does the arsenic melt? What becomes of it?

4. Uses. — In the metallic form arsenic has little use except in making shot. With lead it forms an alloy that is considerably harder than the former metal, and at the same time one which, in the molten condition, is much more mobile. This property of the arsenic alloy is of value in the manufacture of shot by the ordinary method, for the shot made from it are more perfect in shape than those made from a metal more viscous, like lead.

Compounds of Arsenic

EXPERIMENT 172. — To study the characteristics of *arsine*, AsH_3. Prepare a flask for the generation of hydrogen from zinc and sulphuric acid, as on page 39, and attach a jet. After a few moments, or when sufficient time has elapsed for the air to be expelled, wrap a towel around the flask or inclose in a small box with an opening through the cover, as seen in the figure, and light the jet. You have hydrogen burning. Hold a cold porcelain dish against the flame and notice that no deposit forms upon the dish.

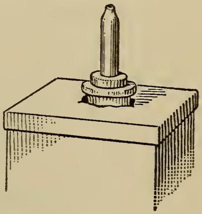


FIG. 59.

Now, add to the hydrogen flask a little arsenic trioxide, dissolved in dilute hydrochloric acid. Again light the jet, and notice how the color of the flame has changed. Hold a cold dish against the jet as before. Is any deposit formed? What that you have already seen does it closely resemble? The gas being generated is arsine. Now, hold a beaker or test-tube over the burning jet, and notice whether there are not two different deposits formed. Can you decide what they are? Write the reaction that takes place when arsine burns.

5. **Arsine.** — Arsine, AsH_3, is also known as arseniureted hydrogen, or hydrogen arsenide. It is a compound of considerable interest, because it is always prepared in testing for arsenic in cases of suspected poisoning. The method used is the one described in the experiment above. This is known as *Marsh's* test, and is so exceedingly delicate that mere traces of arsenic, even so low as one part in several hundred thousand, can be detected. Care should be taken, however, to see that the zinc is

perfectly free from arsenic. Antimony gives a spot considerably like that of arsenic seen above, but the latter may be detected by treating with a solution of bleaching powder, in which the arsenic spots are soluble, while the others are not.

6. Let us study the reactions that take place. First, by the reaction of sulphuric acid and zinc upon each other hydrogen is produced, thus: —

$$Zn + H_2SO_4 = H_2 + ZnSO_4.$$

The hydrogen atoms in the nascent condition, instead of uniting with one another to form molecules of hydrogen, unite with the arsenic present, forming hydrogen arsenide, AsH_3. This may be represented thus: —

$$AsCl_3 + 6\,H = AsH_3 + 3\,HCl.$$

7. **Characteristics of Arsine.** — This is a colorless, exceedingly poisonous gas, which burns with a pale violet flame, giving off white fumes of the trioxide As_2O_3.

$$2\,AsH_3 + 3\,O_2 = As_2O_3 + 3\,H_2O.$$

Both of these products may be seen if a cold beaker or test-tube be held over the burning jet of arsine. If a cold dish is held against the flame, the temperature is lowered below that required for the combustion of arsenic, and it is therefore deposited in the metallic form, while the hydrogen continues to burn. What does the experiment teach regarding the kindling point of hydrogen?

8. **The Oxides of Arsenic.** — Corresponding to the two oxides of phosphorus we have two of arsenic, the *trioxide*, As_2O_3, and *pentoxide*, As_2O_5. Only the former is of importance. It occurs in two or three forms, the white powder being the most common. It is usually sold under

the name "arsenic" or white arsenic, but is also called arsenious acid. It has a sweetish taste, is slightly soluble in cold water, more so in hot, in hydrochloric acid, and in caustic soda. It is very poisonous, but acts somewhat slowly. An antidote for it is ferric hydroxide, prepared by treating a ferric salt in solution with ammonia; the precipitate must be filtered out and washed. Magnesia, MgO, is also suggested, and is used more often because it is to be had already prepared.

9. Arsenic trioxide is used by taxidermists in curing the skins of animals; it is an ingredient of many poisons, but is also often prescribed by physicians as a blood purifier, especially for removing facial eruptions. It is thought to beautify the complexion, and has a tendency to produce fat. Because of the latter property it is sometimes fed to old horses to prepare them for the market. It stimulates the action of the heart and renders breathing easier; on this account it is said to be used by some mountain climbers. These apparent benefits are but temporary, however, and a discontinuance of its use is attended by all the symptoms of serious arsenic poisoning.

EXPERIMENT 173. — Examine a sample of arsenic trioxide and note its general appearances. Test its solubility in diluted hydrochloric acid, also in caustic soda. Which is the better solvent? Use only small quantities of the trioxide. Save the solution.

10. Paris Green; Scheele's Green. — This is a very poisonous, bright green powder, used often for coloring and tinting and as an insect exterminator.

EXPERIMENT 174. — Let the student prepare this compound, thus: To a few cubic centimeters of a solution of copper sulphate in a test-tube add ammonia, drop by drop, until the precipitate which forms at first *just* dissolves. Now, add gradually a solution of arsenic; a bright green precipitate will form. If too blue, not enough arsenic has been added. This is one of the easiest methods of detecting arsenic if present in considerable quantities. It is known as *Scheele's* test.

11. Arsenic Trisulphide, As_2S_3. — This is a bright yellow powder obtained by passing a current of hydrogen sulphide through a solution of arsenic. It is soluble in ammonium carbonate, which distinguishes it from a similar compound of tin, SnS_2, also yellow. It is also soluble in yellow ammonium sulphide, but not in hydrochloric acid.

Experiment 175. — Let the student prepare this compound by passing hydrogen sulphide through a solution of arsenic trioxide in water acidulated with hydrochloric acid. Divide the yellow precipitate into two or three parts and test its solubility in hydrochloric acid and in ammonium sulphide and carbonate.

ANTIMONY: $Sb = 120$

12. Source of Antimony. — This element is found free in very small quantities only, but frequently occurs with the ores of other metals, such as lead, copper, and iron. Its principal ore is *stibnite*, Sb_2S_3, and from this the commercial supply is obtained.

13. Reduction of the Ore. — There are two methods used for reducing antimony ores. The first consists in heating the sulphide in a reverberatory furnace, whereby the ore is reduced to an oxide, thus: —

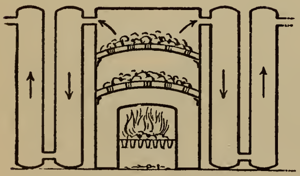


Fig. 60.

$$Sb_2S_3 + 5\ O_2 = Sb_2O_4 + 3\ SO_2.$$

Then the tetroxide, thus formed, is mixed with charcoal, and again heated in a furnace, when metallic antimony is obtained, thus: —

$$Sb_2O_4 + 4\ C = 4\ CO + 2\ Sb.$$

EXPERIMENT 176. — In a cavity in a piece of charcoal place a little antimony tartrate, mixed with sodium carbonate, and moisten with a few drops of water. Now heat strongly with the reducing flame. What do you obtain? Preserve for the next experiment.

14. This illustrates the method of reduction described above, and, it will be noticed, is in accord with the general plan of reducing metallic ores, — first reducing them to the form of an oxide by roasting them, and then deoxidizing them by heating with carbon.

15. Another Method. — This consists in mixing the ore, antimony sulphide, with iron, and melting the whole in a furnace. The iron combines with the sulphur, and precipitates the antimony, thus: —

$$Sb_2S_3 + 3\ Fe = 3\ FeS + 2\ Sb.$$

16. Characteristics of Antimony. — Owing to the fact that, like phosphorus, nitrogen, and other non-metallic elements, antimony forms oxides which are the anhydrides of acids, it is sometimes regarded as a non-metallic element. It is, however, of a highly lustrous metallic appearance, steel-gray in color, notably crystalline in structure, heavy, and so very brittle that it is easily reduced to a powder.

17. Antimony combines energetically with chlorine, bromine, and iodine, in contact with all of which, when finely powdered, it quickly takes fire. Upon bromine, sufficient heat is generated to melt the antimony, and it spins around as does sodium upon water, burning all the time. At ordinary temperatures, the metal does not readily tarnish in the air, but by means of the oxidizing blowpipe flame it is converted into a white oxide, Sb_2O_3. It is only slightly acted upon by hydrochloric acid, but nitric acid converts it into a white powder, and it is readily soluble in aqua regia, forming antimony chloride,

$SbCl_3$. One of its most valuable properties is that of expanding somewhat upon cooling.

Experiment 177. — To illustrate some of the above-mentioned properties. Take the metallic bead obtained in the preceding experiment, and learn whether it is magnetic. Test it with a hammer on an anvil to learn whether it is malleable. Notice its color and appearance. Put a portion of it on charcoal and try the oxidizing flame. What are the results? How does it differ from arsenic treated thus? Test the solubility of the metal in nitric acid; in aqua regia. State results in each case. Boil nearly to dryness the latter solution, and add water. What happens? Treat this with tartaric acid, and state results.

18. Uses. — Because of its property of expanding when it solidifies, antimony is used very extensively in making type metal, britannia ware, and other similar alloys. Antimony may be obtained in a powdered or *amorphous* condition by immersing a strip of zinc in a solution of some antimony salt, as the chloride or tartrate. The principle underlying is the same as that in the second method of reducing the ore, described already. This *antimony black*, as it is called, is a dark-colored, finely divided powder, and is sometimes used in giving plaster figures a metallic appearance.

Compounds of Antimony

19. There was a time when the compounds of antimony were extensively employed in medicine, but owing to their exceedingly poisonous character, their use was prohibited by law, and their applications now are considerably limited.

20. Stibine, Atimoniureted Hydrogen, SbH_3. — This gas, known also as hydrogen antimonide, corresponding to similar compounds of arsenic and phosphorus, is usually prepared from nascent hydrogen and some antimony compound, just as arsine was prepared in Experiment 172. It is a combustible gas, which burns with a green flame, and deposits upon a cold dish held against this flame a black spot resembling that of arsenic, but not so lustrous. It is also less volatile if heated, and is insoluble in a solution of calcium or sodium hypochlorite.

EXPERIMENT 178. — Prepare stibine exactly as you did the arsine, using the same precautions. Test the spots with a solution of bleaching powder or sodium hypochlorite, and verify the statements made above.

21. Oxides of Antimony. — None of the three oxides of antimony is of any importance. The trioxide, Sb_2O_3, and pentoxide, Sb_2O_5, are the anhydrides of the acids, antimonous and antimonic, corresponding to those of nitrogen from the similar oxides.

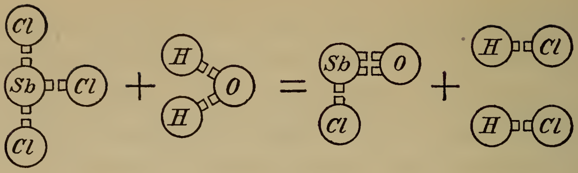
$$Sb_2O_3 + 3\ H_2O = 2\ H_3SbO_3.$$

$$Sb_2O_5 + 3\ H_2O = 2\ H_3SbO_4.$$

22. The Chlorides of Antimony. — When antimony is dissolved in aqua regia, as in Experiment 177, above, and the solution evaporated, antimony trichloride, $SbCl_3$, a white crystalline salt, is obtained. It was formerly known as "butter of antimony," from the thick oily appearance which it assumes before solidifying. Upon adding water to this compound, a white precipitate is formed, which is known as *basic* antimony chloride, or antimony oxychloride, SbOCl. The reaction may be expressed thus : —

$$SbCl_3 + H_2O = SbOCl + 2\ HCl.$$

The trichloride has given up two atoms of its chlorine, and has taken in their place one atom of bivalent oxygen.



This oxychloride is soluble in tartaric acid, but not in water.

23. Antimony Trisulphide, Sb_2S_3. — This is obtained artificially by passing a current of hydrogen sulphide through an antimony solution. It is of a beautiful orange color, soluble in yellow ammonium sulphide, and also in strong hydrochloric acid.

Bismuth : Bi = 208

24. Source of Supply. — Most of the commercial supply of bismuth is obtained from Saxony. It is usually found free, but alloyed with small quantities of several other metals. It also occurs in two ores: the sulphide, Bi_2S_3, known as *bismuthite*, and the oxide, Bi_2O_3.

25. Reduction. — When obtained from native bismuth, as it usually is, the process consists of little more than simply heating to melt the bismuth; the other metals found with it have a higher melting point, and remain unchanged. In the case of the ores, if bismuthite is used, it is treated as the sulphides of other metals are, first converted into an oxide, and then heated with charcoal. Let the student write the reactions representing the two steps.

26. Characteristics. — Like antimony, bismuth is a hard, brittle, distinctly crystalline metal. It is steel-gray in color, having somewhat of a golden reflection, or upon some surfaces a purplish hue. It has a low melting point, being just above tin in this respect, expands upon solidifying, and is permanent in the air at ordinary temperatures; at a red heat it oxidizes to a light yellow powder. It unites readily with bromine and chlorine, and if sifted into them takes fire at once.

Experiment 179. — If no bismuth is to be had in the laboratory, prepare a little by heating bismuth nitrate, mixed with sodium carbonate and moistened, on charcoal with the reducing flame.

Note the color of the metallic bead; test its hardness and malleability, and learn whether it is magnetic. Dissolve a portion of the bead obtained in nitric acid, boil nearly dry, and add water. What forms? Treat with tartaric acid in solution. Compare results with similar tests with antimony. How do they differ?

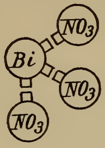
27. Uses. — In the metallic form bismuth has but little use, except in alloys. To these it imparts the properties of low fusing points and of expansibility. For these reasons it is used in stereotyping, and for similar purposes where clearly defined copies are demanded. Bismuth is also used for making safety plugs in boilers, and for very fusible alloys, such as Wood's alloy, which melts at about 60° C.

Experiment 180. — Put into an iron spoon about 2 g. of bismuth, 1 g. of lead, and 1 g. of tin, and melt them. When cold put into a beaker of boiling water. What happens?

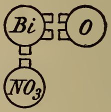
28. Most of the bismuth produced at the smelters is converted into its compounds and used in a medicinal way.

Compounds of Bismuth

29. Two Classes of Compounds. — Like antimony, bismuth forms two classes of compounds: the *ordinary*, and the *basic* or *bismuthyl*. These are best seen in the nitrates, $Bi(NO_3)_3$, in which the bismuth atom has its true valence, three, and in the *basic nitrate*, $BiONO_3$, in which one atom of oxygen has replaced two of the groups of NO_3. It may be graphically shown as follows: —



Ordinary.



Basic (Bismuthyl).

30. The first of these is a white crystalline salt, which is prepared by dissolving metallic bismuth in nitric acid. It has little use, except in the preparation of other compounds of bismuth. The basic nitrate, sold at drug-stores as the subnitrate, or simply as "bismuth," is a white powder, obtained from the ordinary nitrate by the addition of water, whereupon a fine white precipitate falls, thus: —

$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2\ HNO_3,$$

or more properly, considering the water of crystallization,

$$Bi(NO_3)_3,\ 2\ H_2O + H_2O = BiONO_3,\ H_2O + 2\ HNO_3 + H_2O.$$

This is used largely as a cosmetic, and for relieving the irritation of chafed or chapped skin; also in cholera and kindred diseases, and in acute dyspepsia.

31. **Bismuth Trioxide, Bi_2O_3.** — This is also called *bismuth ocher*, the chief ore of bismuth, but may be obtained artificially by heating the metal in the oxidizing flame. It is of a deep yellow color when hot, but yellowish white when cold. Its principal use is as a paint.

32. **Bismuth Trichloride, $BiCl_3$.** — This may be prepared by heating bismuth in chlorine gas. If water is added to it, the basic bismuth chloride, or oxychloride, $BiOCl$, is formed, as is the case with antimony. The latter, however, is soluble in sodium tartrate or tartaric acid, but the former is not. Basic bismuth chloride is a fine white powder, and is used as a paint, known as "pearl white."

33. The Nitrogen Group. — From the similarity of their compounds, and their chemical affinity, nitrogen, phosphorus, arsenic, antimony, and bismuth are often classed together and called the *nitrogen group*. The following table will give a comparative view of their more important compounds: —

N = 14 NITROGEN	P = 31 PHOSPHORUS	As = 75 ARSENIC	Sb = 120 ANTIMONY	Bi = 208 BISMUTH
NH_3	PH_3	AsH_3	SbH_3	——
N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5
——	——	$AsCl_3$	$SbCl_3$	$BiCl_3$
——	——	——	$SbOCl$	$BiOCl$

SUMMARY OF CHAPTER

Comparative Study of Arsenic, Antimony, and Bismuth.
Sources of the metals.
  Wherein alike. Wherein different.
Reduction of the ores.
  Wherein similar — How similar to reduction of other metallic ores.
  In what respects different.
  Description of experiments illustrating methods.
Characteristics of the group.
  Compare two of them with the non-metals.
  Wherein are they all metallic in character.
  Compare in
    Color. Melting point.
    Density. Tendency to oxidize.
    Hardness. Solubility in acids.
    Malleability.

  - State any special characteristics, not common.
  - Compare bismuth and antimony as to certain classes of salts formed by each.
  - Compare arsenic and antimony in the same way.
- Uses of each.
  - Special use for metallic arsenic — Reason.
  - Same for antimony, and reason.
    - Antimony black — How made? — Use?
  - Same for bismuth, and reason.
- Compounds.
  - Compare the hydrogen compounds of arsenic and antimony as to
      - Method of preparing and chemical action.
      - Characteristics of each.
    - How distinguish one from the other?
    - Products formed when AsH_3 burns.
      - Experimental proof.
  - Oxygen compounds.
    - Names and formulæ.
    - Important one of arsenic — Why?
      - Appearance and uses.
      - Physiological action — Compare with antimony.
      - Antidotes. Solvents.
    - Appearance and use of bismuth oxide.
  - Sulphides.
    - Names and formulæ.
    - Method of preparing.
    - Appearance of each.
    - How distinguish As_2S_3 from SnS_2?
    - How distinguish As_2S_3 from Sb_2S_3?
    - How distinguish an antimony salt from one of bismuth?
  - Special compounds.
    - Paris green — Experimental preparation.
      - Appearance — Uses.
    - Butter of antimony — Chemical name and formula.
- Means of identifying.
  - For arsenic — Marsh's test; Scheele's test.
  - For bismuth and antimony.
- Comparison of the nitrogen group.
  - Compounds with hydrogen, oxygen, chlorine, etc.

CHAPTER XXV

IRON, NICKEL, COBALT

IRON: Fe = 56

1. **Distribution.** — Iron, the most useful of all metals, is also the most abundant and most widely distributed. It is found in nearly all clays and soils, and from these is taken up by plants, and through them makes its way into the animal economy. The color of many soils, rocks, and minerals is due to the presence of iron in some form. Pure iron does not occur in any considerable quantities, except in meteorites, of which some weigh many tons. The largest meteorites ever found were discovered by Lieutenant Peary in his Arctic explorations. One of these, weighing nearly one hundred tons, was brought back and placed in the Brooklyn Navy Yard. Meteorites are found to consist of iron, about 93 per cent, and nickel, 7 per cent.

2. **Iron Ores.** — A large number of iron ores are known, among which are the following: —

3. **Magnetite, Fe_3O_4.** — This is also known as *lode-stone*, on account of its magnetic properties.

4. **Hematite, Fe_2O_3.** — This ore received its name from the Greek word for *blood*, because of the red streak it gives on porcelain. It is a very abundant ore: two knobs, Iron Mountain and Pilot Knob, of the Ozark Range in Missouri, consist almost entirely of hematite, in masses ranging all the way from "the size of a pigeon's egg to that of a medium-sized church."

5. **Limonite, $Fe_2O_3, 2\,H_2O$.** — An ore resembling hematite, which gives a yellow streak on porcelain.

6. **Siderite, $FeCO_3$; Spathic Iron Ore.** — This is common in some localities, has a gray to brownish red color, and often contains manganese.

7. **Iron Pyrites, FeS_2,** is a very abundant ore, but on account of the difficulty experienced in reducing it, it is not used, except for the manufacture of sulphuric acid. It is commonly known as "fool's gold."

8. **Reduction of Ores.** — This is accomplished in a blast furnace, the essential features of which are shown in Figure 61. The furnace is from 50 to 75 feet in height, supported by masonry, and strengthened with boiler plate. It is lined inside with fire-brick. Near the bottom some pipes, *PP*, enter the furnace. These are called *tuyères*, or blast-pipes, and furnish a powerful blast of air. Just below these is an opening, *S*, where the slag is drawn off, and below this another opening, *I*, for drawing off the iron.

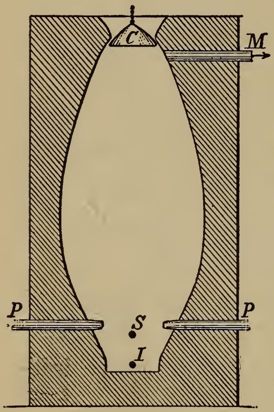


FIG. 61.

9. The furnace is charged from the top; first, wood for kindling being placed in the bottom, then alternate layers of coke and iron ore mixed with limestone. These are all dumped upon the cone-shaped top, *C*, which fits air tight and works automatically. When the ore and other materials fall upon the top, it lowers mechanically and allows the charge to roll into the furnace. Many of the gases formed in the interior of the mass are combustible, and are conducted off through the pipe *M*, and are burned in other furnaces.

