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INTRODUCTION TO MODERN INORGANIC CHEMISTRY

BY

J. W. MELLOR, D.Sc.



WITH ILLUSTRATIONS

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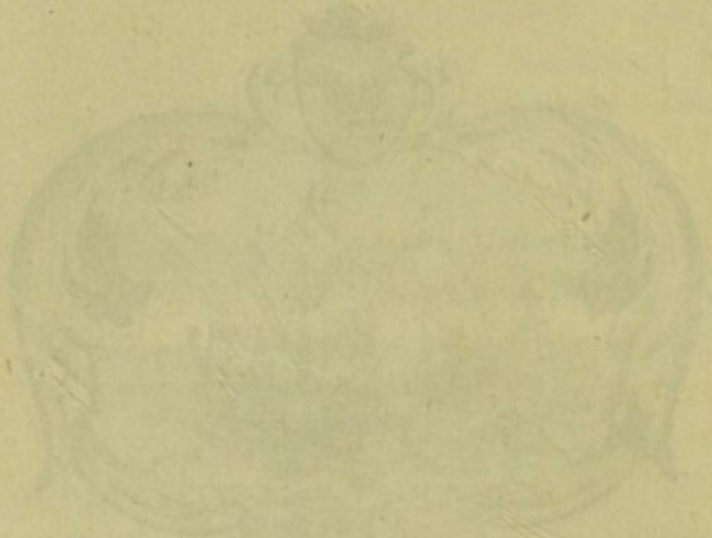
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PREFACE

The true aim of the teacher must be to impart an appreciation of method, and not a knowledge of facts.—K. PEARSON.
The power to recognize and to follow truth cannot be conferred by academical degrees.—PARACELSUS.

IT has been a source of great pleasure to me to find that *Modern Inorganic Chemistry* has made me many new friends. I have prepared a smaller introductory volume to suit students who want to start with a rather simpler book, and I have been persuaded to introduce some pages dealing with a few of the more important compounds which the inorganic chemist borrows from the organic chemist. My larger book can now be regarded as a kind of sequel to the present work. The ideas indicated in the preface to *Modern Inorganic Chemistry* have been my guide here as well as there. Hence I can do no better than reprint them.

Every teacher now recognizes that it is a sheer waste of time to introduce many abstract ideas into an elementary science course without a previous survey of facts from which the generalizations can be derived. In most cases the historical mode of treatment is correct, because the generalizations have usually been developed from a contemplation of the facts; in other cases the historical treatment may involve digressions which would seriously interfere with the efficiency of the course. Obviously, a teacher will try his best to instil the maximum amount of scientific method into the facts—as prescribed by his syllabus and time-table—always remembering that the student gets more lasting benefit from the method than from the facts *per se*. In after-life the scientific method may be retained as a permanent attitude of the mind when the facts themselves are nearly all forgotten. Consequently, the teacher

seeks to develop a certain spirit or attitude of mind which is almost equivalent to a sixth sense ; and therefore the justification for a general course in chemistry must be sought in the mind of the student rather than in the facts of the science. What, then, may a student expect from a general course of chemistry ?

1. *Skill in observation and experiment.*—All are agreed that personal contact with facts is a great advantage. The constant absorption of statements and opinions from text-books makes a student lean so much on authority that he ultimately becomes unfitted for independent observation. Habits of self-reliance, resource, and initiative can be acquired only in the laboratory, or by direct contact with natural phenomena. But practice in observation and experiment is not alone sufficient to develop the scientific faculty. The observational powers of a savage are usually keener than those of a civilized man, and a student may learn to observe without gaining much beyond an increased facility in the art : and he may become very skilful in experimenting without gaining much more than mere dexterity in manipulation.

2. *Memory and knowledge of relevant facts.*—Facts, of course, form the raw material which is refined by scientific methods into science itself. Science can do nothing without facts. Consequently, many facts must be memorized by the neophyte in chemistry. Some students soon learn the trick of amassing and memorizing all kinds of information in a mechanical way. All the facts associated with a phenomenon may not be of equal importance. In practice it is not always easy to discriminate between relevant and irrelevant facts. Still, it is important to confine the attention as closely as possible to relevant and essential facts, and to discard those irrelevant and accidental. The tyro in chemistry must trust his teacher to indicate the more significant facts to be committed to memory, and used as material for exercising his intellect and wits.