Figure 62 shows a perspective view of the blast furnace. The various materials are lifted to the top by elevators; the molten iron is drawn off and molded in trenches in the ground under the shed.

Fig. 62.—Perspective View of Blast Furnace.

10. In accordance with the usual method of reducing metallic ores, the oxides of iron are mixed with coke and limestone and strongly heated. If an ore, not an oxide, is used, it is first calcined to convert it into an oxide. The coke serves as a deoxidizing agent, and the limestone, used as a flux, is melted, and renders the iron ore more fusible. The limestone then combines with the silica always present in the ore, and forms a molten glass, or *slag*, which floats upon the iron and prevents its oxidation by the strong currents of air. The iron thus obtained, nevertheless, absorbs in the intense heat of the furnace considerable quantities of sulphur, phosphorus, carbon, and silica, and in this impure form is not suited to many of the numerous demands for iron. From the blast furnace it is run off through trenches into molds, 2 to 4 feet long, which are called "pigs," and the iron is known as *cast* or *pig* iron. It is very brittle, coarse grained, and contains from 5 to 10 per cent of impurities.

11. Wrought Iron. — This variety is prepared in what are known as *puddling* furnaces. In these the low arching roof deflects the flames downward upon the broken cast iron. The furnace is lined with ferric oxide, Fe_2O_3, and as the cast iron melts, the carbon which it contains combines with the oxygen in the lining. By stirring the molten mass, or *puddling*, as it is called, the whole is gradually purified, until finally, as it is much more difficult to melt pure iron, the whole mass becomes pasty. This pasty mass, *bloom*, as it is called, is then removed and hammered with trip-hammers,

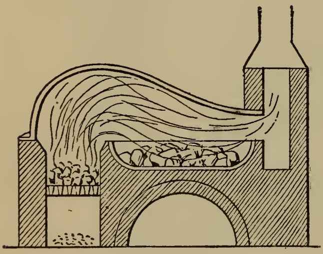


FIG. 63.

a process which drives out any remaining slag, and renders the iron malleable.

12. Steel. — Formerly steel was made from wrought iron by embedding bars of the latter in finely powdered charcoal and keeping at a red heat for about ten days. During this time the bars of iron slowly absorbed more or less carbon, and were converted into steel. Besides the expense and the length of time required in this process, there were two other serious objections to it: first, that there was no possible way of controlling accurately the amount of carbon taken up by the iron, and second, a steel bar was obtained which was not at all uniform in quality and texture.

13. Present Method of Manufacture. — At present, steel is made directly from cast iron, by the Bessemer process. An egg-shaped vessel, called a *converter*, is used. It is securely bound with boiler iron, and is lined with *ganister*, a siliceous earth, fusible only at a very high temperature. The converter, which will hold ten or more tons of iron, is mounted on axes, or trunnions. One of these, *A*, in Fig. 64, is hollow, so that a blast of air may be forced through it when the converter is in a vertical position. This trunnion opens into a pipe, *P*, which extends down the outside of the converter and opens into the *tuyère box*, *B*, beneath the body of the converter. Through the tuyère box, numerous small openings admit the air to the converter and its contents.

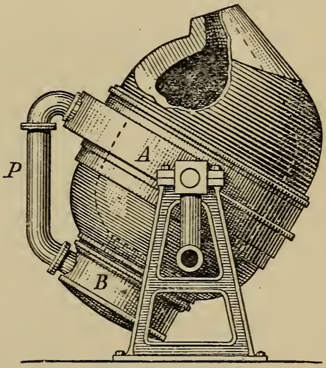


Fig. 64. A Converter.

14. Bessemer Process. — About ten tons of pig iron are placed in a *cupola* furnace, that is, one resembling a blast furnace in most of its details, but considerably smaller. When the iron is melted, it is run into the converter. Immediately the blast of air is turned on, and, bubbling up through the molten iron, the oxygen unites with the carbon and other impurities, burning them out. No heat is used in the operation except what is evolved by the combustion of the impurities themselves. About twenty-five or thirty minutes are required for the completion of the operation, during most of which time a brilliant shower of sparks is thrown from the mouth of the converter. This is represented in colors by the frontispiece. The converter on the right is shown in action; the one on the left, at the close of the process, discharging the molten steel into a pot, from which it will be poured into molds.

15. When the mass of flame and sparks no longer issues from the converter, the workmen know that the cast iron has had its impurities entirely removed, and is now *wrought* iron. Next, a weighed quantity of *spiegeleisen* or manganese iron, containing a known amount of carbon, is thrown into the converter, and in a moment or two the process is complete. In this way, in thirty minutes or less, ten tons of steel are obtained at a cost only a fraction of what it would be by former methods.

16. Basic-lining Process. — If the iron ore contains much phosphorus, the converter is lined with limestone, which, during the process of oxidation, takes up the phosphorus from the iron, and is converted into calcium phosphate. This is known as the *basic-lining process* and was put into practical use by the inventors, Thomas and Gilchrist.

17. Tempering Steel. — Tempering consists in hardening steel, by heating and then suddenly plunging into cold water or oil. Tempered in this way, it becomes much less malleable, but can take and hold a sharp edge. Different instruments require steel that has been heated to different temperatures; thus, surgical instruments after being hardened are again heated to about 225° or till a yellow film of oxide appears upon the surface. For ordinary cutlery, a temperature of about 250° is used, indicated by the appearance of a brown film, while clock and watch springs and such forms as require great elasticity are made of steel heated till blue, or about 290°. By heating any form of steel strongly and then cooling very slowly, the temper is "drawn," or removed, and the metal becomes like ordinary wrought iron.

18. Comparison of the Three Forms. —

CAST IRON.	STEEL.	WROUGHT IRON.
Impurities—5 to 10%.	1 to 2%.	0.36 to 0.5%.
Brittle.	Somewhat malleable.	Very malleable.
Coarse grained.	Fine grained.	Very fine grained.
Cannot be tempered.	May be tempered.	Cannot be tempered.
Lowest melting point.	Medium melting point.	Highest melting point.

19. Uses of Iron. — This is preëminently the "Steel Age." Day by day the uses of iron are increasing. The continual cheapening of both steel and wrought iron by improved methods has caused their use in thousands of ways where wood was formerly demanded. These applications are too well known, however, to need mentioning.

Compounds of Iron

20. Ferrous and Ferric Compounds. — Like several other metals, iron forms two general classes of compounds, the *ferrous* and *ferric*. The former are very unstable, and when exposed to the air gradually change to the ferric. The reaction in the presence of free acid may be indicated thus : —

$$2\ FeSO_4 + H_2SO_4 + O(air) = Fe_2(SO_4)_3 + H_2O.$$

If there is no free acid present, a part of the ferrous salt is converted into the ferric and another part into an insoluble basic salt.

Experiment 181. — *To distinguish between ferrous and ferric salts.* Pulverize a crystal of ferrous sulphate and dissolve in a few cubic centimeters of water; divide into three portions. To one portion add promptly a few drops of ammonium hydroxide, to the second a few drops of potassium sulphocyanide solution, to the third a few drops of potassium ferrocyanide solution. Notice the results in each case. Now dissolve a little ferric chloride or nitrate in water, divide into three parts, and repeat the same tests. Compare results and tabulate as below.

	NH_4OH	KSCy	K_4FeCy_6
$FeSO_4$			
Fe_2Cl_6			

Experiment 182. — *To show the instability of ferrous salts.* Quickly dissolve in cold water a little powdered ferrous sulphate, and divide into two parts. To one add a few drops of ammonium hydroxide, and note the color of the precipitate. Allow both portions to stand for some time. How does the greenish precipitate change in color? Into what is it apparently converted? Has the other portion changed any in appearance? How? Test it with potassium sulphocyanide or ammonia to learn what kind of a salt it is now. What are your conclusions?

21. This experiment will show the tendency of ferrous salts. What is thus accomplished slowly by the action of atmospheric oxygen at ordinary temperatures is effected rapidly by nitric acid at the boiling point. As already seen, this acid is a strong oxidizing agent, readily giving up a part of its oxygen when heated, thus: —

$$2\ HNO_3 + (heat) = H_2O + N_2O_4 + O.$$

This nascent oxygen rapidly attacks any oxidizable substance that may be present. With ferrous chloride in the presence of hydrochloric acid, the following reaction takes place: —

$$2\ FeCl_2 + 2\ HCl + O = Fe_2Cl_6 + H_2O.$$

Experiment 183. — *To show the effects of nitric acid upon a ferrous salt.* Dissolve a little ferrous sulphate in water, add a few drops of sulphuric acid and then some nitric acid, and heat to the boiling point for two or three minutes. Does the solution change any in color? Now test a part of it in two or three ways to learn whether it has been converted into a ferric salt. What are your conclusions?

22. Ferric salts, on the other hand, may be reduced to the ferrous by treatment with hydrogen sulphide or nascent hydrogen. The reaction may be shown thus: —

$$Fe_2Cl_6 + H_2 = 2\ FeCl + 2\ HCl.$$

Experiment 184. — *To prove the above statement.* Put into a test-tube about 5 cc. of a solution of ferric chloride or nitrate and drop into it a good-sized granule of zinc. Now add a little strong sulphuric or hydrochloric acid to cause a rapid evolution of hydrogen. In from 5 to 7 minutes the yellow color of the ferric solution should have disappeared. Test with ammonia or potassium sulphocyanide. What are your conclusions in the matter?

23. How to distinguish Ferrous from Ferric Salts. — From the preceding work it will be learned that ferrous salts in solution are usually colorless or very pale green, while ferric salts are light brown. Potassium sulphocyanide serves as the most delicate method of detecting a ferric salt, because even exceedingly small quantities will show the characteristic wine-red color ; with ferrous salts, however, it shows no reaction, hence will not indicate their presence. Ammonia gives precipitates with both classes of salts, deep reddish brown with the ferric, and greenish with ferrous. Potassium ferrocyanide and ferricyanide may also be used to distinguish between the two.

24. Sulphates of Iron. — *Ferrous sulphate*, $FeSO_4, 7\,H_2O$, the only common ferrous salt, is formed when iron is dissolved in sulphuric acid. It is commonly known as *copperas* or *green vitriol*, and occurs in light green crystals. It is somewhat efflorescent, and gradually gives up its water of crystallization, turning white and breaking up into a powder, anhydrous ferrous sulphate. It is used considerably in making black ink and dyes, also as a deodorizer and disinfectant.

EXPERIMENT 185. — *To show one method of making ink.* Prepare a strong solution of ferrous sulphate, and add to it a little of another solution made by soaking some powdered nutgalls in water. Notice the bluish black color obtained. Allow it to stand a few minutes, and notice whether the color deepens. Now add to the solution a few drops of a solution of oxalic acid. What happens? This suggests a method for removing ink stains without injuring the fiber of the paper or cloth.

25. Ferric Chloride, Fe_2Cl_6. — This is a brownish yellow salt, which rapidly absorbs moisture when exposed to the air. It is obtained when iron is treated with aqua regia or dissolved in hydrochloric acid with the addition of a crystal of potassium chlorate. It has little use except in the laboratory.

26. The Sulphides. — *Ferrous*, FeS; *Ferric*, FeS_2. The former is a dark gray substance somewhat resembling cast iron. It is made by fusing together, in the proportion of their atomic weights, iron and sulphur, and is used extensively in the laboratory for making hydrogen sulphide. *Ferric Sulphide* is the native ore, pyrite, or "fool's gold." It is of a brassy yellow color, and frequently occurs in beautiful cubes or modified forms of the cube. It is very abundant, but has little use except in the preparation of sulphur dioxide for the manufacture of sulphuric acid.

27. The Oxides. — *Ferric*, Fe_2O_3. This is met with in the ore, hematite, already mentioned. It is also formed when iron is exposed to moisture, and is known as *rust.* In the hydrated form, $Fe_2(OH)_6$, ferric hydroxide, it is formed when any ferric solution is treated with ammonia. As a reddish brown precipitate it has already been seen in several of the preceding experiments. It is sometimes used as an antidote for arsenic poisoning. *Magnetite*, Fe_3O_4, is regarded as a mixture, FeO, Fe_2O_3, the first being the unimportant *protoxide.* The greenish precipitate obtained in some of the preceding experiments by adding ammonia to a solution of ferrous sulphate is ferrous hydroxide, $Fe(OH)_2$, or FeO, H_2O; that is, the hydrated form of the protoxide, FeO.

NICKEL: $Ni = 58.7$

28. Distribution. — Like iron, nickel is never found pure except in meteorites, of which, as already stated, it often constitutes from 5 to 7 per cent. Its ores are fairly well distributed, but are nowhere in great abundance, and with them are always associated cobalt and iron.

29. Characteristics of Nickel. — Nickel is a silvery white metal with the faintest yellow tinge; it is susceptible of a very high polish and does not tarnish in the air. It is very hard, melts at about white heat, may be welded like iron, is magnetic, and becomes brittle like cast iron upon the addition of such impurities as cast iron always contains — carbon and silicon. Its density is but little greater than that of iron. It is soluble in nitric acid. In most respects, therefore, it is very similar to iron, and strikingly different in one respect only.

30. Uses. — Nickel is used very extensively in alloys, among them being certain coins; in german silver, consisting of nickel, zinc, and copper; and with steel for armor plating in making what is known as Harveyized steel, noted for its hardness and toughness.

Nickel is also used largely in plating various articles of ornament and utility.

31. Compounds. — The general color of the more common nickel salts is green. Among these may be named the nitrate, $Ni(NO_3)_2$, chloride, $NiCl_2$, sulphate, $NiSO_4$; also $Ni(OH)_2$, nickel hydroxide. This last may be prepared from a solution of any of the preceding salts by adding a few drops of ammonia or caustic potash.

Experiment 186. — To 3 or 4 cc. of a solution of any of the above salts, add a little caustic soda. Describe the precipitate that forms. Test its solubility in hydrochloric acid. Write the two reactions taking place.

32. A fifth compound which may be mentioned is the *sulphide*, NiS. It is prepared, as is the sulphide of other kindred metals, by adding ammonium sulphide to a neutral or alkaline solution of any nickel salt.

Experiment 187. — Add a little ammonium sulphide to 4 or 5 cc. of a solution of any nickel salt. Describe the nickel sulphide that forms. Test its solubility in hydrochloric acid. Also in aqua regia. Write the reactions.

33. Nickel salts fused in a borax bead impart to it a smoky yellow or brown color according to the amount of the nickel present.

Experiment 188. — Make a small loop in the end of a platinum wire, heat it in the burner flame and dip into some powdered borax. Now hold again in the flame until the borax which swells up at first has formed a clear transparent glassy bead. Dip into a solution of some nickel salt, or touch it to a tiny particle of nickel salt and fuse again. If you use the solution, it may be necessary to dip the bead several times. Note the color imparted.

Experiment 189. — *To find the composition of a coin.* Put a "nickel" into an evaporating dish and treat with warm nitric acid for a few minutes. Remove the coin and add a few cubic centimeters of water. Pass a current of hydrogen sulphide through the solution for several minutes, and filter out the black precipitate. After washing it, punch a hole in the bottom of the filter and wash the precipitate through into a beaker with a little nitric acid. Heat until it dissolves. What colored solution is obtained? What metal is indicated by this color? Add ammonia till alkaline; is a deeper blue solution obtained? What metal is it?

Boil nearly to dryness the filtrate from the black precipitate above; note the color. Does this indicate any salts with which you are familiar? Make a borax bead as directed in the preceding section and test the solution; what are your conclusions?

Of what two metals is the coin composed? If you can obtain one of the lighter-colored pennies seen occasionally, test it in the same way.

Cobalt: $Co = 59$

34. Characteristics. — This is a somewhat rare metal that is usually found associated with nickel. It is very similar to iron and nickel in its characteristics, being steel-gray in color, very hard, magnetic, and of about the same melting point. It is permanent in the air. The metal itself has no application in any of the arts.

35. Compounds. — Cobalt forms salts with the three common acids; the *nitrate*, $Co(NO_3)_2$; *chloride*, $CoCl_2$;

and *sulphate*, $CoSO_4$. These are all some shade of red in color, but when heated so as to lose their water of crystallization they become blue.

36. The *hydroxide* and *sulphide* are prepared just as the similar compounds of nickel are.

EXPERIMENT 190. — Prepare the last two as you did the corresponding compounds of nickel in Experiments 186 and 187, and test their solubility in the same way.

37. None of the above has much use except occasionally in the laboratory. There are one or two others, however, which have extensive application in the arts. Among these may be named

38. *Smalt*, a silicate of cobalt. When fused with glass or pottery ware this imparts a beautiful blue color, and is largely used for that purpose. It may be illustrated in the following experiment : —

EXPERIMENT 191. — Prepare a borax bead as you did for nickel, and fuse with it some salt of cobalt. Note the color imparted. If it is too dark to recognize, it is because too much cobalt has been introduced. Break out the bead, and repeat the experiment, using less of the compound.

39. Sympathetic Inks. — They are inks which under ordinary circumstances are invisible, or nearly so, on paper ; when heated or treated by some other method they become legible. Many of these have some compound of cobalt as their basis.

EXPERIMENT 192. — Mix a solution of some compound of cobalt with one of ferrous sulphate. Using this as an ink, write with it upon paper, and when the inscription is dry heat it. Do you obtain a distinct green color, though before it was nearly invisible? In the same way try potassium iodide mixed with the cobalt solution. Results?

SUMMARY OF CHAPTER

- Iron, Nickel, Cobalt.
- Occurrence — Wherein are iron and nickel similar.
  - History of some large meteorites.
  - Some important ores of iron.
    - Names and formulæ.
    - Localities where found.
- Reduction of iron ores — Description of blast furnace.
  - Drawing of essential features.
  - Method of charging the furnace.
  - Chemical action that takes place.
  - Plan of molding *pig* iron.
- Varieties of iron — Three.
  - How different in composition and properties?
  - Description of the *puddling* furnace.
    - Chemical action.
  - Meaning of term *bloom*.
  - Description of the *converter*.
    - Explanation of the chemical changes.
  - Plans used for phosphorus-bearing iron ores.
- Tempering steel.
  - Meaning of the term.
  - Process used.
- Characteristics — Compare iron and nickel as to
  - Color.
  - Hardness.
  - Melting point.
  - Magnetic properties.
  - Susceptibility of polish.
  - Permanency in the air.
  - Several other similarities.
- Uses — Compare nickel and iron.
- Compounds — Classes of iron compounds.
  - Compare them as to stability.
  - Plans for distinguishing the two.
  - Method of converting each into the other. Explain the chemical action in each case.
  - Names of three or four compounds of iron and their uses.
  - Compare the compounds of nickel and cobalt in color and method of preparation.

CHAPTER XXVI

THE PLATINUM GROUP

PLATINUM: Pt = 195

1. Where obtained. — Platinum is a rare metal, usually found uncombined, but almost always associated with *iridium*, and smaller quantities of *palladium* and *osmium*. The greater portion of the commercial supply comes from the Ural Mountains in Russia, though small quantities have been obtained in California, Arizona, and some parts of South America.

2. Characteristics. — Platinum is a hard, silvery white metal, unaffected by the air at any temperature. It is somewhat malleable, but becomes less so if alloyed with a small per cent of iridium, though by this means its hardness is increased. It is a very dense metal, with a specific gravity of 21.5, osmium, the heaviest metal known, having a density of only 22.5. The melting point of platinum is about 1900° C., and it can be fused only by such intense heat as that of the oxyhydrogen blowpipe, or acetylene blast lamp. Like gold, it is soluble only in nitro-hydrochloric acid, forming therewith platinic chloride, $PtCl_4$.

3. Property of occluding Gases. — The most remarkable property of platinum is that of *occluding* or absorbing various gases within its pores. It is estimated that at ordinary temperatures it will absorb 200 times its own volume of oxygen. In the *spongy* form, that is, when finely divided, as in the case of a metallic precipitate, the power of absorption is especially striking. If a current of hydrogen be directed against the platinum sponge, so rapid will be the absorption that almost instantly the metal will become red hot, and in two or three seconds the jet will be ignited.

EXPERIMENT 193. — Repeat Experiment 23 with hydrogen.

4. If into a jar of hydrogen and oxygen, mixed in the proportion of two to one, a platinum sponge be introduced, the gases will be made to unite with explosive violence. This power of occlusion may be seen in the case of certain other gases, as ammonia and common coal gas.

EXPERIMENT 194. — Support upon a ring-stand a small flask containing some strong aqua ammonia; warm it gently so as to secure a constant and rapid evolution of gas from the liquid. Now heat to bright redness in the Bunsen flame a spiral of platinum wire, made by coiling it about a small glass rod, and hold it in the neck of the flask. The wire will continue to glow, and the intensity of the heat will often be increased.

Take this same platinum coil and flatten it a little so as to bring the parts of the spiral closer together; hold it in the Bunsen flame until red hot, then turn off the gas. When the redness has *just* disappeared from the wire, again turn on the gas. The wire will quickly grow red again, and in two or three seconds will re-ignite the escaping gas. This may be repeated over and over again. The same may be tried with a spirit lamp.

5. Platinum Alloys. — Platinum readily alloys with lead, silver, antimony, and other metals which are easily reduced from their compounds; hence it should never be strongly heated in contact with them. It is likewise injured by heating in a smoky flame, or by placing upon red-hot charcoal, which blisters the surface. Platinum vessels are usually cleaned by fusing in them for a few minutes some acid potassium sulphate, $KHSO_4$, and are polished by rubbing gently with a little fine sea-sand.

6. Uses. — The rarity of the metal and the long, complicated processes involved in preparing it in the pure form, make it almost as expensive as gold. It is worth from 50 cents to 75 cents per gram, or about $300 per pound. It is made into wire, foil, and various articles for use in the chemical laboratory, such as crucibles, dishes, tips of forceps, etc. To the chemist it is simply indispensable in analytical work.

SUMMARY OF CHAPTER

- Names of the elements in this group.
- Source of the supply of platinum.
- Characteristics of platinum.
    - Experiments that illustrate these.
- Alloys of platinum.
- Uses and value of the metal.
- Compare with metals studied previously as to
    - Color.
    - Melting point.
    - Density.
    - Tendency to oxidize.
    - Power of occluding gases.
    - Solubility in acids.

CHAPTER XXVII

CHROMIUM AND ITS COMPOUNDS

CHROMIUM: $Cr = 52$

1. Where found. — Chromium is a rare metal which received its name from the Greek word, *chromos*, meaning *color*, and is so named because of the striking colors of most chromium compounds. It occurs chiefly in the Shetland Islands in the form of *chromite*, or chrome iron, Cr_2O_3, FeO, also written $FeCr_2O_4$. It is also found as *crocosite*, $PbCrO_4$, in Siberia, Brazil, and the Philippine Islands.

Compounds of Chromium

2. Classes. — In the metallic form chromium has but little use. Its compounds, however, have various applications. They may be divided into two important classes:

3. Chromium as a True Metal. — Those in which chromium acts as a metallic element, with the power of replacing the hydrogen in acids to form salts. Of these, as in the case of iron, mercury, and others, there are two divisions, the *chromous* and *chromic*, but only the latter are important. As examples, we have chromic chloride, $CrCl_3$, chromic nitrate, $Cr(NO_3)_3$, and chromic sulphate, $Cr_2(SO_4)_3$. These as a rule are green in color, but the double sulphate of potassium and chromium, $K_2Cr_2(SO_4)_4$, is violet. Solutions of the chromic salts are precipitated by caustic potash or ammonia, giving the hydroxide, $Cr(OH)_3$.

4. Chromium as an Acid Producer. — Those in which chromium serves as a non-metallic element, forming acids. Of these there are three classes, but only two merit notice, the *chromates* and the *dichromates*. The chromates are based on the theoretical chromic acid, H_2CrO_4, wherein the chromium atom is that which distinguishes the acid, as does the sulphur in sulphuric acid, H_2SO_4. The general color of the chromates is yellow, though there are some exceptions. The best-known example is potassium chromate, K_2CrO_4.

EXPERIMENT 195. — *To prepare some other chromates.* To 3 or 4 cc. of a solution of potassium chromate in a test-tube add a few drops of lead nitrate or acetate in solution. Notice the color of the lead chromate formed. In the same way prepare some barium chromate by using barium chloride with the potassium chromate. Compare its color with the preceding. Now prepare some silver chromate by using silver nitrate solution with the potassium chromate. Note its appearance.

5. Potassium Dichromate, $K_2Cr_2O_7$, orange-red in color, is the best-known example of the dichromates.

Tabular view of the compounds: —

I. Chromium as a true metal: —
  1. Chromous.
  2. Chromic —
    a. Chloride, $CrCl_3$.
    b. Nitrate, $Cr(NO_3)_3$.
    c. Sulphate, $Cr_2(SO_4)_3$.

II. Chromium as an acid former: —
  1. Chromates —
    a. Potassium, K_2CrO_4.
    b. Lead, $PbCrO_4$.
    c. Barium, $BaCrO_4$.
  2. Dichromates —
    a. Potassium, $K_2Cr_2O_7$.

6. Conversion of One Class of Compounds into Another. — Though the chromium salts are stable, they may easily be converted from one into another. By adding a little acid and passing a current of hydrogen sulphide through a solution of potassium chromate, the latter is changed into a salt of the first class (chromic). The change of color to green indicates that the reduction has taken place; at the same time free sulphur is precipitated. Thus: —

$$2\ K_2CrO_4 + 3\ H_2S + 10\ HCl = 4\ KCl + 2\ CrCl_3 + 8\ H_2O + 3\ S.$$

Experiment 196. *To prove the above.* — Put into a test-tube a few cubic centimeters of a solution of potassium chromate, and add a little hydrochloric acid. Now pass through the solution a current of hydrogen sulphide. What change in color is noticed? Is the sulphur precipitated?

7. Sulphur dioxide has a like reducing effect upon a chromate solution.

Experiment 197. — Put into a test-tube 4 or 5 cc. of a solution of sodium sulphite, Na_2SO_3, and a little hydrochloric or sulphuric acid. Notice that sulphur dioxide gas is being liberated. Now add a little potassium chromate or dichromate. How does the chromium solution change in color? If sodium sulphite is not to be had, fill a bottle with sulphur dioxide gas, pour in the dichromate, and shake.

Experiment 198. *To show the reduction of the dichromates to the chromic salts.* — Put into an evaporating dish 10 or 15 cc. of a solution of potassium dichromate, add some hydrochloric acid, and boil a few minutes. The addition of a little alcohol will hasten the action. Notice the change in color. What compound of chromium is probably formed?

8. The above experiments prove that either the chromates or dichromates may be reduced to salts of the first class. The reaction that takes place in the latter is as follows: —

$$K_2Cr_2O_7 + 14\ HCl = 2\ KCl + 2\ CrCl_3 + 7\ H_2O + 6\ Cl.$$

Experiment 199. — To 2 or 3 cc. of potassium chromate solution in a test-tube add a few drops of hydrochloric or nitric acid. How does its color change? What other salt of chromium in solution does it resemble? In like manner treat 2 or 3 cc. of potassium dichromate solution with a few drops of caustic potash or any alkali. Notice the change in color; what chemical change has taken place?

9. It will be seen by the above experiments that the chromates and dichromates may readily be converted, the one into the other. The reactions taking place are shown thus: —

$$2\ K_2CrO_4 + 2\ HCl = K_2Cr_2O_7 + 2\ KCl + H_2O,$$

and $$K_2Cr_2O_7 + 2\ KOH = 2\ K_2CrO_4 + H_2O.$$

10. The Oxides of Chromium. — *Cr_2O_3 and CrO_3, chromium sesquioxide and trioxide.* The former is basic in properties, the latter acid. The former is green, and is used in imparting a green color to glass and enamel; the latter is a dark red crystalline solid.

Experiment 200. — Make a borax bead and dip it into a solution of some chromium salt, then fuse in the burner flame. If a good color is not secured the first time, repeat the operation.

11. Chromium trioxide may be prepared by adding strong sulphuric acid to a saturated solution of potassium dichromate. After standing for some time, beautiful red needle-like crystals separate from the liquid, thus: —

$$K_2Cr_2O_7 + H_2SO_4 = 2\ CrO_3 + K_2SO_4 + H_2O.$$

These cannot be filtered out by ordinary methods, as the trioxide is a strong oxidizing agent and readily gives up a part of its oxygen to any organic compound, itself being changed into the sesquioxide, thus: —

$$2\ CrO_3 = Cr_2O_3 + 3\ O.$$

12. Chromium trioxide is theoretically the anhydride of chromic acid, H_2CrO_4, and seemingly ought to produce it when added to water, thus :—

$$CrO_3 + H_2O = H_2CrO_4.$$

But the action is merely one of solution, and the acid is not formed.

13. Chromic Hydroxide, $Cr(OH)_3$.— This is a green precipitate formed when ammonia or caustic potash is added to any chromic salt, as the chloride or sulphate.

$$CrCl_3 + 3\ KOH = Cr(OH)_3 + 3\ KCl.$$

14. Uses of the Compounds.— Some of the uses of chromium compounds, among others those of the sesquioxide and of lead chromate, have been mentioned. Both the chromate and dichromate of potassium are used as reagents in the laboratory, and in the arts for dyeing and calico printing. If the reaction,

$$K_2Cr_2O_7 + 8\ HCl = 2\ KCl + 2\ CrCl_3 + 4\ H_2O + 3\ O,$$

is studied, it will be seen that potassium dichromate, treated with hydrochloric acid, is a strong oxidizing agent. Each molecule gives up three atoms of oxygen. If no other salt is present, this nascent oxygen unites with the hydrogen in six additional molecules of hydrochloric acid, thus :—

$$6\ HCl + 3O = 3\ H_2O + 6\ Cl.$$

Combining the last two reactions, it will be seen that we have the one given on page 319, showing the reduction of potassium dichromate to chromic chloride. However, if any oxidizable salt be present, as, for example, a ferrous compound, the nascent oxygen readily converts it from the ferrous to the ferric condition. This is shown in the following reaction: —

$$2\,FeCl_2 + 2\,HCl + O = Fe_2Cl_6 + H_2O.$$

On account of this property, potassium dichromate is frequently used by chemists in estimating the amount of iron present in a solution.

Experiment 201. — *To illustrate this use and the oxidizing power of potassium dichromate.* Dissolve a little ferrous sulphate in a few cubic centimeters of water and add some hydrochloric acid. Now add gradually drop by drop a solution of potassium dichromate. Notice how the solution changes to green. Test a portion of it with potassium sulphocyanide and learn whether the solution has been oxidized to the ferric condition. What are your conclusions? Study some of the foregoing reactions and see whether you can determine why the solution became green.

SUMMARY OF CHAPTER

Origin of the term *chromium*. Why applied to this metal.
Classification of the chromium compounds.
  Names and formulæ of the most important.
Relation of the classes of compounds.
  Method of converting those of second class to first.
  Indication of the change.
  Method of converting chromates into dichromates, and *vice versa.*
Compare the two oxides in
  Appearance.
  Properties.
Commercial uses of certain compounds.
  Chromium sesquioxide.
  Chrome yellow.
Laboratory uses.
  What uses as a reagent.
  How used as an oxidizing agent.
  Experiment to illustrate.

CHAPTER XXVIII

MANGANESE AND ITS COMPOUNDS

MANGANESE: Mn = 55

1. Where found.—This is a somewhat rare metal, often associated with iron ores. The most abundant natural compound is the dioxide, MnO_2, known as *pyrolusite.* In the metallic form, manganese has little use, but some of its compounds are valuable.

Compounds of Manganese

2. Classes. — These may be classified as follows: —

3. As a Metal. — Those in which manganese acts as a metal, that is, having the power of replacing hydrogen in acids. These may be divided into

a. Manganous,
b. Manganic,

of which only the former are important. The most common of these are *manganous chloride*, $MnCl_2$, and *manganous sulphate*, $MnSO_4$, both crystalline salts, pink in color. From these may be prepared the *hydroxide*, $Mn(OH)_2$, by adding ammonia to a solution of either salt; also the *sulphide*, MnS, by adding ammonium sulphide.

EXPERIMENT 202. — Using a solution of either manganous chloride or sulphate, prepare the hydroxide and sulphide as indicated above and describe their appearance. Test their solubility in hydrochloric acid. State results.

4. Manganese Dioxide. — In this connection we shall notice the most important of the oxides, MnO_2, *manganese dioxide.* It is a black compound, and is used in preparing oxygen, bromine, chlorine, and iodine. Notice the similarity in method of the last three.

Cl	MnO_2	$+ 2\,NaCl +$	$2\,H_2SO_4$	$= Cl_2 +$	$MnSO_4 +$	$Na_2SO_4 +$	$2\,H_2O$
Br	“	$+ 2\,NaBr +$	“	$= Br_2 +$	“ +	“ +	“
I	“	$+ 2\,NaI +$	“	$= I_2 +$	“ +	“ +	“

5. As an Acid Former. — Compounds in which manganese serves as an acid-forming element. Of these, there are two classes,

a. Manganates,

b. Permanganates.

The first of these is based upon a theoretical acid, *manganic,* H_2MnO_4, and none is of special interest to us. The best-known example of the second is potassium permanganate, $KMnO_4$.

6. Potassium Permanganate. — This is a dark purple crystalline salt, soluble in water. It is used frequently in the laboratory as a reagent, in a technical way for the estimation of iron in iron ores, and for the testing and purification of cistern water. Like nitric acid and potassium dichromate (see pages 88, 321), it is a strong oxidizing agent. When treated with hydrochloric or sulphuric acid, it gives up oxygen, thus: —

$$2\,KMnO_4 + 6\,HCl = 2\,KCl + 2\,MnCl_2 + 3\,H_2O + 5\,O;$$

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O.$$

The nascent oxygen thus obtained may be used in oxidizing ferrous salts to the ferric condition, or in destroying (oxidizing) the organic matter contained in a solution. In the case of the iron the reaction may be shown thus: —

$$10\ FeSO_4 + 8\ H_2SO_4 + 2\ KMnO_4$$
$$= K_2SO_4 + 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + 4\ H_2O;$$

or, the five atoms of oxygen set free as shown above decompose five additional molecules of sulphuric acid, thus: —

$$5\ O + 5\ H_2SO_4 = 5\ H_2O + \text{—}\ (SO_4)_5.$$

Then the five (SO_4) groups or *ions* unite with the $10\ FeSO_4$, forming the ferric salt, $5\ Fe_2(SO_4)_3$. Sometimes it is written thus: —

$$10\ FeO + 5\ O = 5\ Fe_2O_3,$$

which expresses in a simple form the same change from a ferrous to a ferric condition.

EXPERIMENT 203. — *To show the oxidizing power of potassium permanganate.* To a fresh solution of ferrous sulphate add one or two cubic centimeters of sulphuric acid, and then slowly, drop by drop, potassium permanganate until the solution *just begins* to turn pink. Now test it with potassium sulphocyanide or ammonium hydroxide. Have you obtained a ferric salt? In this connection study the preceding reactions.

In the same way test some cistern water that has an offensive odor. Before adding the permanganate heat the water nearly to boiling. Does it lose its odor by this treatment? In the same way try some cistern water discolored with cedar shingles; is the color removed? Try also a strong solution of logwood; can you remove the dark color?

What instances can you give in which nitric acid has served as an oxidizing agent? Potassium dichromate?

7. The sulphuric acid is added simply to dissolve a dark-colored precipitate that would otherwise form and obscure the results. In purifying cisterns, of course the acid cannot be used, but the brown solid in a short time settles to the bottom and remains there. The amount of organic matter in cistern water may be learned by measuring the amount of potassium permanganate added before the water begins to turn pink. Sometimes a manganese solution or salt is proved by the color it imparts to the borax bead.

Experiment 204. — Prepare a bead as in the case of nickel or cobalt, and fuse with some salt of manganese. Notice the beautiful color imparted.

SUMMARY OF COMPOUNDS

- *Class I*
  A true metal in its chemism.
  1. Manganous
     - *a.* Chloride, $MnCl_2$.
     - *b.* Sulphate, $MnSO_4$.
     - *c.* Hydroxide, $Mn(OH)_2$.
     - *d.* Sulphide, MnS.
  2. Manganic, Dioxide, MnO_2.
- *Class II*
  An acid-forming element.
  1. Manganates, not important.
  2. Permanganates, Potassium, $KMnO_4$.

Compare the above compounds with those of chromium and note the few differences.

SUMMARY OF CHAPTER

- Occurrence of manganese.
  - How associated. Chief ore.
- Classification of its compounds.
  - Compare with the compounds of chromium, showing wherein similar and wherein different.
- Uses of certain compounds.
  - Manganese dioxide.
    - Appearance.
    - What laboratory uses.
    - What commercial uses.
  - Potassium permanganate.
    - Appearance.
    - Laboratory uses. Experiments to illustrate.
    - Practical uses. Experiment to illustrate.

APPENDIX A

QUALITATIVE ANALYSIS

It is not intended in the following pages to give anything like a complete system of qualitative analysis. Such would be impossible, keeping within the necessary bounds of a high-school text. As a matter of reference, however, and to meet the demand of any who may care to pursue to some extent this line of work, the following brief outline is offered.

The student has noticed already that a reagent which will precipitate some metals from their solutions may have no effect upon various other metals. Taking advantage of this fact, we are able to divide the metals into groups, and then to separate the members of these groups one from another. Accordingly, depending upon the reagents used for precipitating the metals, five divisions are usually made as follows: —

Group I	1. Lead 2. Mercury (*ous* salts) 3. Silver	Precipitated as chlorides, $PbCl_2$, Hg_2Cl_2, $AgCl$, by using hydrochloric acid.
Group II	Antimony Tin Arsenic Mercury (*ic* salts) Copper Bismuth Cadmium	Precipitated as sulphides Sb_2S_3, SnS or SnS_2, etc., with sulphureted hydrogen. The first three are soluble in yellow ammonium sulphide or sodium sulphide; the others, not.

Group III	Iron Aluminum Chromium Cobalt Nickel Manganese Zinc	The first three are precipitated as hydroxides with ammonia, and constitute division *one* of this group. The last four are precipitated by ammonium sulphide as sulphides.
Group IV	Calcium Strontium Barium Magnesium	Precipitated as carbonates, $CaCO_3$, $SrCO_3$, etc., with ammonium carbonate from an alkaline solution.
Group V	Lithium Ammonium Sodium Potassium	Not precipitated by any common reagents. Most of them usually tested by color imparted to flame, or the spectrum.

The General Plan. — Suppose now we have a solution which may contain salts of any or all of the above metals. By adding hydrochloric acid, those of the first group would be precipitated and their chlorides separated by filtering. The filtrate would contain the remaining four groups. This would now be treated with hydrogen sulphide, whereby the second group metals may be precipitated and filtered out. In a similar way the separation of the third, fourth, and fifth groups would be effected. All that remains is to separate the metals of each individual group and prove their presence by means of some distinctive test.

Ionic Theory. — A clear understanding of the processes underlying any qualitative analysis is rendered much easier by what is known as the *Ionic* theory. It has long been observed that certain elements or groups of elements always give the same distinctive tests with certain reagents. For example, a silver solution gives the same characteristic precipitate with any soluble chloride, whether it be hydrochloric acid, sodium chloride, or any other.

Suppose in analyzing an unknown solution we have found four bases and four acid radicals: each base might have been combined with each of the acid groups, making in all sixteen possible cases. Were we compelled to test for each one of these possible compounds, analysis would be very tedious; but, as already stated, each base affords the same test as if it existed alone.

It seems, therefore, that when substances are dissolved, they become more or less dissociated. For example, hydrochloric acid becomes largely broken up into hydrogen and chlorine atoms; potassium chlorate into potassium, K and ClO_3, groups. As the solution becomes more dilute, this dissociation as a rule increases.

Ions. — These dissociated atoms or groups of atoms are called *ions*, and the process itself, *ionization*. They are regarded as being charged with electricity, and are of two kinds, *anions* or negative ions, and *cathions* or positive ions. The metals, ammonium, and hydrogen are cathions; the acid radicals and elements, like NO_3 and Cl, and the group HO, hydroxyl, are anions. This is often called the theory of *electrolytic dissociation*, and concisely stated is that when compound substances are dissolved in water, they are to a greater or less extent broken up into their constituent anions and cathions.

Application of the Theory. — In the brief space of this text it is impossible to make application of the theory to any extent. For this the student is referred to Ostwald's *Analytical Chemistry*, translated by McGowan. An illustration may, however, make the theory somewhat clearer. Suppose we have a solution containing lead nitrate, $Pb(NO_3)_2$, silver nitrate, $AgNO_3$, and mercurous nitrate, $HgNO_3$. According to the ionic theory, the solution contains, not molecules of the three compounds mentioned, but largely individual ions of Pb, Ag, Hg, and (NO_3); hence, tests need be made only for these four. Now, when we add dilute hydrochloric acid, we introduce two other ions, H and Cl. When those of Pb, Ag, and Hg meet with the Cl ions, compounds form, which in the main are insoluble in water, hence are not dissociated or broken up into ions, and therefore fall as precipitates. The same is true in any other chemical reactions.

Details of the Work. Group I. — Take about two-thirds of the unknown solution, "Solution A," and add to it a little hydrochloric acid; if any of the first group metals are present, they will come down as a white precipitate. Filter out and save the clear filtrate for work with the remaining groups. We will label this "Solution B." To be sure that enough hydrochloric acid has been used, add a drop or two to this filtrate. If it becomes turbid more must be added, and the whole solution again passed through the filter paper. Now wash the precipitate on the paper two or three times with cold water, and throw out the wash water. Next punch a hole in the bottom of the paper, and by directing a stream of water from the wash bottle upon the precipitate wash it through into a beaker. Do not use too much water, however; usually 50 to 75 cc. will be sufficient. If the precipitate is not easily loosened by the stream of water, remove it with a spatula or stirring rod, and add it to what has already been washed into the beaker. Next, heat this to the boiling point and after a minute or two filter quickly.

If any precipitate remains upon the filter, wash once or twice with hot water.

Tests for Lead and Mercury. — Lead chloride is very soluble in hot water, and if it was present it will now be found in the filtrate. Test a portion of it with potassium dichromate, $K_2Cr_2O_7$; another portion, with potassium iodide, KI, or sulphuric acid. The first two give distinctive yellow precipitates, the third, a heavy white one, somewhat soluble in water, but almost entirely insoluble in alcohol. Any precipitate left on the filter paper above will contain the mercurous and silver chlorides, if any were present. The latter of these is very soluble in ammonia; so pour upon the filter paper a few cubic centimeters of ammonium hydroxide. If mercury is present, the precipitate will turn black, and further proof is unnecessary.