3. *Ability to reason and think in a logical systematic way.*—A student must learn to reflect on the available

data bearing on the problem in hand; and to explain a phenomenon by drawing legitimate inferences from approved evidence. It is a mistake to postpone the exercise and discipline of the thinking faculties until a student has memorized a vast accumulation of facts. It is necessary to form habits of reflection and thought as early as possible. Exercise means growth. It is far easier to acquire a mass of facts than to learn to draw a sound inference as to what the facts prove. The thinking faculty can be developed only through the student's own individual efforts. Just as the memory, in some subtle way, grows more vigorous with use, so the exercise of the thinking faculties enhances the power to think. Every exercise of the reason, said Sir Humphry Davy in 1811, strengthens the habit of correct thinking, and adds something to the influence and power of common sense. Vague indefinite observing is usually followed by muddled inchoate thinking. Clear thinking pre-supposes clear seeing.

4. *Cultivation of the imagination.*—Some teachers have very pronounced objections to the introduction of scientific theories in an elementary course; they claim that "it is not scientific to present and discuss, say, the atomic theory in an elementary chemistry course." It might be asked what constitutes an elementary course? It would be a great mistake to suppose that science has no need for the imagination, for it is very true, as K. Pearson has said, that "disciplined imagination has been at the bottom of all great scientific discoveries"; and, as W. A. Fiske has said, that "every hypothesis and law of science is the result of a vivid imagination." Imagination helps to complete the picture outlined by observation and inference. The picture must, of course, be tested and criticized in every conceivable way to make sure that it is not a mirage among the purpled morning clouds to be dispelled by the dawning light.

5. *Development of a critical and impartial judgment.*—The imagination, though very useful, is a most dangerous ally;

and a sharp line of demarcation must be observed between valid or legitimate deductions from the evidence, and what has been supplied by the imagination. Each proposition must be judged solely on its merits. There must be no shirking of the facts, no exaggeration, no distortion of the naked truth. The mind must be kept open and free from prejudice. The student must learn not to prejudge data and phenomena by ideas formed independently of the things themselves. A teacher soon accumulates remarkable examples of the influence of expectation on judgment. If a practical class knows what quantitative result "ought" to be obtained, it is surprising how much nearer that result the majority will get than if the true result were unknown—and this without dishonest intentions. Rigorous honesty and absolute impartiality in dealing with approved evidence are indispensable. A complete absence of bias can alone give reality and meaning to scientific truths.

I have to thank several authorities for permission to use a number of quotations and a selection of questions from college examination papers. The source of each is indicated in the text. The original wording of the examination questions has been slightly modified in a very few cases. I have pleasure in thanking a number of friends for reading portions of the proofs. I gratefully acknowledge the help I have consciously and sub-consciously received from the examination and review of a large number of text-books during the past few years. I am also indebted to Mr. F. J. Austin for the photography.

J. W. M.

THE VILLAS,
STOKE-ON-TRENT.

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INTRODUCTION TO MODERN INORGANIC CHEMISTRY

CHAPTER I

The Physical Properties of Atmospheric Air

§ 1. What is Air?

> The generality of men are so accustomed to judge of things by their senses, that because the air is invisible, they ascribe but little to it, and think it but one remove from nothing.—Robert Boyle (1673).

We are surrounded on all sides by a subtle transparent invisible air, and we appear to be living at the bottom of a vast ocean of air much as the flat-fish live at the bottom of the sea. We cannot usually see, taste, or feel the air, and comparatively few have any definite idea of its nature, and are seldom cognizant of its presence. Many of the old philosophers even doubted the materiality of air, and denied that it has substance or weight. The existence of air is perceptible to the senses only when it offers resistance to rapid movements, and when it itself is in motion. Wind is air in motion, and wind has sufficient energy to propel our sailing-ships, to drive the machinery of our windmills, and, when stirred by cyclonic blast, to uproot trees, sweep away buildings, and lash the surface of the ocean into wild monster waves.

All known solids and liquids possess two attributes—weight and extension in space—which appear to be permanent and

essential qualities abiding in *all known kinds of matter ;* whereas other properties—colour, odour, etc.—appear to be secondary or accidental attributes because they are peculiar to *specific forms of matter.* The question whether air is or is not a form of matter remained open for hundreds of years before a definite answer could be returned, because the answer naturally turns on two other questions : Does air occupy space ? Does air possess weight ?

§ 2. Does Air occupy Space ?

The old Grecian philosophers were not favourably disposed to knowledge obtained by observation and experiment ; they appear to have been so very proud of their intellectual superiority that they purposely refrained from checking the truth of their conjectures about natural things by comparing them with facts. Consequently, it is not common to find experimental observations cited in their voluminous writings. Anaxagoras, who flourished about 500 B.C., was exceptional in that he used two experiments as the base of his argument to prove that air is material. He said : (i) A blown bladder resists compression ; and (ii) The inside of an inverted drinking-glass, when plunged beneath the surface of water, remains perfectly dry. He might have added that this phenomenon would not obtain unless something inside the vessel prevented the ingress of the water. A similar experiment is mentioned by Hero of Alexandria, about 117 B.C., to prove that air is matter.