TABLE I

SEPARATION OF LEAD, MERCURY, AND SILVER

To the unknown solution, add HCl, filter out the chlorides, and wash the precipitates. Save the filtrate for determining metals of Group II and those following. Mark it "Solution B." Transfer the precipitates to a beaker; add H_2O, and boil. Filter, and wash with hot water, if any precipitate remains. Test filtrate for Pb as in 1. Determine Hg and Ag in the precipitate as in 2 and 3.	1. Test the hot water filtrate for Pb with $K_2Cr_2O_7$, KI, and H_2SO_4. For results, see preceding work.
	2. To the precipitate left undissolved by the hot water, add NH_4OH. If it turns black, mercurous salts are indicated. Test filtrate that runs through, for Ag by 3, below.
	3. To the filtrate from 2, above, add HNO_3 till odor of NH_3 is no longer perceptible. A white precipitate indicates silver.

Test for Silver. — To determine whether silver is present put the ammonia solution that has just filtered through into a test-tube and add nitric acid until no longer alkaline. This will be known by the absence of the odor of ammonia. If there is any silver present, a white precipitate will form, which may again be dissolved by adding ammonia.

Group II. — Through "Solution B," the filtrate from the chlorides of the first group, pass a current of hydrogen sulphide, until, after shaking the solution, the odor of the gas is very perceptible. Any metals of this group will now be in the form of sulphides. Warm somewhat to collect the precipitates, and filter quickly. Preserve the filtrate, "Solution C," for determining metals of the third and succeeding groups.

Now wash the precipitates left on the filter and reject the wash water. Transfer the precipitates to an evaporating dish and add a few cubic centimeters of yellow ammonium sulphide or sodium sulphide in solution, and warm gently for several minutes. This will dissolve the sulphides of division 1 of this group, that is, those of arsenic, tin, and antimony; while those in the second division, mercuric salts, copper, bismuth, cadmium, and, as lead chloride is somewhat soluble in water, sometimes lead, will remain as precipitates. It should be stated, however, that copper sulphide is partially soluble in strong yellow ammonium sulphide; hence, when its presence is suspected from the color of the original solution, it is better to use sodium sulphide to separate division one from two.

When the sulphides have been digested as stated, filter and wash the remaining precipitate with water to which a drop or two of ammonium sulphide has been added. Save the filtrate to test for arsenic, tin, and antimony.

Test for Mercury. — Transfer the precipitates of mercury, copper, etc., to a beaker, add a few cubic centimeters of dilute nitric acid, and boil. All the sulphides will dissolve except that of mercury, which will remain as a heavy black residue. Disregard any dark-colored particles that remain floating upon the liquid, for they consist merely of sulphur colored with small portions of the black sulphides not yet dissolved. The student can prove this by collecting them upon a small loop in a platinum wire and igniting in the bunsen flame. The mass will burn with characteristic flame and odor. The indications of mercury shown by the black residue may be verified by filtering out, washing, and dissolving in *aqua regia*. Boil to dryness, take up with water, and test one portion with stannous chloride. A white precipitate, turning gray when heated, or when more of the stannous solution is added, is distinctive. Test another portion with potassium iodide, adding a drop at a time. A bright red precipitate, soluble in excess of the reagent, should form.

The filtrate from the mercuric sulphide, containing copper, bismuth, etc., should be boiled nearly to dryness, and water added to dissolve the salts. Before proceeding farther, it is always better, if lead has been found in the first group, to test a small portion of this solution in water in a test-tube with sulphuric acid and a little alcohol added. If a precipitate of lead sulphate forms, it must be removed in the same way from the whole solution, using very little sulphuric acid.

Test for Copper. — Now add ammonia to the solution, from which you have removed the lead, until alkaline.

If the solution turns darker blue, copper is indicated; at the same time bismuth will come down as a fine white precipitate. As the quantity of bismuth in solution is usually small, the student must be careful not to overlook it; at the same time he must not mistake for bismuth a fine sediment sometimes carelessly allowed to collect in the reagent bottle used for ammonia.

Test for Cadmium. — To determine whether cadmium is present, after filtering out the bismuth, add to the blue solution potassium cyanide in solution, drop by drop, until the blue color has entirely disappeared; then pass a current of hydrogen sulphide, by which the cadmium, if present, will be precipitated as a bright yellow sulphide.

Tests for Arsenic, Tin, and Antimony. — For separating and determining the presence of arsenic, tin, and antimony, various plans have been suggested, but nearly all are more or less tedious and require considerable care. The following plan, perhaps, is as satisfactory as any. To the ammonium sulphide solution of these metals, saved above, add dilute hydrochloric acid till the solution is no longer alkaline. The three metals will again be precipitated as sulphides. If the precipitate is pale yellow, or nearly white, and small in quantity, it probably consists mainly of sulphur, and none of the metals need be sought. If it is dark colored, gold or platinum may be present, or if copper has been found in the other division of this group, and ammonium sulphide was used instead of sodium sulphide, the precipitate may be only copper. Filter, and throw out the filtrate, as it contains no metals. Wash the precipitate, as usual, and transfer it to a beaker. Now add a little strong hydrochloric acid and warm gently; the sulphides of antimony and tin will dissolve, but the arsenic will be unaffected. Filter, and test the filtrate as follows: put into it a bright iron wire or nail, and after warming gently let it stand about fifteen minutes. The antimony is reduced to the metallic form, and the stannic chloride to the stannous. Filter or decant and test the solution for tin with mercuric chloride. The results are those given in testing for mercury with stannous chloride in the other division of this same group.

Wash thoroughly the precipitated antimony, and add to it a little strong hydrochloric acid and a few drops of nitric acid. The antimony will dissolve. Boil the solution nearly dry and add water. A white precipitate indicates antimony, which may be verified by passing a current of hydrogen sulphide through the solution. An orange-colored precipitate will result.

The arsenic left undissolved by the hydrochloric acid above may be tested in several ways. Transfer the arsenic sulphide to a beaker, add to it some strong nitric acid, and heat. The arsenic will dissolve. Now fill a test-tube about half full of a solution of ammonium molybdate, add to it a few drops of the arsenic solution prepared above, and boil. A yellow crystalline precipitate indicates arsenic.

Sometimes the following method works satisfactorily. After adding concentrated hydrochloric acid to dissolve the precipitates of antimony and tin sulphide obtained from the ammonium sulphide solution, decant the clear solution into a test-tube. Now slowly pour hydrogen sulphide water down the inside of the tube. Presently the antimony will begin to precipitate, forming an orange-colored ring of the sulphide. Continue adding the hydrogen sulphide solution, when above the antimony a ring of yellow stannic sulphide will form.

TABLE FOR GROUP II

Through “Solution B,” from Group I, pass H_2S till saturated, filter out sulphides, wash; save filtrate, “Solution C,” for Group III, Table III. Transfer precipitate to evaporating dish, and digest for a few minutes in $(NH_4)_2S_2$ or Na_2S. Again filter and wash. Save filtrate for 2, and precipitate for 1, below.	2. Acidulate the filtrate with HCl, filter, and wash. Transfer precipitate to a beaker, add strong HCl, and warm. Filter and test filtrate by *a* and *b*, and the precipitate by *c*.	*a.* Put into the filtrate a bright iron wire or nail and let stand about 15 minutes. A black scaly precipitate of antimony forms. Filter out and test by *b.* To the filtrate add $HgCl_2$, drop by drop, as a test for the tin.
		b. Dissolve the precipitated antimony in *aqua regia*, boil nearly dry, and add water. A white precipitate indicates antimony, verified by H_2S, which gives orange-colored precipitate.
		c. Heat the precipitate of arsenic sulphide with a little nitric acid and add some ammonium molybdate solution. A yellow crystalline precipitate will indicate arsenic.
	1. Precipitate may contain Pb, Hg, Cu, Bi, Cd. Add dilute HNO_3, and boil. Any heavy black residue will indicate Hg. Filter and wash. Boil filtrate nearly dry, take up with H_2O, and test small portion for Pb. If present, remove by adding C_2H_5OH and H_2SO_4 to whole, and filter. Add NH_4OH to filtrate till alkaline.	*a.* Deep blue color indicates copper.
		b. White precipitate indicates bismuth. To verify, filter out, dissolve in HCl, boil nearly dry, and add H_2O. While precipitate forms, filter.
		c. After filtering out the bismuth, add KCy solution till the blue color has disappeared. Pass a current of H_2S. A yellow precipitate indicates cadmium.

Group III. — Like Group II, this is also usually separated into two divisions for convenience in analysis. The first includes iron, aluminum, and chromium, precipitated by ammonia; the second, manganese, zinc, nickel, and cobalt, with ammonium sulphide as the precipitant.

To "Solution C," the filtrate saved from Group II, after filtering out the sulphides, add a few drops of nitric acid and boil a short time. Now add ammonium chloride, NH_4Cl, and ammonium hydroxide till alkaline. The latter reagent precipitates the metals of the first division as hydroxides. Warm the solution, filter and wash as usual. Save the filtrate for the second division of this group and the succeeding groups. Transfer the hydroxides of iron, chromium, and aluminum to a beaker, add 20 or 25 cc. of strong potassium hydroxide solution, and boil several minutes. This will dissolve the aluminum and leave the others unchanged. Filter and wash. To a portion of the filtrate, after acidulating with hydrochloric acid, add ammonia till alkaline. A white, flaky, sometimes starchy precipitate indicates aluminum.

Test for Iron. — Take a portion of the iron and chromium precipitate left undissolved and add hydrochloric acid. Test the solution obtained for iron, by using either potassium sulphocyanide, KSCy, or potassium ferrocyanide.

Test for Chromium. — Next, take a rectangular piece of platinum foil and bend up the sides so as to form a small boat or pan. A piece of broken porcelain dish may serve the same purpose, but more heat will be needed. Put into the boat the remaining iron and chromium precipitate, add an equal amount of potassium nitrate, KNO_3, and as much sodium carbonate, Na_2CO_3, and heat red hot until the whole mass has fused well together. Upon cooling, if chromium is present, it will assume a yellowish appearance. Put the boat and contents into a beaker containing a little water and dissolve the mass. Acidulate the solution with acetic acid and test a portion with silver nitrate. A brick or blood red precipitate of silver chromate, Ag_2CrO_4, indicates the presence of chromium. Test another portion with lead acetate, $Pb(C_2H_3O_2)_2$.

Tests for Nickel and Cobalt. — To the filtrate saved for the second division of this group, add some ammonium sulphide. If precipitates of light color are obtained, nickel and cobalt are not present, as their sulphides are black. If nickel is present, the filtrate will often be of a dark-brown color, which is apt to lead the student to think the solution is not filtering well. Disregard this, mark it "Solution D," and save for work with the fourth group. After washing the precipitates, transfer them to a beaker and treat with dilute hydrochloric acid; the sulphides of zinc and manganese will dissolve, while those of nickel and cobalt will remain as a black residue. Filter and wash. Test the black residue with the borax bead; cobalt gives the well-known blue in the oxidizing flame, and nickel, yellow to brown or black, according to the amount introduced into the bead. If both metals are present, the cobalt blue will obscure the brown, and further tests are necessary; for these the student is referred to any manual on qualitative analysis.

Tests for Zinc and Manganese. — To the solution supposed to contain zinc and manganese, after boiling for two or three minutes, add caustic potash till strongly alkaline. Allow it to stand for some time, for manganese precipitates slowly. If present, it may be filtered out and the precipitate tested with the borax bead. It imparts a beautiful amethyst color. Acidulate the filtrate with acetic acid and add ammonium sulphide till alkaline. A white precipitate indicates zinc. This is usually verified by heating on charcoal, moistened with a solution of cobaltous nitrate. A green mass is obtained; aluminum compounds treated in the same way give a blue mass.

TABLE FOR GROUP III

To "Solution C" from Group II add a few drops HNO_3, and boil; then NH_4Cl and NH_4OH till alkaline. Filter and wash. Save filtrate for second division of this group, and test by 2. Test precipitates obtained for Fe, Cr, Al, by 1.	2. Add $(NH_4)_2S$ to precipitate Ni, Co, Zn, Mn as sulphides. Filter and save filtrate ("Solution D") for Group IV. Treat precipitate with dilute HCl; filter and test filtrate by *c* and *d*. Test any black residue by *d* and *e*.	*a.* Test for Co with borax bead — blue.
		b. If Ni is present with no cobalt, borax bead will become yellow to brown in oxidizing flame.
		c. Add considerable excess of KOH and let stand for some time. A slow-forming precipitate indicates Mn. Filter and test filtrate by *d*. Verify Mn with borax bead. Amethyst color.
		d. Acidulate filtrate from *c* with acetic acid, add $(NH_4)_2S$ till just alkaline. Zinc forms white precipitate of ZnS.
	1. Add strong KOH solution to the hydroxides and boil. Filter and test filtrate by *a*; precipitate remaining by *b* and *c*.	*a.* Filtrate may contain aluminum. Acidulate with HCl, add NH_4OH or $(NH_4)_2CO_3$. A white precipitate of aluminum hydroxide shows the presence of the metal.
		b. Dissolve a small portion of the precipitate in HCl and test for iron with KSCy, K_4FeCy_6, or NH_4OH.
		c. Fuse the remainder in platinum dish with KNO_3 and Na_2CO_3. Dissolve in H_2O, acidulate with $HC_2H_3O_2$. Test for Cr with $AgNO_3$, also with $Pb(C_2H_3O_2)_2$.

Group IV. — For this use "Solution D" saved from Group III. It is better to make a preliminary test before proceeding with the whole. To do this, add to a small portion of the solution to be analyzed a little disodium phosphate. If a white precipitate forms, some of the metals at least are present, and all must be tested for. If so, add to the whole ammonium chloride, ammonium hydroxide, and ammonium carbonate. A white precipitate may contain calcium, strontium, and barium in the form of carbonates ; filter and wash. Save the filtrate to test for magnesium and fifth-group metals.

Test for Barium, Strontium, etc. — Transfer the precipitates to a beaker and dissolve in acetic acid. Test a small portion of this with potassium dichromate ; a light yellow precipitate indicates barium, which may be verified by the flame test. If present remove it from the entire solution by adding the dichromate and filtering. To the filtrate add caustic potash till alkaline and a little more potassium dichromate, when the strontium, if present, will be precipitated, as strontium chromate is insoluble in alkaline solutions. Remove this by filtering, and test the filtrate for calcium by adding ammonium oxalate. This gives a fine white precipitate of calcium oxalate. It is customary to verify the strontium by the flame test, as its salts impart a crimson color which is very persistent.

There are other plans for effecting a separation of the metals of this group, of which the following is frequently used. After removing the barium, to a small portion of the filtrate add a little strong solution of calcium sulphate. If a white precipitate forms, strontium is present and must be removed. Add to the remainder of the solution a very little sulphuric acid ; the strontium will slowly precipitate. After a few minutes filter and test filtrate for calcium. To do this add sufficient ammonia to neutralize any excess of sulphuric acid present, and then add ammonium oxalate solution as in other methods.

To a small portion of the filtrate saved above, after precipitating the barium, strontium, and calcium with ammonium carbonate, add a little disodium phosphate; a white precipitate which may form slowly will indicate magnesium.

TABLE FOR GROUP IV

To filtrate, “Solution D,” from Group III, add NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$, when a preliminary test has shown the presence of some metals of this group. Filter and wash. Save filtrate and test for Mg by 4. Transfer precipitates to beaker and dissolve in acetic acid. Treat solution as in 1.	1. To a small portion of the solution, add a little $K_2Cr_2O_7$ solution. If Ba is present, indicated by the forming of a light yellow precipitate, treat the whole of the solution in the same way, and filter. The Ba precipitate may be verified by flame test. Test the filtrate by 2.
	2. Render the filtrate alkaline by adding KOH, and then add a little more $K_2Cr_2O_7$. If strontium is present, it will be precipitated and may be filtered out. Or, from the filtrate from 1 above, the strontium may be removed by adding a little sulphuric acid. Let it stand a few minutes and then filter, and test filtrate for Ca by 3. The precipitate may be verified by flame test.
	3. When the barium and strontium have been removed, if the filtrate is not already alkaline, render it so by adding NH_4OH. Then add ammonium oxalate; white precipitate is distinctive of calcium. May be verified by flame test, orange-yellow.
	4. To a small portion of the filtrate saved from “Solution D,” add a little disodium phosphate. A white precipitate indicates magnesium, distinctive in the absence of other metals of this group. Filter, and save filtrate for Group V, “Solution E.”

Group V. Sodium, Potassium, Lithium. — The salts of the metals of this group are all soluble in water, hence none of the reagents used in the previous steps of analysis precipitate them. The flame, especially with the spectroscope, is usually all that is necessary for their identification.

As sodium is so widely distributed, a slight test for it may nearly always be obtained, but the student must learn to disregard any except a decidedly strong indication. As already seen, if sodium is present, the potassium flame can be perceived only by making the observation through a sheet of cobalt glass. Before making these flame tests, boil the solution, saved from Group IV, to dryness, and heat gently until ammonia fumes are no longer driven off. Dissolve the residue in water, and acidulate with hydrochloric acid.

Sodium gives bright yellow flame,
Potassium gives violet flame,
Lithium gives bright red flame, lasting but a moment.

Potassium may also be tested in another way. To the solution used in making the flame tests, add some platinic chloride in solution and a little alcohol. Allow it to stand for some time, stirring occasionally with a glass rod. A small quantity of a yellow precipitate of potassic-platinic chloride, K_2PtCl_6, is slowly deposited. A large watch crystal serves well for making this test.

Test for Ammonia. — Ammonia must be looked for in the original solution, as so many ammonium compounds are used as reagents in making the analysis. Put a few cubic centimeters of the original solution into a beaker and add caustic soda or potash until strongly alkaline. Moisten the under side of a watch crystal with a drop of water and upon it place a short strip of red litmus paper. Put the crystal over the beaker, and warm the solution gently. If ammonia is present, it will be liberated by the non-volatile alkali added, and will turn the litmus paper blue.

TABLE FOR GROUP V

Boil filtrate from Table IV to dryness, ignite to expel NH_4 compounds, dissolve in H_2O and acidulate with HCl. Test for Na, K, Li, by flame as in 1; K by wet method, as in 2; NH_4, as in 3.	1. Make test with platinum wire; Na gives yellow; K, violet when alone; Li, red. Use cobalt glass, if Na is present, to distinguish the violet rays.
	2. Sometimes K must be detected otherwise than by the flame test. To the acidulated solution, add $PtCl_4$; a yellow precipitate, slowly forming, indicates K.
	3. To a portion of the original solution, add caustic soda or potash till alkaline, and warm gently. Suspend a strip of red litmus in the fumes arising. If it turns blue, NH_4 is indicated.

The five tables given above simply show in condensed form the methods already described; and when the student has once seen the details and understands them, he will find the tables very convenient for rapid work. For a successful analysis, neatness is absolutely essential, and great care must be used in washing the precipitates so as to remove all of the metals contained in the filtrate.

Detection of Acids. — As a rule, the beginner will only meet with a few of the more common acids, and these only will be noticed here. They may be placed in groups, somewhat as the metals are, according as they are affected by certain reagents.

Group I. — This includes those which form a precipitate with barium chloride. The only one with which the student will meet often is sulphuric acid. As already seen, this gives with barium chloride, barium sulphate, $BaSO_4$, insoluble in all acids.

If the solution be neutral, phosphoric acid or the phosphates also give a white precipitate with barium chloride; but this is soluble in hydrochloric acid. After being thus dissolved, if the solution be made alkaline with ammonia, the precipitate will again fall.

Sulphurous and thiosulphuric acids are usually put in this group. They may be easily distinguished, however. To the solution add a little strong hydrochloric acid; both sulphurous and thiosulphuric acid and their salts will give off fumes of sulphur dioxide which may be readily detected. The latter, however, at the same time, throws down a milky or pale yellow precipitate of sulphur, while the former remains clear. The reaction is shown below: —

$$Na_2SO_3 + 2\,HCl = 2\,NaCl + H_2O + SO_2 \text{ (sulphurous)},$$

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + H_2O + SO_2 + S \text{ (thiosulphuric)}.$$

Group II. — This includes such as form no precipitate with barium chloride, but do with silver nitrate. The most common are: —

Hydrochloric, HCl, curdy white precipitate, very soluble in ammonia.

Hydrobromic, HBr, pale yellowish white precipitate, slowly soluble in ammonia.

Hydriodic, HI, pale yellow precipitate, *very slightly* soluble in ammonia.

Methods for testing each of these and its compounds have been given in the text, and the student is referred to them.

Hydrogen sulphide, H_2S, if free, is known by the odor. In the form of compounds, it may usually be detected by adding some acid and heating, whereby the gas is liberated and its characteristic odor becomes perceptible.

Group III. — Here belong those acids which form no precipitate with either barium chloride or silver nitrate. The only common one is nitric, but the salts of nitrous and chloric acids, HNO_2 and $HClO_3$, especially those of the latter, have occasional use in the laboratory. A plan for testing and distinguishing between nitrous and nitric acids was given in the text. The following plan, however, usually works satisfactorily, and by some is preferred to the other. Into a test-tube, containing the solution to be tested, drop a crystal of ferrous sulphate, and then pour down the sides of the tube a few drops of strong sulphuric acid. A brown ring will form about the crystal of ferrous sulphate.