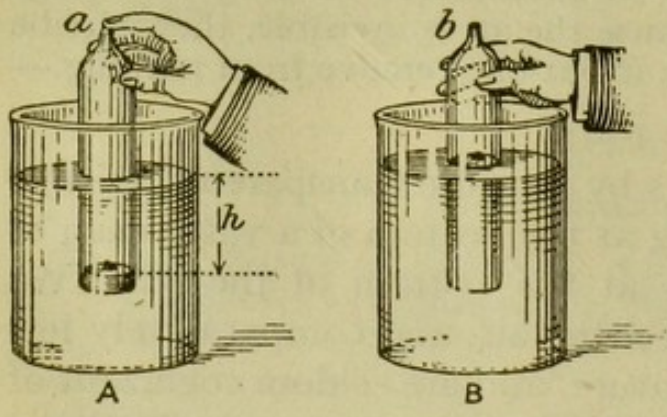


FIG. 1.—Modern form of Hero's Experiment (117 B.C.).

The idea of Hero's experiment is illustrated in Fig. 1. A glass cylinder with a very narrow orifice *a* at one end and open at the other is pressed into a vessel of water, while the narrow orifice is closed by the finger as shown in Fig. 1, *A*. The water scarcely

rises at all into the cylinder, and the space inside the cylinder, represented by *h*, Fig. 1, is occupied by air. When the finger closing the narrow orifice is removed, *b*, water enters the cylinder until sufficient air has been expelled to allow the water inside to rise to the same level [1] as the water outside the cylinder (*B*, Fig. 1). The rush of air as it escapes from the cylinder at *b* can be felt by placing the hand just over the orifice.

If a bottle with its mouth upwards be plunged beneath the surface of water, bubbles of air leave the bottle as water enters ; and conversely, if a bottle full of water be held mouth downwards in air, bubbles of air enter as water leaves the bottle. These experiments might be multiplied indefinitely. All confirm the conclusion : **Air is a substance which occupies space.**

§ 3. Does Air possess Weight?

Aristotle (*c.* 400 B.C.), another celebrated Grecian philosopher, *asserted* that air has weight, and he thought that he had proved this when he said that an utrem—bladder or leather bottle—weighed less when "empty" than when "inflated" with air. Unless the air was under compression in Aristotle's experiment, the bladder must have weighed the same whether "inflated" or "empty," because air weighs nothing when weighed in air. Accordingly, doubts arose as to the truth of Aristotle's statement, because others tried in vain to verify the experiment.[2] The question was, however, definitely settled by Galileo Galilei, in 1632, and he was the first to prove by direct weighing that **air is a substance which possesses weight.** Galilei proved conclusively that a copper globe full of air weighs less than the same copper globe filled with compressed air. After the invention of the air-pump by Otto von Guericke, about 1650, it was comparatively easy to find the actual weight of a given volume of air.

[1] The level of the water inside the cylinder can be readily shown at a distance by the aid of a piece of floating cork.

[2] For instance, Simplicius said that a certain amount of moisture must have condensed from the breath when Aristotle inflated the bladder with air from the lungs, and that Aristotle must have weighed the condensed moisture, not air.

Experiment to determine the weight of a given volume of air.—A glass globe or litre flask *A*, Fig. 2, fitted with a stopcock *a*, is exhausted by means of the air-pump, and then suspended from one arm of a delicate balance, and counterpoised by shot, or by another similar globe *B* on the other arm of the balance. The globe *A* is then filled with air by opening the stopcock *a*, and, when it is again suspended from the arm of the balance, it descends, owing to the weight of the air it then contains. Weights are added to the other pan until equilibrium is restored. The weight so added represents the weight of the air in the globe. Suppose that 1·26 grms. were needed. The air is again removed from the globe *A*, and the stopcock opened while the mouth of the globe is immersed in water, at, say, 4°. The globe fills with water. The

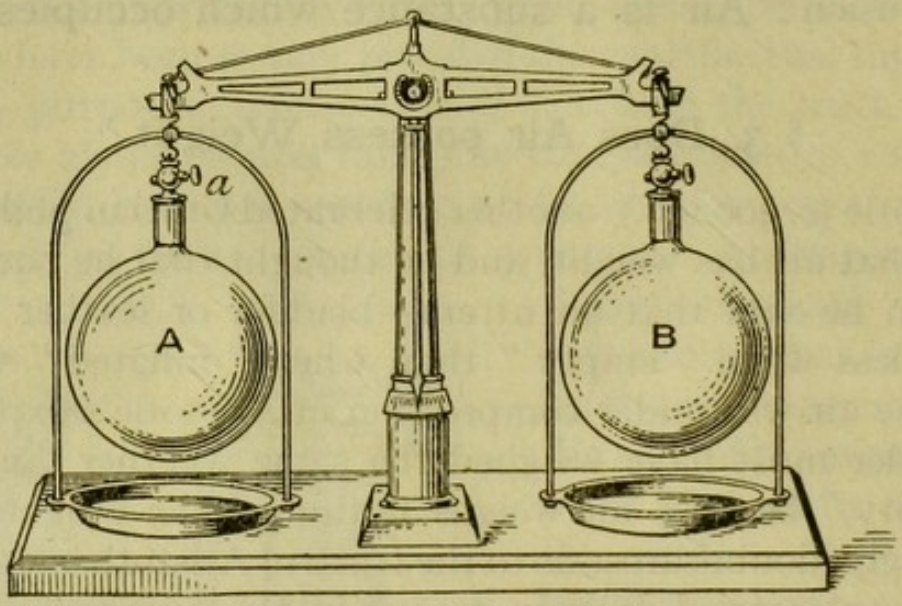


FIG. 2.—Weighing Air.

stopcock is then closed, and the outside of the globe dried. The globe and contents are then weighed. Suppose that 1050 grms. are needed, the globe then contains 1050 c.c. of water, since one cubic centimetre of water, by definition, weighs one gram at 4°.[1] The experiment shows that 1050 c.c. of air at the time of the experiment weighed 1·26 grms., or that 1000 c.c. of air weigh 1·2 grms. Certain corrections are required. The more important of these will appear towards the end of this chapter.

Refined experiments made by trained men, working with

[1] If the temperature exceeded 4°, a correction would be required, because water expands with a rise of temperature. The correction required can be read from Tables of the Specific Gravity of Water at different temperatures, which have been compiled from actual measurements and are to be found in books of reference.

the best available apparatus, and taking all known precautions to secure constant conditions, show that **under standard conditions, 1000 c.c. of dry air weigh 1·293 grams.** Hence, like all other known forms of matter, air is a material substance which both occupies space and possesses weight.

§ 4. Faith in Authority.

Errors of experiment.—When the student first tries to weigh air in the laboratory, he is almost sure to be disconcerted on finding that his own numbers deviate from one another. However carefully he works, each measurement will differ from the others, unless, of course, a very crude balance is employed. However skilful the worker, **it is impossible to make an exact measurement without committing a small error of experiment.** The more skilful the experimenter, the less the magnitude of the experimental error; but the very best men working under the very best conditions can rarely get two measurements to coincide perfectly. Hence **it is usual to make a series of measurements of any given phenomenon, and to select the arithmetical mean as the best representative value.** The experimental error is then represented by the deviations from the arithmetical mean. In the preceding experiment—even after correcting his result by the method to be described later—the student will have done very well if he gets numbers with an experimental error deviating less than one per cent. from the arithmetical mean.

Still further, the student will most assuredly find that the best representative value of his own measurements deviates from 1·293 grams per litre. It has just been emphasized that this number is the result of work by specially trained men provided with the best available apparatus. It is but to be expected that the student will require some practice before he can acquire the accuracy, deftness, and skill of an expert chemist. There is no reason to suppose that the 'prentice hand of the beginner will be less awkward in the chemical laboratory than when he first entered the swimming bath or first mounted a bicycle. It is not permitted every one to

"touch the record" in running or swimming, nor yet in chemical manipulation.

The numerical constants accepted by chemists can be regarded as concordant records made by a number of investigators who have been proved worthy of confidence. The student will find that he has to accept by faith the results of a great many measurements—the so-called constants—made by others. Faith is belief based on suitable evidence outside personal experience. This faith in authority is not the blind faith of the unreasoning kind so prevalent in the Middle Ages, but, as H. C. Bolton said, it is a rational belief in the concurrent testimony of individuals who have recorded the results of their experiments and observations, and whose statements can be verified.

§ 5. Nature's Horror of a Vacuum.

An experiment.—A flask is fitted with a rubber stopper, glass tube and stopcock, as indicated in Fig. 3. The tube is connected with an air-pump, and the flask exhausted. The stopcock is closed, and the tube dipped beneath the surface of some water, preferably coloured with a few drops of red ink. The stopcock is then opened and the rush of water entering the flask forms a spray or fountain inside the flask, Fig. 3.