The chlorates, for example, potassium chlorate, $KClO_3$, heated with sulphuric acid, yield chlorine, and chlorine peroxide, a very explosive gas. Usually, if sulphuric acid is added to a crystal of the chlorate, a sharp explosion occurs, throwing the materials out of the tube.

Group IV. — We might place here certain organic acids, which require special tests for identification. The only common one is acetic, $HC_2H_3O_2$, though the student occasionally meets with one or two others. Acetic acid and its salts are tested by adding a solution of ferric chloride and boiling. The solution becomes a deep red color which may be destroyed by using hydrochloric acid or mercuric chloride.

Oxalic acid, $H_2C_2O_4$, might be placed here, though more properly in Group I, as its salts form a white precipitate with barium chloride in neutral or alkaline solutions; this precipitate is soluble in hydrochloric acid, but not in acetic.

Preliminary Work. — Before testing any solution for acids, the metals present should be determined, otherwise the student may be greatly misled. If any are present which would interfere with necessary tests, that is, if there are any which would form precipitates with the reagents necessarily used in making the acid tests, they must be removed before proceeding with the determination.

Again, if the unknown substance is in solution, it would be useless to look for the acids whose salts are insoluble in water. For example, if we have found lead or barium present in a given solution, obviously it would be unnecessary to look for sulphuric acid. Hence a knowledge of the solubility of salts is very important, and the following incomplete table is given, showing the solubility of a few of the more common salts:—

Acetates, soluble in water.
Bromides, nearly all soluble; exceptions, those of first group metals and mercuric.
Carbonates, only those of Group V, the alkali metals.
Chlorides, nearly all, Group I excepted.
Iodides, nearly all, Group I excepted, also certain iodides of bismuth and copper.
Nitrates, all soluble.
Nitrites, nearly all soluble.
Phosphates, only those of Group V.
Sulphates, many insoluble, such as those of barium, mercury, lead, and silver; and calcium and strontium, nearly so.
Sulphites, only those of Group V.
Sulphides, only those of Groups IV and V.

If the substance, of which the acid radical is to be determined, is not in solution, it is often of great advantage to make certain preliminary tests. Put a small portion of it into a test-tube and add a little strong sulphuric acid. Warm gently, and notice the color and odor of the gas obtained. The more common are shown below: —

Acetates, odor of vinegar, no color.

Bromides, sickening odor, brown color, resembling that of nitrogen tetroxide. Odor is more offensive and peculiarly irritating to the eyes.

Carbonates, strong effervescence, no special odor, colorless gas.

Chlorides, very irritating gas (HCl), colorless.

Iodides, peculiar odor, resembling weak chlorine, violet color.

Nitrates, very irritating gas, no color.

Nitrites, irritating gas, brown in color; not so offensive as bromine.

Phosphates, no special action.

Sulphates, no special action.

Sulphites, suffocating gas (SO_2), colorless.

Sulphides, offensive odor (H_2S), colorless.

Thiosulphates, suffocating gas (SO_2), colorless.

The student must remember that these are merely preliminary steps and must be verified by distinctive tests already described.

APPENDIX B

SOME ADDITIONAL QUANTITATIVE WORK

It is believed that all the quantitative work that the ordinary class can do has been introduced into the text. There may be occasions, however, when it will seem desirable to vary the work or even to furnish more to certain students; to meet such a demand, the following experiments are offered.

1. To estimate Amount of Carbon Dioxide in any carbonate soluble in acids. (Adapted from Fresenius.)

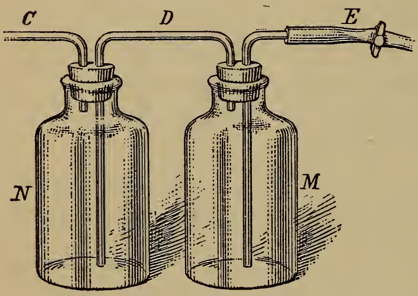


Fig. 65.

Fit two small bottles with rubber stoppers and glass tubing, as shown in the figure. *E* is a short piece of rubber tubing which may be closed air-tight by means of a screw clamp. The carbonate to be used, calcite for example, $CaCO_3$, is accurately weighed, placed in *M*, and covered with water. *N* is filled over half full of pure concentrated sulphuric acid. Find the weight of the whole, which should not exceed 60 to 70 g., tighten the clamp at *E*, and test the apparatus to see that it is air-tight.

Now by suction at *C*, partially exhaust the air in *N*; this will have a like effect upon *M*, and upon readmitting the air to *N* the acid will be forced over into *M*. The carbonate will thus be decomposed, and the carbon dioxide will escape into *N*, being dried as it bubbles through the acid. When the carbonate has all been decomposed, and the evolution of gas has ceased, open the clamp at *E*, and by means of an aspirator or by suction remove the carbon dioxide from *M* and *N*, and when the apparatus has become cool, weigh again. The loss represents the amount of carbon dioxide expelled by the acid.

Carbonate used (for example) . .	1.0 g.
Apparatus and contents, say . .	68.0 g.

After decomposition by acid: —

Total weight	x g.
Loss	$68.0 - x$.

$$CO_2 = 68 - x \text{ g.}$$

2. To determine the Water of Crystallization in a Compound. — This is usually done by heating a known weight of the compound, and noting the loss. To illustrate, put into a small porcelain crucible, the weight of which is known, about a gram of magnesium sulphate, and weigh carefully. Support the crucible in a clay triangle upon an iron ring-stand. With the Bunsen burner heat cautiously at first, increasing to red heat, cool slowly and weigh. Heat a second time four or five minutes and weigh again. Do this until two successive weighings show the same results, then calculate the per cent of water of crystallization.

Tabulate results thus: —

Weight of crucible + $MgSO_4$ . . .	a
Weight of crucible alone	b
Weight of $MgSO_4$	$a - b$

After the second and third heating, when weight was the same:—

Crucible + $MgSO_4$	c
Loss	$a - c$

In the same way try some other salt containing water of crystallization, as, for example, common alum or copper sulphate.

3. Volumetric Composition of the Air. — As the air, disregarding the impurities and small portions of other gases present, consists of oxygen and nitrogen, we can remove the former by exploding with hydrogen and then measure the residue. For example, suppose we pass into the eudiometer 20 cc. of air and then 10 cc. of hydrogen. We now have a total amount of 30 cc.; pass an electric spark to explode the hydrogen and oxygen. As two parts of hydrogen unite with one of oxygen, one-third of the loss would represent the oxygen, and the other two-thirds the hydrogen, which has combined to form water. The residue will contain the nitrogen of the air and any excess of hydrogen. Take the quantities used above:—

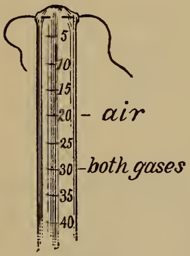


Fig. 66.

Air	20 cc.
Air + H	30 cc.
Residue after exploding . . .	18 cc.
Loss	12 cc.

$\frac{1}{3}$ of loss = 4 cc., the oxygen of air used.

20 cc. air = 4 cc. oxygen + 16 cc., nitrogen of air.

Let the student arrange his own apparatus for the above experiment, making all corrections necessary for accurate results, and prove the usual statement that air is one-fifth oxygen and four-fifths nitrogen.

4. The Volumetric Composition of Ammonia. — The composition of ammonia may be determined, but the experiment requires time and is somewhat tedious. The plan is as follows: into a eudiometer, over mercury, introduce a few cubic centimeters of dry ammonia gas, and pass sparks from an induction coil for twenty or thirty minutes or until the volume of the ammonia seems no longer to increase. This, in accordance with the law of Gay-Lussac, should now be double what was introduced into the eudiometer. Next add sufficient oxygen to explode with the hydrogen obtained from the ammonia, and pass a spark. It is obvious, from the proportions in which hydrogen and oxygen combine, that two-thirds of the loss represents the hydrogen, which, subtracted from the volume of the gases after electrolysis, gives the amount of nitrogen contained in the ammonia. Take the following example: —

Ammonia gas introduced . . .	8 cc.
Vol. of mixed gases after passing sparks,	16 cc.
Oxygen added	8 cc.
Total amount	24 cc.
Residue after exploding . . .	6 cc.
Loss	18 cc.
Two-thirds of loss = hydrogen, which was obtained from the ammonia gas .	12 cc.
Volume of mixed gases	16 cc.
Subtract volume of H	12 cc.
Volume of N	4 cc.

This proves that hydrogen and nitrogen unite in the proportion of three to one to form ammonia; furthermore we have seen that the four volumes of the mixed gases upon combining are condensed to two.

Let the student arrange his own apparatus, taking every precaution to insure accuracy, and, using different quantities from those mentioned above, prove the truth of the preceding statements.

5. Composition by Volume of Hydrochloric Acid. — This may be learned by the interaction of sodium and hydrochloric acid, by which is formed common salt and free hydrogen. In order to lessen the rapidity of the reaction, an amalgam of sodium should be used. This may be prepared by putting a small quantity of mercury into a mortar, and then, by means of forceps, thrusting small pieces of sodium, one at a time, into the mercury. Do this until a pasty mass is obtained, which upon cooling becomes solid. In preparing the amalgam do not hold the face too close to the mortar, as the combination sometimes takes place with considerable violence.

The hydrochloric acid gas for this experiment must be dried, either by bubbling through strong sulphuric acid or by passing through a drying tube containing bits of porcelain or pumice stone moistened with sulphuric acid. The gas may be generated by the reaction of common salt with dilute sulphuric acid, four parts of water to about five of acid. If dried by passing through sulphuric acid, the rapidity of evolution of gas may be observed and regulated by increasing or decreasing the amount of heat applied.

It is better, if possible, to collect the gas over mercury rather than by downward displacement, for in this way it may be obtained free from air.

For this experiment, some straight graduated tube should be used, such as the eudiometer shown in some of the illustrations for the synthesis of gases. If this is not to be had, you may use a burette, the capacity of which, both above and below the graduations, is accurately known. (See Fig. 67 for the general arrangement of the apparatus.) When the graduated tube is completely filled with gas, put around it, as near the mouth as possible, a paper test-tube holder. This is made by folding a sheet of paper into a strip about an inch wide; for use it is simply placed around the tube as shown in the accompanying figure at *N*, and grasped tightly between the thumb and fingers. The paper, being a poor conductor of heat, serves to prevent the transmission of the warmth of the hand to the glass so as to expand the hydrochloric acid.

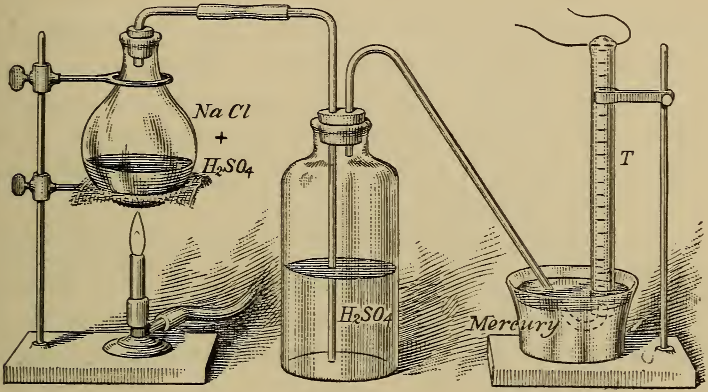


FIG. 67.

By means of this holder seize the tube, hold the thumb firmly over its mouth, and place in an upright position. Next,

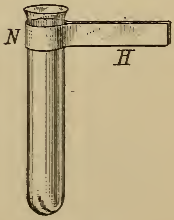


FIG. 68.

quickly drop into the tube a few grams of the sodium amalgam already prepared, and instantly replace the thumb, holding it as tightly as possible. Tip the tube back and forth a few times to hasten the action, and when this seems complete, place the mouth of the tube beneath the surface of the mercury and remove the thumb. The mercury instantly rises in the tube to fill the space formerly occupied by the chlorine, but now existing in the form of solid sodium chloride. Measure accurately the amount of gas remaining, and compare with the capacity of the tube; what are your conclusions? Test the residual gas with a light; what is it? What evidence have you that common salt is formed?

If the student finds he cannot hold his thumb tightly enough over the mouth of the tube to prevent leakage, he may use a short rubber stopper instead, and after the reaction of the sodium with the gas the tube may be opened over water.

6. **Analytic Proof of the Composition of Hydrochloric Acid.** — This may be furnished by the electrolysis of hydrochloric acid and the measurement of the gases obtained. Let the student arrange his own apparatus, and, taking such precautions as are necessary to avoid possible errors (mentioned in describing certain forms of electrolytic apparatus), make the experiment, and note results.

APPENDIX C

LABORATORY SUGGESTIONS

1. Neatness. — To the best success in any chemical experiment neatness is absolutely essential; indeed, the merest traces of substances foreign to those with which we are working may cause a complete failure of the experiment. A student hardly knows what neatness is until he has had a thorough training in chemical analysis.

The apparatus should always be *clean* when put away, and then before using should be rinsed with pure water. Never lay a cork or stopper down upon the table, as it will gather dust and thus pollute the reagent. If you desire to use some solution contained in a bottle, take the stopper between the first and second fingers with the palm of the hand upward and remove it from the bottle; then without laying it down seize the bottle with the thumb on one side and the fingers on the other. In this way the stopper will not come in contact with the side of the bottle and soil it, neither will dust and dirt be gathered from the table. The reagent bottles should be frequently wiped, as they soon become more or less covered with deposits which form from the gases generated in the laboratory. The table also should be kept clean, and water and other liquids should not be allowed to remain if accidentally spilled.

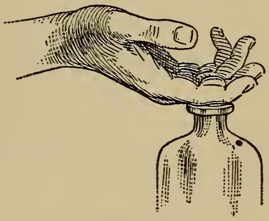


FIG. 69.

2. Order.— Great advantage will also be secured by having everything in its allotted place. Especially is this true of the reagent bottles, and the more there are of these the more important it is that they should be kept in order. For the larger schools probably about twenty reagent bottles will be furnished each student, and these will be arranged upon two shelves, one above the other. In such case, the following order is suggested as being as good as any: —

Lower Shelf

Beginning at left hand: —

Sulphuric Acid	Hydric Sulphate	H_2SO_4
Hydrochloric Acid	Hydric Chloride	HCl
Nitric Acid	Hydric Nitrate	HNO_3
Ammonium Hydroxide or Hydrate		NH_4OH
Ammonium Chloride		NH_4Cl
Ammonium Sulphide		$(NH_4)_2S$
Ammonium Carbonate		$(NH_4)_2CO_3$
Barium Chloride		$BaCl_2$
Potassium Dichromate	Potass. Acid Chromate	$K_2Cr_2O_7$
Potassium Ferrocyanide		K_4FeCy_6

Upper Shelf

Calcium Hydroxide or Hydrate		$Ca(OH)_2$
Mercuric Chloride		$HgCl_2$
Silver Nitrate	Argentic Nitrate	$AgNO_3$
Ferric Chloride		Fe_2Cl_6
Acetic Acid	Hydric Acetate	$HC_2H_3O_2$
Lead Acetate	Plumbic Acetate	$Pb(C_2H_3O_2)_2$
Potassium Iodide		KI
Sodium Carbonate	Crystals or powder	Na_2CO_3
Borax, powdered		$Na_2B_4O_7$

Some of the above reagents are known by different names, and in such cases two of them, the most common, have been given above.

3. Apparatus needed. — Each student should be assigned a locker where he may safely keep the apparatus supplied to him, and for the care of this he should be held responsible. The following apparatus is suggested: —

3 Test-tubes, $5 \times \frac{1}{2}$.
3 Test-tubes, $6 \times \frac{1}{2}$.
3 Test-tubes, $6 \times \frac{3}{4}$.
1 Evaporating Dish, small.
1 Evaporating Dish, medium.
1 Beaker, 2 oz.
1 Small Flask, $2\frac{1}{2}$ oz.
1 Delivery Tube.
1 Test-tube Brush.
1 Pair Forceps.
1 Glass Stirring Rod.
1 Blowpipe.
1 Platinum Wire.
1 Rubber Cork, one hole.
1 Rubber Cork, two holes.
1 Small Mortar.

Directions will be given later for preparing the delivery tube, stirring rod, and some other desirable apparatus.

The student should also have the following, and will furnish them himself: —

An apron, reaching to the ankles. This may be made of denim, oil cloth, or rubber cloth. The last is the most serviceable in many ways, but is the most expensive.

A Towel.
A Bar of Soap.
A Small Magnet.
An Iron Spoon.
A Clay Pipe.
A Candle.
A Small Triangular File.

The candle will be needed very frequently during the first half of the work in studying the properties of gases.

Common Property. — In addition to the individual property assigned above, certain articles on account of their size or for other reasons are used in common. There should be enough of them so that each member of the class may be supplied. Among these may be named: —

An Iron Pan, 8×14 and about $2\frac{1}{2}$ inches deep, to be used for a pneumatic trough.

Test-tube Rack.
Bunsen Burner, with Connections.
Wire Gauze.
Iron Ring-stand.
Funnel.
Wash-bottle (?).
Sand Bath.

MANIPULATIONS

4. Cutting Glass. — To cut tubing, with a sharp-cornered file scratch the glass entirely around where you desire to cut it. Now grasp the tube with both hands, the fingers above, and the thumbs below nearly meeting at the line scratched by the file. Now bend the tube downward and pull strongly apart at the same time. With a little practice good square cuts may be made. The rough ends thus secured will cut any rubber connections used. To prevent this hold them in the Bunsen flame until the glass by becoming softened loses its sharp edges.

Sometimes it becomes necessary to cut a bottle or large tube in two; this may be done in two ways, but both depend upon the unequal heating of the glass. Tie around a bottle where you desire to cut it an ordinary twine string; saturate it with kerosene and ignite it. Sometimes it will be found necessary to apply the oil the second time, as soon as the first has ceased to burn, and again ignite it. In this way, if the oil has been applied carefully, a narrow line extending around the bottle is heated strongly, and if the glass be cooled suddenly by pouring over it cold water, the bottle will be neatly severed.

5. To prepare a Delivery Tube. — This may be made of rubber and glass tubing, or of glass alone. The former is often preferable because it allows of more freedom in manipulation. If made entirely of glass, two bends are necessary, and one should be within an inch of the end. Hold the tubing in the Bunsen burner, moving it back and forth and rolling it around so as to warm all portions equally. When the glass begins to soften, allow its own weight to bend it, and take care that you do not form a right-angled tube, but one of a gentle curve like the elbow of a stove pipe. When the bend has cooled just a little, close the openings at the bottom of the burner and hold the glass in the luminous flame until it is well covered with soot. This will cause the glass to cool slowly and hence make it less liable to fracture. Complete by making the second bend in the same way, forming an obtuse angle as shown in the figure. If rubber connections are used, a second bend is unnecessary.

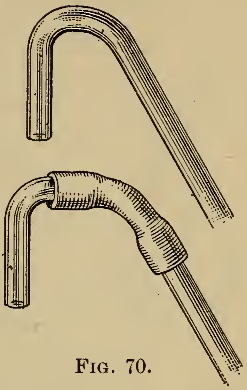


FIG. 70.

6. To make a Jet. — Frequently a tube drawn to a fine point is desirable. Take a piece of glass tubing 5 or 6 inches in length and heat as in making a delivery tube. When it begins to soften, draw it slowly apart until a tube of small diameter is obtained at the center, as shown in *a* in the adjoining figure. When somewhat cooled, cut in two at *a*; then make a bend in one of the shorter tubes, as shown in *b*. Round off the sharp edges and anneal as previously described. You will now have two *jets*, one straight and one bent, for both of which you will find uses.

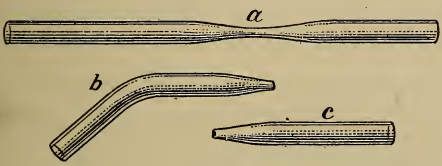


FIG. 71.

7. To make a Wash-bottle. — Any good-sized bottle or flask will do for this. The tube, *a*, should be drawn to a jet as shown in the figure, and after being bent should reach nearly to the bottom of the flask. The other tube after being bent should just reach through the cork. By blowing through *b*, a jet of water may be directed wherever desired; or if a larger stream is desired, it may be poured out at *b*. The bottle is more convenient if the jet, *a*, is attached to the rest of the tube by a rubber tube 2 or 3 inches long; the stream of water may then be turned readily in any direction.

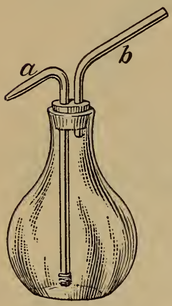


Fig. 72.

The wash-bottle is indispensable for qualitative work in washing precipitates. A rubber band should be slipped over the lower end of the tube, *a*, so that if it strikes the side of the flask in removing the cork and tubing it will not be broken. If the lockers are too small to receive the wash-bottle, one may be used in common by the students working at each laboratory table or section. In such case it is better for each student to have a short tube with rubber connections to attach to *b*, whenever he desires to use the bottle.

8. To repair a Test-tube. — Test-tubes are frequently broken by the beginner, but they may be easily mended, and will then be almost as useful as at first. Hold the broken end in a hot Bunsen burner flame, roll the tube about to heat all sides evenly. When the glass becomes soft, by means of a glass rod, which will cohere to the softened tube, draw off the viscous portion, and thus seal the tube. Usually a small mass of softened glass will remain upon the end of the tube. This must be drawn off in the same way, until the bottom is very thin, like the rest of the tube. Then by alternately heating and blowing into the tube, it may be rounded out and made almost as perfect as a new tube. After a little practice students may become skillful at this work.

9. Blowpipe Work. — In metallurgy, the blowpipe must be used frequently, and two kinds of flames are employed, the *reducing* and the *oxidizing*. In preparing for *either one*, turn down the jet to about a quarter its usual force, or until you have a flame not much larger than that of a good-sized candle, and close the openings at the bottom so as to render it luminous. In the figure, *a* shows the small luminous flame ready for the use of the blowpipe, *b* shows the reducing flame. The tip of the blowpipe is placed in the outer *edge* of the flame, and a gentle but steady stream of air forced into the flame. In this way a small *luminous* cone, *l*, will remain in about the center of the flame, and in this the metallic oxide should be held. This luminous portion contains red-hot particles of carbon, and they have the power of reducing oxides of metals to the metallic condition. If this luminous cone is not apparent, too much air is being forced into the gas. Either blow more gently, or turn the gas on a little stronger. With a little practice the student will learn to breathe and blow at the same time, and will not find the work especially tiresome.

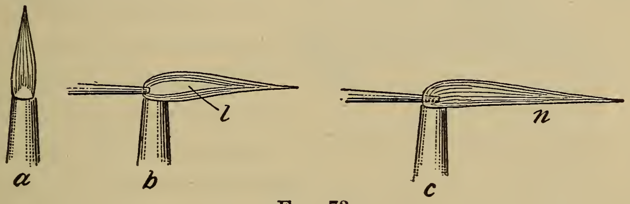


FIG. 73.

For the oxidizing flame, *c*, above, the tip of the blowpipe is placed in the very center of the jet. In this way the air introduced and the gas become thoroughly mixed, and complete combustion ensues. The cone should be perfectly non-luminous, and the metal to be oxidized should be held about where *n* is in the cut. The flame is exceedingly hot, and having an excess of oxygen readily reduces to oxides such metals as are oxidizable.

10. Collecting Gases. — There are several methods for collecting gases, varying according to the characters of the gases. Those which are insoluble in water are usually collected *over water.* Students will find an ordinary baking pan, 2 inches deep and about 6 inches broad by 12 long, sufficiently large. The bottle to receive the gas is first filled with water and inverted over the pan, Fig. 74. This is done by holding tightly a sheet of paper or glass over the mouth of the bottle until inverted and placed under the water in the pan. The delivery tube, *T*, dips under the bottle and conducts the gas from the generating flask, *G*, into the bottle.

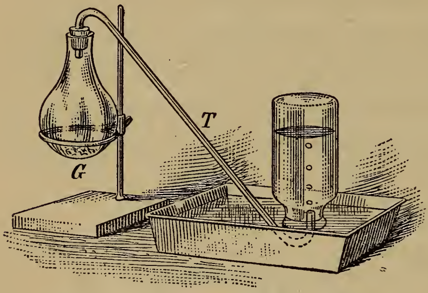


Fig. 74. — Collecting over water.

11. Collecting by Downward Displacement. — Gases soluble in water obviously cannot be collected by the method already described. If it is necessary to have them absolutely pure, mercury is frequently substituted for the water. Ordinarily, however, if *heavier* than air they are collected by *downward displacement.* By this method the bottle is simply left standing upon the table,

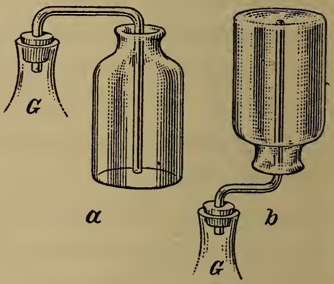


Fig. 75.

and the delivery tube reaches down into the bottle. Thus the heavier gas is introduced below the air, and gradually displaces it. Such gases as chlorine or carbon dioxide are collected in this way. If the gas is lighter than air and soluble in water, it is usually collected by *upward displacement.* The receiving bottle is held in an inverted position, and the delivery tube runs up to the bottom of the bottle, gradually displacing the air in the bottle. In Fig. 75, *a* shows the arrangement for collecting by *downward displacement*, and *b*, that for *upward displacement.*

12. Measurements.—Frequent reference is made throughout this work to the cubic centimeter and gram, and the student should have fairly definite ideas of these terms. This can come only by practice. For the volumetric, a test-tube and beaker may be graduated. From a burette run into a test-tube 1 cc. of water; indicate its height by fastening upon the tube just above the lowest part of the meniscus a narrow strip of mucilage paper. Add another cubic centimeter and mark the height in the same way. Thus graduate the tube up to 5 cc.; mark it also for the 10 cc. Now that the graduation may be permanent, with a file scratch carefully the marks, after which the paper may be removed; *a* shows the meniscus for each cubic centimeter, and *b* the small strip of paper. In the same way graduate a beaker for 5, 10, 15, 20, and 25 cc.

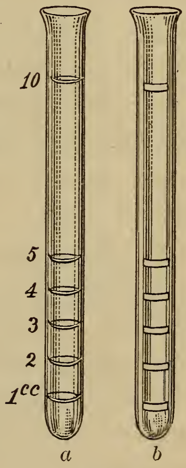


Fig. 76.

As different compounds vary so greatly in density, it is more difficult to obtain an accurate idea of a gram, but the student should be able to approximate it. Put upon one scale pan of a balance a small evaporating dish, and counterbalance it with shot or sand upon the other. Then add a gram weight to the shot. Into the evaporating dish now slowly add common salt until the gram weight is balanced. Thus try some other amount, as 2 g. or 5 g.

If the classes are large, one portion may be graduating the test-tubes and beakers, while another is doing the gravimetric work. This will greatly expedite matters.

13. Precipitates. — A precipitate is any solid matter thrown down in a solution by adding to it some reagent. It may be very dense, so as to be quite jelly-like, or it may form merely a cloud in the solution. To illustrate, put one drop of sulphuric acid into a beaker half or two-thirds full of water and add 2 or 3 cc. of barium chloride solution. The dilute solution should thus give a slight precipitate only. Now powder about a gram of ferrous sulphate and dissolve in as little water as possible, 2 or 3 cc., then add a few drops of ammonia. A thick gelatinous precipitate should form.

14. Decanting and Filtering. — These are processes for separating a precipitate from the solution in which it is formed. When the precipitate is one that has considerable density and settles quickly, leaving a clear solution, this supernatant liquid may be *decanted* or poured off. There is no objection to this method unless the presence of small particles of the precipitate in the decanted portion, or of the solution in the precipitate, will interfere with subsequent tests. To illustrate, a solution of lead acetate may be precipitated with hydrochloric acid, and after warming slightly and allowing the precipitate to settle, the solution may be decanted.

But in cases where the separation must be complete, *filtration* is necessary, that is, passing the solution through a filter paper. There are two ways of folding filters: the simplest, and one used when the precipitate is to be removed from the paper, is as follows: fold the paper to form a semicircle, *b*, then this to form a quadrant, making one fold slightly smaller than the other. This is done because funnels are seldom perfectly made, and one "quarter" will fit them better than another. Usually this is the larger. Now open out one of the quarters, and press down neatly into the funnel. If the quarter tried does not seem to fit, the other one may do so better. Now moisten with a little water, and with the fingers press the paper against the sides of the funnel to remove any air bubbles that may exist there. In filtering, pour in slowly at first, especially if the precipitate is very finely divided. If the solution does not come through clear, it may be necessary to filter again through the same filter paper. The pores will soon become partially filled, and the filtrate will be perfectly clear.

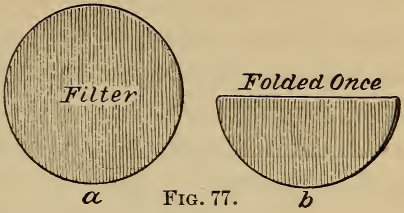


FIG. 77.

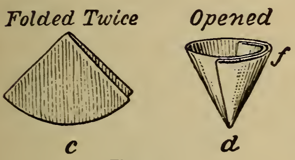


FIG. 78.

FIG. 79.

In filtering, the stem of the funnel should always be made to touch the side of the beaker or vessel into which the liquid is being passed, so that no drops may spatter out. Furthermore, in pouring a liquid from any vessel, it should always be allowed to run down a moistened stirring rod into the funnel. By observing these precautions, neatness in transferring liquids from one vessel to another will be secured.

15. **Opening Bottles.** — The common acids and aqua ammonia, as well as some other reagents, are frequently put up in bottles with glass stoppers. They are sealed by dipping the stopper into melted paraffin before inserting into the bottle. To remove the stopper the paraffin must be melted. This may be done by turning down the gas-jet moderately low, taking the bottle in both hands, holding the neck over the flame, not too close, and rolling it rapidly around so as to heat all sides alike. Be careful to heat the glass only gently. In a moment or two the wax will be melted and the stopper may be very easily removed. With a little practice bottles may be opened in this way without ever breaking or cracking. Be careful, however, in removing the stopper, never to have the face directly over the bottle.

16. **Platinum Wires.** —These are used in making *flame* and *borax-bead* tests for various metals. For the sake of convenience in handling, they are generally fused into a short piece of glass tubing. Take a few inches of small-size tubing and draw out, as in making a jet such as has already been described for use in testing the combustibility of gases. Cut the glass in two, as before, and insert the platinum wire into the tubing to

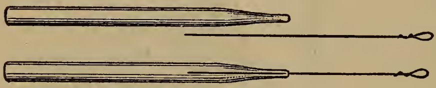


FIG. 80.

a distance of 3 or 4 cm.; again hold in the flame until the glass is softened. Upon cooling, the wire will be securely fastened in the tubing. (See Fig. 80.)

17. Electrolytic Apparatus. — If necessary, the student may prepare his own apparatus for experiments in electrolysis out of other apparatus that he will find at hand. Take two pieces of heavy platinum wire, each about a foot long, and make into spiral coils by wrapping around a pencil. Leave two or three inches straight at one end, as shown at *a*, Fig. 81.

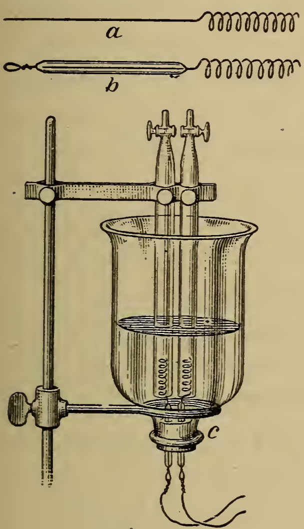


FIG. 81.

Fit to a short-necked bell jar with an open top a rubber cork with two small holes, and support the bell jar upon an iron ring-stand, fastening it securely in position. Next, take two pieces of small glass tubing, each long enough to reach through the cork *c*, and extend just into the body of the jar. Insert the straight ends of the two platinum spirals, already made, through these tubes, and fuse the glass at the ends so as to fasten the wires firmly in the glass; make a small loop in the wire at the lower end. See *b* in the figure. Insert the two electrodes thus prepared through the holes in the cork, and see that everything is water tight.

Next take two burettes with glass stop-cocks and determine accurately the capacity of each below the point of graduation, that is, from *m* to *n* in Fig. 82. This must be done if we desire to measure accurately the amount of gas collected. Now by means of clamps support these two burettes inverted over the two spiral electrodes, and the apparatus is complete. For use, fill the bell jar with the liquid to be electrolyzed to some distance above the mouth of the burettes. Attach a rubber tube to the tip of the burettes, open the stop-cock, and by suction fill each with the liquid and close the stop-cock. Turn on the current, and the capacity of each burette above the point of graduation having been determined, the amount of gas which collects in each tube is quickly read.

FIG. 82.

Instead of the burettes, test-tubes 8 inches by one-half in diameter may be used with good results, except that the gases cannot be accurately measured.

18. A Simple Electrolytic Apparatus. — Occasionally it may be desired to electrolyze a substance without separating the gaseous products. For such purposes a very simple form of apparatus may be employed, as shown in the figure. Prepare the two electrodes as described for the more complicated form, and fit them to a 3-hole stopper as shown in Fig. 83. Through the other opening pass a bent delivery tube, T, for conducting off the mixed gases which will collect in the top of the bottle when the current is passed.

FIG. 83.

Such apparatus as this may be used to show the explosive character of the mixture of hydrogen and oxygen obtained by the electrolysis of water, or of hydrogen and chlorine resulting from the decomposition of hydrochloric acid. To prevent the contents of the bottle becoming too warm, it should be placed in a vessel of cold water. Use hydrochloric acid of specific gravity about 1.1, and allow the current to pass for some time before collecting the gases, in order that the liquid may become saturated with the chlorine. If it is desired to collect bottles of the mixed gases over water, let the water be first saturated with common salt.

19. Eudiometers. — The eudiometer is an instrument used to test the composition of mixed gases. The most convenient form for all purposes is the U-shaped one, in which mercury is used to confine the gases. The air left in one limb of the tube serves as an air cushion to receive the shock of the explosion. The straight eudiometer, however, is cheaper, and with a few additional attachments may be used satisfactorily. *A* in the figure is an open-top bell jar, such as has been used in other experiments. The neck of *A* is closed with a tight-fitting, 1-hole rubber stopper, through which passes a glass tube having an enlargement blown upon the lower end, at *B*. Another rubber cork, which must fit the eudiometer, *E*, *very* tightly, is put upon the glass tube as shown in the figure. This must also fit *very* tightly. *T* is simply a piece of glass tubing about one inch in diameter, which should have a capacity somewhat greater than *E*. It is closed at the

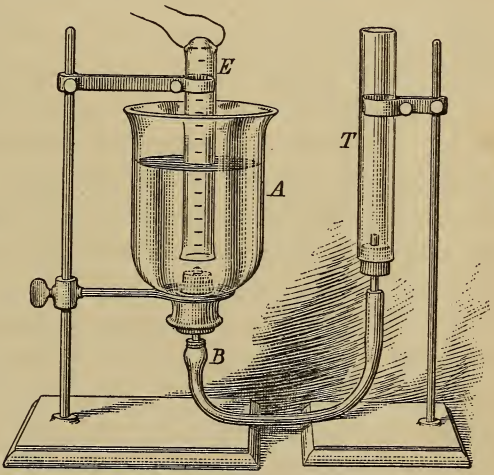


FIG. 84.

lower end with a cork, through which passes a short glass tube. A rubber tube connects the two portions of the apparatus, and just above *B* is fastened by some fine insulated copper wire wrapped about it.

For use the eudiometer is filled with water and supported in position over *A*. The gases to be exploded are introduced separately, and each measured carefully, the eudiometer being held by a paper test-tube holder at such height that the water stands at the same level inside and outside. Now press *E* firmly down upon its cork, and lower *T* as much as possible in order that the confined gases may have the pressure upon them reduced; grasp the rubber tubing near *B* *firmly* with the thumb and finger, and pass the spark. After the explosion, adjust the level inside and outside of *E* as when the gases were introduced, and measure the residue. If this adjustment cannot be secured by lowering *E*, it may remain connected as when the spark was passed, and the level secured by changing the height of *T*.

20. Aspirators and Aspirating Bottles. — As an aid in filtering certain classes of precipitates, an aspirator is frequently used. This acts upon the principle of the Sprengel air-pump. The aspirator consists merely of two tubes, *A* and *B*, secured at right angles to each other. *A* is attached to a water faucet, and *B*, by means of heavy-walled rubber tubing, to a filter flask. As the water flows through *A*, the air is gradually withdrawn from the flask; the pressure being thus removed from beneath the filter containing the precipitate, the liquid is forced through much more rapidly.

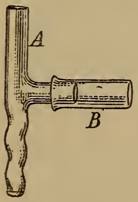


FIG. 85.

The filter flask is usually shaped like an Erlenmeyer flask (see Fig. 86), and has a side tube for connecting with the aspirator at *B*. It is made of heavy glass so as to withstand any ordinary atmospheric pressure. For use it is fitted with a rubber stopper having one hole, through which the stem of a funnel is inserted. In the apex of the funnel is placed a small platinum cone, perforated with minute openings. This cone is used to prevent the breaking of the filter paper by the atmospheric pressure; at the same time the numerous small holes permit the outflow of the filtrate with comparative freedom.

FIG. 87.

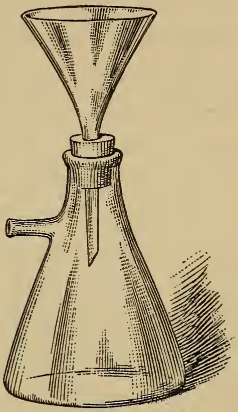


FIG. 86.

For certain experiments an aspirating bottle is almost indispensable. For example, suppose the experimenter desires to cause a regular flow of air or of some other gas through some vessel, suitable apparatus is necessary and may be very easily made. Large bottles, holding 3 or 4 liters, will serve best. To each fit a cork with two holes, and insert glass tubing as shown in the accompanying figure. The bent tube, *G*, has attached a short piece of flexible rubber tubing, upon which is placed a screw clamp, at *H*. By means of this the flow of gas issuing

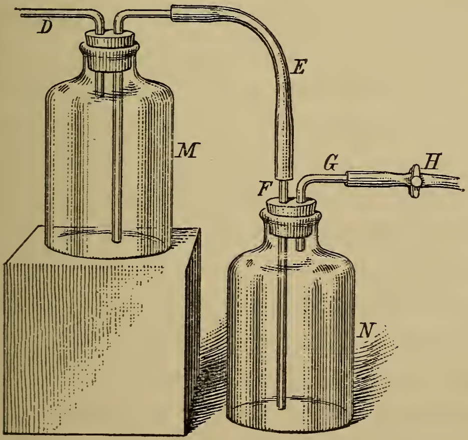


FIG. 88.

from *N* is regulated. The bottle, *M*, is placed upon a box so as to elevate it considerably above *N*. A rubber tube, *E*, connects the two bottles, and, being flexible, allows of the elevation of either bottle above the other.

If you desire to fill *N* with any gas not soluble in water, place both down upon the table, and fill *N* completely with water. Open the clamp at *H*, and insert the cork with the tubing into *N*. The water will be forced out into *G*, and expel the air therefrom ; this done, connect at *H* with the generating flask (not shown in the figure), after having waited until all air has been expelled from it. By the gas pressure, the water will be forced from *N* over into *M*; continue until *N* is nearly filled, close the clamp at *H* tightly, and remove the generator. Elevate *M* to its position upon the box, and the aspirator is ready for use.

By simply opening the screw clamp, the siphon connecting the two bottles transfers the water from *M* to *N* as rapidly as the exit of gas at *H* will allow. If the gas has been permitted to fill completely the bottle *N*, and has forced the water out of the siphon tube, it is only necessary to apply a little pressure at *D*. If a dry gas is desired, it must be obtained by passage from *N* through some suitable drying tube attached at *H*. If the gas to be used is ordinary air, the action of this apparatus may be made continuous, except for a momentary delay in changing the connections, by placing first *M*, and then *N*, upon the box, and connecting the receiver with the tubes, *G* and *D*, respectively.

The apparatus may be used in this way for showing the presence of carbon dioxide in air, by forcing it through lime-water. In other cases, where the amount of gas needed is not in excess of the capacity of the bottle *N*, this apparatus will work with entire satisfaction.

21. Gas Generators. — It is often desirable to have a generator, automatic in action, which will furnish a steady flow of gas and be ready for use at a moment's notice. Kipp's apparatus meets such a demand; but at much less expense one which works equally well may be prepared for any laboratory. In the figure, *A* is a bottle of about 500 cc. capacity, fitted with a cork and tube at *P*, to keep out dust. Through the bottom at *K*, with a glass drill, make a hole and insert a rubber cork with one perforation.

Through *B* near the bottom drill a hole and insert a rubber cork with a glass tube and short rubber connection clamped with a Hoffman screw. This is for the purpose of drawing off the spent acid. In the top of *B* fit a stopper with two holes; through one of these pass a long tube reaching to the bottom of *B* and extending up into *A*. To the other hole fit the bent tube, *D*, which has rubber connections for joining with any other apparatus. When not in use, this is kept tightly closed with a screw clamp.

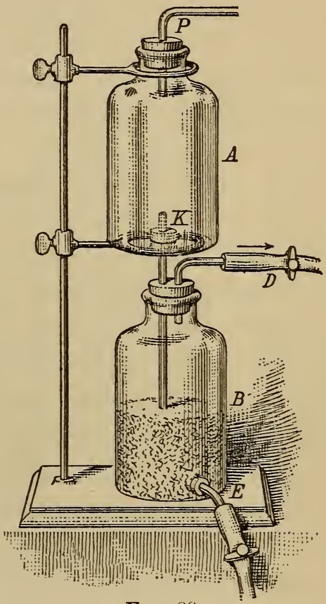


FIG. 89.

If you desire to use this apparatus as a hydrogen generator, place a half pound or more of zinc in *B*, close tightly the screw clamp at *D*, and pour diluted sulphuric or hydrochloric acid into *A* until about two-thirds full. Open the screw clamp; the acid will run down into the lower bottle and will continue to react with the zinc as long as the gas has free exit at *D*. If, however, the clamp is closed, the pressure in *B* soon becomes sufficient to force the acid up the longer tube into the upper bottle, and the evolution of gas ceases.

The bottle, *A*, is held in position by a clamp at the neck, and rests upon a ring of the support. The holes at *K* and *E* may be drilled by using a large file broken off, together with emery dust. To use the generator for hydrogen sulphide or carbon dioxide, the zinc would be replaced with ferrous sulphide or marble.

22. Correction of Barometric Reading. — In the various problems given in the text in connection with the Law of Charles, it was assumed without being stated that we were dealing with dry gases. Further than this, in the quantitative work with gases, certain corrections have been neglected. For exact work, however, in the measurement of gases, not only must the temperature be known, and the barometric pressure as well, but also certain other facts. If the gas has been collected over water, the exact volume will not be obtained by methods already used, for the reason that the presence of water vapor increases the tension of the gas, and hence the volume. In reducing the volume of gases, therefore, to standard conditions, allowance must be made for this tension. This has been carefully estimated, and for the ordinary range of temperature is shown below: —

19° C. . . .	16.35 mm.	22.0° C. . .	19.66 mm.
19.5° C. . .	16.86 "	22.5° C. . .	20.27 "
20.0° C. . .	17.39 "	23.0° C. . .	20.89 "
20.5° C. . .	17.94 "	23.5° C. . .	21.53 "
21.0° C. . .	18.50 "	24.0° C. . .	22.18 "
21.5° C. . .	19.07 "	24.5° C. . .	22.86 "

To illustrate, suppose we have 40 cc. of gas, the temperature of the room being 21° C., the barometric pressure 740. According to the law, stated previously, —

$$V : V' :: P' : P,$$

or

$$V = \frac{V' \times P'}{P},$$

in which V represents volume under standard pressure P, which is 760, V' the given volume of gas under the pressure P'. Substituting, —

$$V = \frac{40 \times 740}{760}.$$

But making correction for aqueous tension, we have

$$V = \frac{V' \times (P' - p)}{P},$$

in which p is the tension of the aqueous vapor. From the table given above, we find that at 21° C. this is 18.5 mm. Substituting in the formula, we have, —

$$V = \frac{40 \times (740 - 18.5)}{760},$$

which will give the *true* volume of the gas under standard conditions.

23. Drying Tubes. — Drying may usually be accomplished by forcing a strong current of air through the tube by means of a foot-bellows, if the tube has been previously moistened with alcohol, the process will be materially hastened. In like manner flasks may be dried. By means of rubber tubing connect a glass tube, long enough to reach to the bottom of the flask, to a foot-bellows, and direct a strong current of air into the flask.

24. Recording Results of Experiments. — In the first place, the student should understand exactly what he is expected to learn from the experiment; then he must know what steps are necessary in order to secure the correct results. Do not make the mistake of drawing conclusions before the experiment is complete, and then endeavoring to make the results conform to your preconceived ideas. Learn to see everything that occurs, and draw your conclusions in accordance with what really happens.

These results should be recorded in suitable note-books, and, were it possible, always completed in the laboratory. Note the results neatly and concisely in good rhetorical sentences. When they admit of being tabulated, such a form is always desirable. If the notes are not written up in the laboratory, a brief record should be made there, and at home put into permanent form in the note-book without delay. These records should be examined frequently by the teacher, at least after the completion of each distinctive portion of the work; for instance, in studying the halogen group, when the work in chlorine has been done, the notes should be examined; after that in bromine is completed, a similar examination should take place.

PREPARING SOLUTIONS

25. For ordinary work, reagents which are "commercially pure" will do, and are much cheaper. It is better to use distilled water in making up all solutions, but for some, such as caustic potash, soda, and such as form precipitates with water that is more or less "hard," pure water is essential.

26. Acids — Hydrochloric, Nitric, and Sulphuric. — For ordinary work these acids should be diluted with twice their own volume of water. In the case of the last acid the water must be added very cautiously, as great heat is generated. It is better to take what water is to be used in diluting the acid, and very gradually add the sulphuric acid to it. Acetic acid may also be diluted. When an acid stronger than the one prepared in this way is demanded, it is so stated in the text.

27. **Ammonia.** — Ordinary aqua ammonia should be diluted with about three parts of water.

28. **Ammonium Chloride.** — This should be made up with about 100 g. of the salt to a liter of water.

29. **Ammonium Carbonate.** — About 200 g. to liter.

30. **Ammonium Oxalate.** — About 40 g. to liter.

31. **Ammonium Sulphide.** — This may be prepared by the teacher if preferred. It is done by taking ammonium hydroxide as diluted above and passing into it a current of hydrogen sulphide until saturated. If yellow ammonium sulphide, $(NH_4)_2S_x$, is desired, add to the ammonia at the beginning a little sulphur in the form of flowers. When the solution is saturated, it is customary to add to it about two-thirds as much more of the ammonium hydroxide.

32. **Barium Chloride.** — About 100 g. to the liter.

33. **Potassium Dichromate.** — About 50 g. to the liter.

34. **Potassium Ferrocyanide.** — About 75 g. to the liter.

35. **Calcium Hydroxide.** — Saturated solution.

36. **Mercuric Chloride.** — Saturated solution.

37. **Mercurous Nitrate.** — About 50 g. to the liter, with about one-twentieth part of nitric acid added. Otherwise a basic salt forms in the solution. It is a very good plan to put a few drops of mercury into the bottle containing the solution.

38. Silver Nitrate. — About 50 g. to the liter. Keep the solution in an amber-colored bottle and away from contact with organic substances.

39. Ferric Chloride. — About 50 g. to the liter.

40. Ferrous Sulphate. — This must be made up as desired. About 100 g. to the liter.

41. Lead Acetate. — About 100 g. to the liter.

42. Potassium Iodide. — About 50 g. to the liter.

OTHER SOLUTIONS USED OCCASIONALLY

43. Arsenic Chloride. — Dissolve arsenious oxide, As_2O_3, in caustic soda, and then add hydrochloric acid until the solution gives an acid reaction.

44. Antimony Chloride. — Add hydrochloric acid to water until well acidulated, and then a small quantity of antimony trichloride; a solution of antimony may be obtained from the antimony tartrate in the same way.

45. Bismuth Nitrate. — This must be prepared in the same manner as the antimony chloride. Dissolve a few crystals of the salt in water to which considerable nitric acid has been added.

46. Calcium Chloride. — About 100 g. to the liter.

47. Calcium Sulphate. — Saturated solution.

48. Cobalt Nitrate. — About 50 g. to liter.

49. Chromium Chloride. — Prepare as indicated in the text. To a solution of potassium dichromate add about one-twentieth as much hydrochloric acid and a little alcohol, and boil. The green solution obtained will be chromium chloride.

50. Copper Sulphate. — About 50 g. to liter.

51. Di-sodium Phosphate. — About 100 g. to liter.

52. Potassium Cyanide. — About 100 g. to liter.

53. Potassium Chromate. — About 50 g. to liter.

54. Potassium Hydroxide. — About 100 g. to liter.

55. Sodium Hydroxide. — About 100 g. to liter.

56. Magnesium Sulphate. — About 100 g. to liter.

57. Sodium Carbonate. — About 100 g. to liter.

58. Lead Nitrate. — About 100 g. to liter.

59. Stannous Chloride. — First add about one-twentieth part of hydrochloric acid to the water, and then about 75 g. of the solid to a liter. It is better to put a piece of granulated tin into the solution.

60. Cochineal Solution. — Grind up the solid in a mortar and dissolve in water or in a 10 per cent solution of alcohol.

61. Indigo Solution. — Treat about 1 g. of indigo with about 10 g. of sulphuric acid. After standing several days, dissolve the whole in water.

62. Litmus Solution. — Dissolve the blue solid, powdered, in water.

63. Phenol-phthalein. — Dissolve about 1 g. in 100 cc. of 50 per cent alcohol.

64. Ammonium Molybdate. — Dissolve 15 g. of ammonium molybdate crystals in 100 cc. of aqua ammonia as prepared above. To this add an equal volume of distilled water, and finally 125 cc. of nitric acid, specific gravity about 1.4.

SUPPLIES NEEDED

65. Chemicals. — For ten students.

Acid, Acetic	1 lb.	Ammonium, Carbonate	1 lb.
" Hydrochloric	10 "	" Chloride	1 "
" Nitric	6 "	" Hydroxide	8 "
" Oxalic	½ "	" Nitrate	½ "
" Sulphuric	10 "	" Sulphate	⅛ "
" Tartaric	½ "	Antimony, Metallic	¼ "
Alcohol	1 qt.	" Potassium Tartrate	¼ "
Alum	1 lb.		

Arsenic, Metallic	$\frac{1}{4}$ lb.
“ Trioxide	$\frac{1}{4}$ “
Barium Chloride	$\frac{1}{4}$ “
Bismuth, Metallic	$\frac{1}{2}$ “
“ Nitrate	$\frac{1}{4}$ “
Bleaching Powder	$\frac{1}{4}$ “
Calcium, Carbide	$\frac{1}{2}$ “
“ Chloride	$\frac{1}{4}$ “
“ Fluoride	$\frac{1}{4}$ “
“ Sulphate	$\frac{1}{4}$ “
Carbon Disulphide	$\frac{1}{4}$ “
Charcoal, Powdered, animal,	$\frac{1}{2}$ “
“ Stick	1 doz.
“ Wood, powdered,	$\frac{1}{2}$ lb.
Cobalt Nitrate	$\frac{1}{4}$ “
Cochineal	$\frac{1}{8}$ “
Copper, Metallic, turnings	2 “
“ Nitrate	$\frac{1}{8}$ “
“ Sulphate	$\frac{1}{4}$ “
Ether	$\frac{1}{4}$ “
Indigo	$\frac{1}{16}$ “
Iodine	$\frac{1}{16}$ “
Iron, Filings	$\frac{1}{2}$ “
“ Chloride	$\frac{1}{2}$ “
“ Sulphate	$\frac{1}{2}$ “
“ Sulphide	2 “
Lead, Metallic	$\frac{1}{2}$ “
“ Acetate	$\frac{1}{4}$ “
“ Nitrate	$\frac{1}{2}$ “
“ Oxide, Litharge	$\frac{1}{4}$ “
“ “ Minium	$\frac{1}{4}$ “
Litmus	$\frac{1}{16}$ lb.
“ Papers, Red and Blue, each	$\frac{1}{2}$ q.
Magnesium Ribbon	$\frac{1}{16}$ lb.
“ Powdered	$\frac{1}{4}$ “
“ Sulphate	$\frac{1}{4}$ “
Manganese Chloride	$\frac{1}{4}$ “
“ Dioxide	1 “

Mercury, Metallic	$\frac{1}{2}$ lb.
“ Bichloride	$\frac{1}{4}$ “
Mercuric Nitrate	$\frac{1}{4}$ “
“ Oxide	$\frac{1}{2}$ “
Mercurous Nitrate	$\frac{1}{4}$ “
Phosphorus, Ordinary	$\frac{1}{16}$ “
Potassium, Metallic	$\frac{1}{16}$ “
“ Bromide	$\frac{1}{4}$ “
“ Carbonate	$\frac{1}{2}$ “
“ Chlorate	1 “
“ Chromate	$\frac{1}{4}$ “
“ Cyanide	$\frac{1}{8}$ “
“ Dichromate	$\frac{1}{2}$ “
“ Ferrocyanide	$\frac{1}{4}$ “
“ Iodide	$\frac{1}{2}$ “
“ Hydroxide, sticks,	1 “
“ Nitrate	$\frac{1}{2}$ “
“ Nitrite	$\frac{1}{4}$ “
“ Permanganate	$\frac{1}{4}$ “
“ Sulphocyanide	$\frac{1}{4}$ “
Silver Nitrate	$\frac{1}{8}$ “
Sodium, Metallic	$\frac{1}{8}$ “
“ Borate (Borax)	$\frac{1}{2}$ “
“ Carbonate	1 “
“ Chloride	1 “
“ Hydroxide, sticks	1 “
“ Phosphate, Di	$\frac{1}{8}$ “
“ Sulphite	$\frac{1}{4}$ “
“ Thiosulphate	$\frac{1}{2}$ “
Starch	$\frac{1}{2}$ “
Strontium Nitrate	$\frac{1}{4}$ “
Sugar	1 “
Sulphur, roll	1 “
“ flowers	1 “
Tin, Metallic	$\frac{1}{2}$ “
“ Chloride	$\frac{1}{4}$ “
Turpentine	$\frac{1}{4}$ “
Zinc, Granulated	2 “
“ Dust	$\frac{1}{2}$ “

APPENDIX D

REFERENCE LIBRARY

No text on chemistry can hope to give more than a glimpse at the subject. Naturally, therefore, it should be the aim of every teacher to build up a reference library for the use of himself and students. Among the many good books to be obtained, the following are suggested: —

Newth's Inorganic Chemistry — Longmans.
Newth's Chemical Lecture Experiments — Longmans.
Mendeleëff's Principles of Chemistry — Longmans.
Ostwald's Outlines of General Chemistry — Macmillan.
Ostwald's Foundations of Analytical Chemistry — Macmillan.
Walker-Dobbin's Chemical Theory for Beginners — Macmillan.
Roscoe and Schorlemmer's Treatise on Chemistry, Vols. I and II — Appleton.
Remsen's Chemistry, Advanced Course — Holt.
Remsen's Theoretical Chemistry — Lee.
Ramsay's Experimental Proofs of Chemical Theory — Macmillan.
Cornish's Practical Proofs of Chemical Laws — Longmans.
Johnston's Chemistry of Common Life — Appleton.
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Ramsay's Gases of the Atmosphere — Macmillan.
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Sutton's Volumetric Analysis — Blakiston.
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Alembic Club Reprints — Chemical Pub. Co., Easton, Pa.
  Foundations of the Atomic Theory.
  Experiments on Air.
  Foundations of the Molecular Theory.
  Discovery of Oxygen.
  Elementary Nature of Chlorine.
  Liquefaction of Gases.
  Early History of Chlorine.
Muir's Heroes of Science — Young & Co.
Shenstone's Glass Blowing — Longmans.
Thorpe's Chemical Preparations — Ginn.

APPENDIX E

BIOGRAPHICAL

THE following are among those who have contributed to chemical literature or to the advancement of the science.

AGE OF ALCHEMY

Geber. — Arabian alchemist of eighth century; author of several chemical works, and discoverer of *aqua regia.*

Albertus Magnus. — Died 1280. Advanced the theory that the metals were composed of water, arsenic, and sulphur.

Bacon, Roger. — Thirteenth century. English alchemist. Advocated experimental proof of chemical theory. Inventor of gunpowder.

Valentine, Basil. — Fifteenth century. Wrote several works on chemistry. Probably a fictitious name of *Johann Thölde.*

MEDICAL ERA OF CHEMISTRY

Paracelsus, a name coined for himself by *Theophrastus Bombastus von Hohenheim.* — Early part of the sixteenth century. By his study and preparation of a large number of medicines, he earned for himself the title, "Father of Medicine."

Libavius. — Died in 1616. Proceeded with the work begun by Paracelsus. Wrote a Handbook of Chemistry.

Van Helmont, Jean Baptiste. — 1577–1644. Discovered several gases.

Boyle, Robert. — 1627–1691. Real founder of the sciences of physics and chemistry. Formulated Boyle's Law, and advanced the true theory as to the composition of matter.

Becher, Johann Joachim. — 1635–1682. German chemist. Author of theory that when a metal burns *terra pinguis* escapes from it.

AGE OF PHLOGISTON

Stahl, Georg Ernst. — 1660–1734. Founder of the phlogistic theory of combustion, that all combustible substances contained an *unknown something* called *phlogiston* which escaped when the substance burned. It was an outgrowth of Becher's theory.

Hoffmann, Christoph Ludwig. — 1721–1807. Physicist and chemist. His theory of the reduction of a metal was about the same as that held to-day. He believed that the *calces* of the metals contained the metals themselves and some other substance, which he called *sal acidum.*

Black, Joseph. — 1728–1799. Professor of chemistry in Edinburgh. Discovered carbon dioxide and proved that the carbonates of the alkalies and alkaline earths are not elements.

Cavendish, Henry.—1731–1810. Discovered hydrogen; studied the composition of water and the air, and made a large number of experiments with the latter. Prepared nitric acid by synthesis.

Priestley, Joseph.—1733–1804. Discoverer of oxygen, and strong advocate of phlogistic theory.

Scheele, Carl Wilhelm. — 1742–1786. Discoverer of chlorine; made some investigations in organic chemistry; prepared glycerine and prussic acid.

MODERN ERA OF CHEMISTRY

This coincides roughly with the nineteenth century.

Lavoisier, Antoine Laurent.—1743–1794. Founder of modern chemistry. Made a beginning in quantitative work, and overthrew the theory of phlogiston. Advanced the idea of the conservation of matter.

Gay-Lussac, Joseph Louis. — 1778–1850. Author of the law of combination of gases by volume. Made an extensive study of the general properties of gases; determined the relation between the volume of a gas and its temperature, thus supplementing Boyle's work.

Berzelius, Johann Jacob, Baron. — 1779–1848. Studied the atomic weights of the elements; improved the usual methods of chemical analysis, and investigated the law of combining proportions.

Proust, Louis Joseph.—1760–1826. Advocated the theory that the elements combine always in definite proportions, now known as the "Law of Definite Proportions."

Dalton, John. — 1766–1844. Advanced the atomic theory of matter, and formulated the "Law of Multiple Proportions."

Berthollet, Claude Louis. — 1748–1822. Made a long series of experiments, studying the behavior of ammonia, hydrogen sulphide, chlorine, and other gases.

Davy, Sir Humphry. — 1778–1829. Studied the properties of various gases; proved that the alkalies, caustic soda and potash, are not elements.

Dulong and *Petit.* — Early part of nineteenth century. Made a study of the metals. Formulated the law that the specific heats of the metals are inversely proportional to their atomic weights.

Dumas, Jean Baptiste André. — 1800–1884. Made an extensive study of vapor densities.

Faraday, Michael. — 1791–1867. Succeeded in liquefying many of the gases; studied physical chemistry, and determined the effects of an electric current upon electrolytes. He formulated the "Law of Definite Electrolytic Action," that an electric current decomposes electrolytes so that equivalent amounts of the substance are liberated at the kathode and anode.

Liebig, Justus, Freiherr von. — 1803–1873. Studied organic chemistry; investigated the phenomenon of isomerism.

Mendeleëff, Dmitri Ivanovich. — Born 1834. Russian chemist. Formulated the "Periodic Law of the Elements." Author of general chemistry.

Pictet and *Cailletet.* — Physico-chemists of the present time. They have done much work in producing low temperatures, and in liquefying air, hydrogen, and oxygen.

Ramsay, William. — Born 1852. Discoverer of argon in 1894. English scientist of to-day.

Dewar, James. — Born 1842. English scientist of the present time. Has studied carefully low temperatures.

Moissan, Henry. — French chemist of the present time. Has succeeded in preparing artificial diamonds; has also studied carefully the properties of liquid fluorine.

MEANING OF ALCHEMISTIC TERMS

The student in attempting to read the reports of the chemists of the eighteenth century will find much difficulty in understanding the alchemistic terms so universally employed. The following are among those most commonly met with, and are given to encourage the student to read these accounts himself. The Alembic Club Reprints, mentioned among the books suitable for reference, furnish the most desirable portions of the writings of such investigators as Scheele, Dalton, Priestley, and others. It will be noticed that often several terms are used for the same substance. This was in accordance with the plans of alchemy to keep secret the discoveries and mystify any who might attempt to decipher the records.

OLD TERMS	PRESENT MEANING
Acid	Anhydride (oxide).
Acid of chalk	Carbon dioxide.
Acidum salis	Chlorine.
Aer fixus	Carbon dioxide.
Air	Gas.
Alkali of tartar	Potassium carbonate.
Aqua fortis	Nitric acid.
Aqua regis	Aqua regia.
Azotic gas	Nitrogen.
Blanc d'Espagne	Bismuth Subnitrate.
Calx	Oxide.
Calx of silver	Silver carbonate.
Colcothar	Ferric oxide.
Dephlogisticated air	Oxygen.
Draco mitigatus	Mercurous chloride.
Fire air	Oxygen.
Fixed air	Carbon dioxide.
Fixed alkali	Sodium carbonate.
Gas fuliginosum	Combustible gas.

Old Terms	Present Meaning
Gas pingue	Combustible gas.
Gas siccum	Combustible gas.
Gas sylvestre	Carbon dioxide.
Grey calx of lead	Lead sesquioxide.
Hartshorn	Ammonia.
Liver of Sulphur	Potassium persulphide.
Magnesia alba	Magnesium carbonate.
Marcasite	Ferric sulphide.
Marine acid	Hydrochloric acid.
Mephitic air	Nitrogen.
Mercurius calcinatus	Mercuric oxide.
Mercurius dulcis	Mercurous chloride.
Mercurius Niter	Mercuric nitrate.
Mercurius precipitatus per se	Mercuric oxide.
Mercurius precipitatus ruber	Mercuric oxide.
Mercurius sublimatus	Mercuric chloride.
Mercurius vitae	Antimony oxychloride.
Mors metallorum	Mercuric chloride.
Niter	Potassium nitrate.
Nitrous air	Nitrogen dioxide.
Nitrous gas	Nitrogen dioxide.
Phlogiston	A hypothetical substance, believed to exist in all combustible bodies.
Phlogistic air	Nitrogen.
Pulvis angelicus	Antimony oxychloride.
Spirit of niter	Nitric acid.
Spirit of sulphur	Sulphuric acid.
Spiritus igneo aerius	Oxygen.
Spiritus salis	Hydrochloric acid.
Terra pinguis	Same meaning as phlogiston.
Usifur	Artificial mercuric sulphide.
Vital air	Oxygen.
Vitriol	Sulphate.
Vitriolated tartar	Potassium sulphate.
Volatile alkali	Ammonium Carbonate.

TABLE OF THE ELEMENTS AND THEIR ATOMIC WEIGHTS

Name	Symbol	Atomic Weights	
		O = 16	H = 1
Aluminum	Al	27.1	26.9
Antimony	Sb	120.	119.5
Argon	A	39.9	?
Arsenic	As	75.	74.45
Barium	Ba	137.4	136.4
Bismuth	Bi	208.5	206.5
Boron	B	11.	10.9
Bromine	Br	79.96	79.34
Cadmium	Cd	112.4	111.55
Cæsium	Cs	133.	131.9
Calcium	Ca	40.	39.8
Carbon	C	12.	11.9
Cerium	Ce	140.	138.0
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.	58.55
Columbium	Cb	94.	93.0
Copper	Cu	63.6	63.1
Erbium	E	166.	164.7
Fluorine	F	19.	18.9
Gadolinium	Gd	156.	155.8
Gallium	Ga	70.	69.5
Germanium	Ge	72.	71.9
Glucinum	Gl	9.1	9.0
Gold	Au	197.2	195.7
Helium	He	4.	?
Hydrogen	H	1.01	1.0
Indium	In	114.	113.
Iodine	I	126.85	125.89
Iridium	Ir	193.	191.7
Iron	Fe	56.	55.5
Krypton	Kr	81.8	?

TABLE OF THE ELEMENTS AND THEIR ATOMIC WEIGHTS — *Continued*

NAME	SYMBOL	ATOMIC WEIGHTS	
		$O = 16$	$H = 1$
Lanthanum	La	138.	137.6
Lead	Pb	206.9	205.36
Lithium	Li	7.	6.97
Magnesium	Mg	24.36	24.1
Manganese	Mn	55.	54.6
Mercury	Hg	200.3	198.50
Molybdenum	Mo	96.	95.3
Neodymium	Nd	143.6	142.5
Neon	Ne	20.	?
Nickel	Ni	58.7	58.25
Nitrogen	N	14.04	13.93
Osmium	Os	191.	189.6
Oxygen	O	16.	15.88
Palladium	Pd	106.	106.2
Phosphorus	P	31.	30.75
Platinum	Pt	194.8	193.4
Potassium	K	39.15	38.82
Praseodymium	Pr	140.5	139.4
Rhodium	Rh	103.	102.2
Rubidium	Rb	85.4	84.75
Ruthenium	Ru	101.7	100.9
Samarium	Sm	150.	149.2
Scandium	Sc	44.1	43.8
Selenium	Se	79.1	78.6
Silicon	Si	28.4	28.2
Silver	Ag	107.93	107.11
Sodium	Na	23.05	22.88
Strontium	Sr	87.6	86.95
Sulphur	S	32.06	31.83
Tantalum	Ta	183.	181.5
Tellurium	Te	127.	126.5
Terbium	Tr	160.	158.8

TABLE OF THE ELEMENTS AND THEIR ATOMIC WEIGHTS — *Continued*

NAME	SYMBOL	ATOMIC WEIGHTS	
		O = 16	H = 1
Thallium	Tl	204.1	202.61
Thorium	Th	232.5	230.8
Thulium	Tm	171.	169.4
Tin	Sn	118.5	118.1
Titanium	Ti	48.1	47.8
Tungsten	W	184.	182.6
Uranium	U	239.5	237.8
Vanadium	V	51.2	51.0
Xenon	X	128.	?
Ytterbium	Yt	173.	171.9
Yttrium	Y	89.	88.3
Zinc	Zn	65.4	64.9
Zirconium	Zr	90.7	89.7

The above table shows two columns of atomic weights; the first assumes O = 16 as the standard, the second, H = 1.

GLOSSARY OF CHEMICALS AND MINERALS

Agate. A variety of quartz, occurring often in variegated colors, arranged concentrically.

alabaster. A fine-grained, white variety of gypsum.

alum. A double sulphate, of general formula, $M_2R_2(SO_4)_4\ 24\ H_2O$.

alumina. Aluminum oxide, Al_2O_3.

amethyst. A variety of quartz.

anthracite. Natural coal, possessing little or no oil or other volatile products. Hard coal.

antichlor. A reagent used to neutralize chlorine when in excess.

aragonite. A variety of calcite, $CaCO_3$.

argentite. Native silver sulphide.

arsenic. The popular name for arsenic trioxide.

arsenious acid. Another name for arsenic trioxide.

arsine. Hydrogen arsenide, AsH_3.

azurite. An ore of copper, blue in color, composition $Cu(OH)_2$, $2\ CuCO_3$.

Baryta. Barium oxide.

baryta water. Barium hydroxide.

bauxite. A hydrated oxide of aluminum, Al_2O_3, H_2O, used as a source for aluminum.

benzene. A light oil obtained from petroleum, composition C_6H_6.

bicarbonate of soda. Cooking soda, $NaHCO_3$.

bismuth ocher. Bismuth oxide, Bi_2O_3.

bismuthite. Native bismuth sulphide.

bituminous. Containing bitumen or oil. Applied to soft coals.

blanc de fard. Bismuth subnitrate, $BiONO_3$.

blende. Native zinc sulphide.

blue vitriol. Copper sulphate.

borax. Sodium diborate, $Na_2B_4O_7$.

braunite. Native Mn_2O_3.

butter of antimony. An old name for antimony trichloride.

Calamine. An ore of zinc, Zn_2SiO_4, H_2O.

calchopyrite. A sulphide of iron and copper, Cu_2S, Fe_2S_3.

calcite. Crystallized calcium carbonate.

calomel. Mercurous chloride, Hg_2Cl_2.

carbonado. A variety of diamond occurring in black pebbles or masses.

carborundum. A hard substance, made by combining, at high temperatures, silica and carbon.

cassiterite. Native stannic oxide, SnO_2, the chief ore of tin.

caustic potash. Potassium hydroxide.

caustic soda. Sodium hydroxide.

celestite. Strontium sulphate.

cement. A variety of lime prepared from limestone, containing from 40 to 50 per cent of slate.

chalcedony. A variety of quartz.

chalk. A soft variety of limestone, composed of the shells of diatoms.

chloride of lime. A common name for bleaching powder.

chrome alum. A sulphate of potassium and chromium.

chrome red. Basic lead chromate, Pb_2CrO_5.

chrome yellow. Lead chromate, $PbCrO_4$.

cinnabar. The chief ore of mercury, HgS.

clay. A hydrated silicate of aluminum, containing various impurities.

colcothar. Ferric oxide, Fe_2O_3.

copperas. Ferrous sulphate.

corrosive sublimate. Mercuric chloride, $HgCl_2$.

corundum. Anhydrous alumina, uncrystallized.

cryolite. A fluoride of sodium and aluminum, $NaAlF_4$.

Dolomite. A native carbonate of magnesium and calcium.

Emerald. (Oriental.) Crystallized alumina, green in color.

emery. Massive, opaque alumina.

epsom salts. Magnesium sulphate.

euchlorine. A solution of chlorine in water.

Fat lime. Lime made from pure limestone.

feldspar. A silicate of potassium and aluminum, which, decomposed, forms clay.

fool's gold. Ferric sulphide, Fe_2S_3.

fuller's earth. A variety of clay.

fuming liquor of Libavius. Anhydrous stannic chloride.

Galena. The chief ore of lead, PbS.

green vitriol. Ferrous sulphate.

gypsum. Native calcium sulphate.

Hartshorn. An old term for ammonia.

heavy spar. Native barium sulphate.

hematite. An important ore of iron, of the composition Fe_2O_3.

horn silver. Native silver chloride.

hydraulic cement. Lime containing from 10 to 30 per cent of silica, having the property of hardening under water.

hypo. The photographer's name for sodium thiosulphate.

Iceland spar. A transparent, crystalline variety of calcium carbonate.

infusorial earth. A grayish white earth, composed largely of silica, resulting from the secretion of diatoms.

Jeweler's rouge. An oxide of iron, red in color, used in polishing and as a pigment.

Kaolin. A pure variety of clay, formed by the decomposition of feldspar.

kelp. The ashes of seaweeds, used as a source of certain potash salts and of iodine.

kerosene. Popularly called *coal oil.* An oil obtained by the distillation of petroleum.

kieserite. Native magnesium sulphate.

kupfer nickel. Nickel arsenide, $NiAs$.

Labarraque's solution. Sodium hypochlorite.

lac sulphuris. Sulphur precipitated from a solution of it in lime-water.

laughing gas. Nitrous oxide, N_2O.

lean lime. Lime made from impure limestone.

lime. Calcium oxide, CaO.

limestone. Calcium carbonate, uncrystallized.

lime-water. Calcium hydroxide.

litharge. Impure lead oxide, PbO.

lunar caustic. A commercial term for silver nitrate.

Magnesia. Magnesium oxide.

magnesite. Native magnesium carbonate.

magnetic pyrites. A mixture of FeS and Fe_2S_3. This mixture is given its name because of magnetic properties.

malachite. An ore of copper, $CuCO_3$, $Cu(OH)_2$.

marble. Crystallized limestone.

marcasite. A variety of ferric sulphide, FeS_2.

massicot. Lead oxide, PbO.

milk of lime. Calcium hydroxide, containing more or less lime in suspension.

milk of sulphur. Same as *lac sulphuris*.

minium. Red lead, Pb_3O_4.

mispickel. An important ore of arsenic, FeSAs.

Naphtha. A light oil, obtained from petroleum.

Nessler's solution. A solution used in testing for ammonia.

niter. Another name for potassium nitrate.

Nordhausen's acid. The same as *fuming* sulphuric acid, $H_2S_2O_7$.

Oil of vitriol. Sulphuric acid.

opal. A variety of silica, SiO_2.

oriental. A term applied to the true emerald and certain other gems, to distinguish them from less valuable stones similar in appearance.

orpiment. A sulphide of arsenic, yellow in color, having composition As_2S_3.

Paraffin. A wax obtained in the later distillation of petroleum.

Paris green. A popular name for Scheele's and Schweinfurth's green, compounds of arsenic.

pearl ash. Pure potassium carbonate.

pearl white. Bismuth oxychloride, BiOCl.

petroleum. Rock oil, found native in various parts of the world.

plaster of Paris. Calcined calcium sulphate.

plastic sulphur. A dark-colored, allotropic form of sulphur, somewhat resembling rubber.

potash. Another name for commercial potassium carbonate. Also a loose name for potassium chlorate.

powder of Algaroth. A variable compound of antimony, approximately SbOCl.

purple of Cassius. A purplish-colored precipitate obtained in testing a solution of gold with stannous chloride.

pyrites. A common name for ferric sulphide, FeS_2.

pyrolusite. Native manganese dioxide.

Quartz. Silicon dioxide.

quicklime. The same as lime.

Realgar. Red sulphide of arsenic, As_2S_2.

red lead. The same as *minium*.

red precipitate. Mercuric oxide.

rose quartz. A variety of quartz, somewhat pink in color.

Sal ammoniac. Ammonium chloride.

sal soda. Sodium carbonate.
salt. The common name for sodium chloride.
salt cake. Sodium sulphate.
saltpeter. Potassium nitrate.
sapphire. Crystallized alumina.
Scheele's green. Copper arsenite, $CuHAsO_3$.
silica. Silicon dioxide.
slaked lime. Lime treated with water.
smalt. A silicate of cobalt and potassium.
smoky quartz. A variety of silica, brown or smoky in color.
soda. Same as *sal soda*.
soda, cooking. Same as sodium bicarbonate, $NaHCO_3$.
spathic iron. Native iron carbonate, $FeCO_3$.
specular iron. A variety of hematite.
spiegeleisen. A variety of iron containing manganese and carbon.
stibine. Same as antimoniureted hydrogen, SbH_3.
strontianite. Native strontium carbonate.
subnitrate of bismuth. Basic bismuth nitrate, $BiONO_3$.
sugar of lead. Lead acetate.
Topaz. Crystallized alumina with small quantity of coloring matter.
Vermilion. Artificial mercuric sulphide.
White arsenic. Arsenic trioxide.
white lead. Basic lead carbonate, used as a paint.
white vitriol. Zinc sulphate.
witherite. Native barium carbonate.
Zinc white. Zinc oxide, ZnO, used as a paint.

GLOSSARY OF TECHNICAL TERMS IN CHEMISTRY

Acidify. To make acid.
acidulate. To add acid to, until no longer alkaline or neutral.
actinic. Referring to light rays, having the power to effect chemical changes.
air-bath. A small oven used for drying substances.
alkali. A compound of hydrogen, oxygen, and some metallic element, soluble in water, having the power to neutralize acids; as caustic soda, NaOH.
allotropic. Literally, *another form;* a term applied to the unusual form of an element.

allotropism. The phenomenon of existing in two or more forms.

alloy. The product resulting from fusing together two or more metals.

amalgam. An alloy, one constituent of which is mercury.

amorphous. Without any special form, uncrystallized, massive.

anæsthetic. An agent used to produce insensibility.

anhydride. An oxide, usually non-metallic, which forms some acid upon the addition of water.

anhydrous. Without water. An anhydrous salt is one from which the water of crystallization has been removed.

anion. A negative ion. See *ion.*

antiseptic. A substance used to prevent decay, or to destroy noxious germs.

argentiferous. Silver-bearing.

aspirator. Apparatus used to secure the passage of air or any other gas through certain vessels.

assay. Determination of the quantity of the various constituents of a metallic ore.

Basic. Having the properties of an alkali or base.

binary. A compound consisting of two elements.

brightening. The sudden brilliant appearance of the silver assay when the lead has all been removed by cupellation.

bumping. A term applied to the violent boiling of the liquid in a vessel, causing it to jump.

burette. A graduated tube, with stop-cock, used in volumetric work for measuring accurately a liquid.

Calcine. To heat strongly.

carbureting. Adding hydrocarbon compounds to an illuminating gas, as in making *water gas.*

cathion. An electropositive ion.

cementation. An old process of making steel by imbedding wrought iron in powdered charcoal and heating several days.

chemism. The so-called affinity that one element or substance has for another.

commercial. A term applied to chemicals as usually furnished to the trade; not absolutely pure; in distinction from chemically pure reagents.

concentrated. Strong; undiluted.

converter. A large, egg-shaped furnace, used in making steel from cast iron and in purifying copper.

c. p. Chemically pure.

crucible. A small vessel, made to withstand great heat. Named from the Latin word *crux*, because the old alchemists thus marked their crucibles.

crystalline. Composed of crystals.

cupel. A small cup, made of bone ashes; used by assayers in determining the gold and silver in an ore.

cupellation. The process of separating lead and silver by the oxidation of the former.

Decant. To pour off the liquid from a precipitate, after the latter has settled.

decrepitate. To burst in pieces with a crackling sound, as many salts do when heated with the blowpipe.

deflagrate. To burn vigorously.

deflagrating spoon. A small metallic cup or spoon with a long wire handle attached. Used for holding combustible substances when burning in oxygen or other gases.

deliquesce. To take up moisture from the air.

deoxidizing agent. See *reducing agent.*

desiccate. To dry.

desiccator. A vessel used in drying or keeping dry a substance which is to be weighed accurately.

destructive distillation. The process of heating in closed retorts a substance to such a temperature as to effect its decomposition.

digest. To warm gently.

disinfectant. A substance used to cleanse and purify unwholesome places, as well as to destroy disease germs.

displacement. A method of collecting a gas in a vessel filled with air, or some other gas, depending upon the difference in density of the two.

dissociate. To break up a compound body into parts.

distill. To evaporate a liquid and condense again in another vessel.

distillate. The liquid obtained in the process of distillation.

dyad. An element having a valence of two.

Ebullition. Rapid boiling.

effervescence. The act of bubbling, as seen upon the application of an acid to a carbonate.

effloresce. To give up at ordinary temperatures the water of crystallization.

electrode. The terminal of a battery.

electro-positive. A term applied to elements attracted to the negative electrode.

equivalence. A term sometimes used instead of valence.

escharotic. An agent which corrodes or destroys; a caustic.

evolve. To set free.

excess. A quantity more than sufficient to secure certain chemical action.

Filtrate. The liquid obtained after passing through the filter paper, in removing the precipitate.

fixed. The opposite of *volatile.*

flocculent. Flaky.

flux. Any substance used to lower the melting point of another; as limestone with iron ore in the blast furnace.

formula. A combination of symbols used to represent a molecule of a compound body.

fractional distillation. The process of separating by distillation the several constituents of a mixture of liquids, by means of their different boiling points.

Gangue. The impurities contained in an ore or mineral.

gelatinous. Like starch paste in appearance.

generate. To produce or set free, as a gas.

germicide. A substance used to destroy bacteria or germs.

granulated. In irregularly shaped small particles, secured by pouring the fused metal into cold water.

graphitoidal. Resembling graphite.

gravimetric. Measurement or estimation by weight.

Halogen. Literally, *salt producer;* applied to the members of the chlorine group.

hydrated. Containing water.

hydroxyl. A term applied to the radical OH.

hygroscopic. Applied to substances which readily absorb moisture from the air.

Ignite. To set fire to.

indicator. A substance used to show the completion of a chemical reaction.

inflammable. Combustible.

ion. An atom or group of atoms in a solution, which serves as a carrier of electricity.

ionization. The separation of a substance into ions.

isomeric. Applied to substances having the same percentage composition, though differing in characteristics.

isomorphous. Of the same crystalline form.

Leach. To treat with water; to remove the soluble salts from a mixture of substances by means of water.

liquation. The process of separating one metal from another by cautiously fusing, so that one will flow out before the melting point of the other is reached.

lixiviate. Synonymous with *leach.*

lute. To seal air-tight.

Manipulation. Setting up or arranging apparatus for experiment.

matte. A mixture of metallic sulphides obtained in the early stages of the reduction of copper ores, containing lead, silver, etc.

meniscus. The upper curved surface of a liquid contained in a small tube.

monad. An element the valence of which is one.

mono-basic. A term applied to an acid having only one replaceable atom of hydrogen.

mordant. A substance used to set the color in dyeing.

mother liquor. The liquid remaining after the principal salt contained in solution has been removed by crystallization.

Nascent. Applied to a gas when first liberated from its compound. It is believed to exist then in the atomic condition.

native. Not in combination, free.

neutral. Neither acid nor alkaline.

neutralization. The combination of an acid with an alkali so as to destroy the properties of each, and produce a salt.

nitrogenous. Containing nitrogen. Organic matter containing nitrogen is thus characterized.

Occlude. To condense upon the surface or within the pores. Especially seen in the action of platinum upon hydrogen.

oxidation. The union of a substance with oxygen.

oxidizing agent. A substance which readily gives up a portion of its oxygen to combine with some other substance.

oxygenized. Containing considerable oxygen.

Paste. A special variety of glass, used sometimes for making imitation diamonds.

pigs. The term applied to cast iron as molded when first drawn from the blast furnace. Applied also to the molds themselves.

pipette. A small graduated glass tube used in measuring small quantities of a liquid.

pneumatic. Pertaining to gases; applied to the trough or pan used in collecting gases.

polymerism. A term referring to the cases of compounds which have the same percentage composition, but different molecular weights.

precipitate. A solid thrown down in a liquid by some reagent.

Qualitative analysis. The determination of the kind of matter which enters into a substance.

quantitative analysis. The determination of the amount of a substance contained in a compound.

Radical. A group of elements which seems to act as a single element.

reaction. The action of two or more substances upon each other.

reagent. A substance used to bring about some chemical change.

reducing agent. A substance used to convert a compound from a higher to a lower order, as from an *ic* to an *ous* compound; or, to remove the oxygen from an oxide.

residual. That which remains.

reverberatory. A variety of furnace, usually of low, arching ceiling. See Fig. 57 in text.

roast. To heat strongly; to oxidize metallic ores, expelling the sulphur as SO_2.

Sand-bath. A small iron saucer containing sand, used the same as a wire screen in protecting glassware when being heated.

saturated. Fully satisfied; containing all it can hold.

scintillate. To burn with sparks.

siliceous earth. Material consisting largely of silica.

slag. The dark-colored glass formed in the reduction of metallic ores from the flux used and the gangue present.

solvent. A liquid which dissolves some particular substance.

spit. Silver on being melted absorbs considerable oxygen. Upon cooling it again expels this, sometimes with considerable energy, throwing out fine particles of the molten silver. This is termed spitting.

stable. Not easily decomposed.

sublimate. The substance obtained by sublimation.

sublimation. The vaporizing of a solid and recondensing. The same in reference to solids that distillation is with liquids.

supernatant. Said of a liquid overlying a precipitate after the latter has subsided.

suspension. Said of a solid in the form of fine particles floating throughout the liquid.

symbol. A letter or letters representing an atom of an element.

Thio. From a Greek word, meaning *sulphur.*

treat. To apply or add to.

triad. An element having a valence of three.

tubulated. Applied to a flask having a small tube-like opening in the side, fitted with a stop-cock.

tubulure. A small, tube-like opening.

tuyère. A blast or air pipe for conducting the strong currents of air into the blast furnace.

Valence. The power which an atom or group of elements has of combining with some other element taken as a standard.

volatile. Easy to vaporize.

volatilize. To drive off in the form of vapor.

volumetric. Estimation of the quantity of a substance by measuring.

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