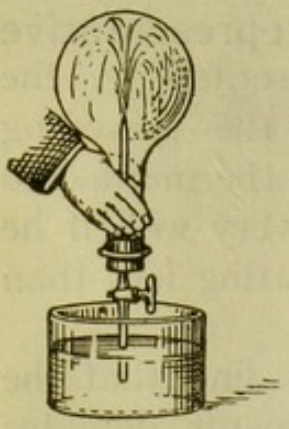


FIG. 3.—Rush of Water into a Vacuum.

An hypothesis to explain the experiment.—Why does the water enter the flask? Prior to 1644 it was believed that Nature abhors a vacuum, and that Nature's horror of a vacuum made the water rush into the evacuated flask immediately the way was open. Instead of accepting Aristotle's plausible conjecture, hypothesis, or guess in blind faith, let us compare it with other phenomena so as to find if it explains them equally well. It does not follow that because we have found *an* explanation we have found *the* right one.

Confirmatory facts.—When a glass bottle is filled with

water, closed by pressing the palm of the hand on the open mouth of the bottle, the bottle turned upside down, and the hand removed while the mouth of the bottle is immersed in water, the water remains in the bottle, Fig. 4.

After pouring water from a tumbler, it may be perfectly true to say that the tumbler is empty, so far as the water is concerned, but it is not empty in an absolute sense, because air entered the tumbler when water ran out. If an inverted cylinder or bottle filled with air be gradually reversed under water while its mouth is held beneath that of another cylinder filled with water, Fig. 5, the bubbles of air from the one cylinder rise into the other and

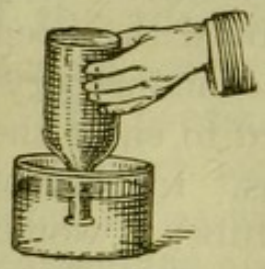


FIG. 4.—Column of Water supported in Bottle.

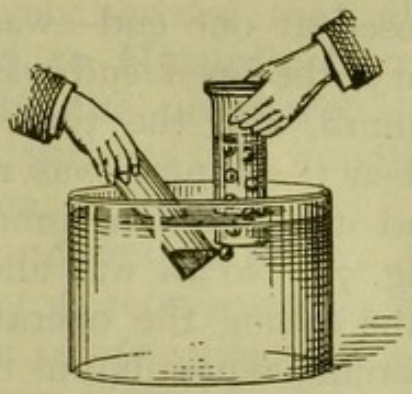


FIG. 5.—Transferring Gases from one Cylinder to another.

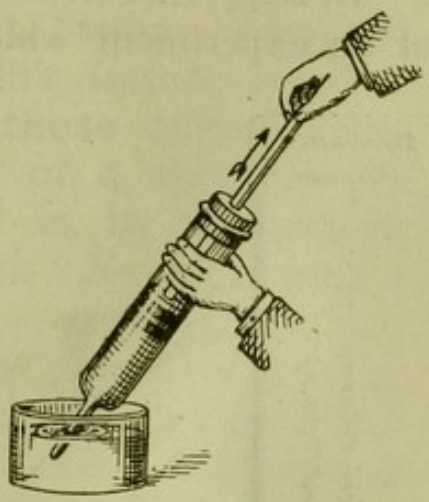


FIG. 6.—The ascent of Water in the Cylinder of a Pump.

gradually displace the water. In this way, air can be transferred from one cylinder to another.

Again, dip the tip of a glass syringe with its piston depressed, into a vessel of water, Fig. 6; raise the piston and the water will rise in the cylinder at the same time. All these experiments are readily explained by Nature's horror of a vacuum.

About 1630 Galilei noticed that a pump which worked satisfactorily when the water in the reservoir was at a certain height, appeared useless when the water had subsided to a lower level. Thinking that there was something wrong with the valves of the pump, Galilei wrote—

I sent for a workman to mend it. He told me that this defect

was owing to nothing but to the water being too low, and hence not suffering itself to be raised to such a height; and he added that neither pump nor any other machine which raised water by attraction could ever raise the water a hair's breadth more than 33 to 34 feet; and, let the pump be big or little, that this is the utmost height.

This free translation from Galilei's writings makes it appear as if Nature's repugnance to a vacuum extends only up to about 33 feet.

§ 6. Death of the Hypothesis: Nature abhors a Vacuum.

In 1644, E. Torricelli, a pupil of Galilei, published an account of an experiment which puzzled the philosophers of his time. A glass tube—about four feet long, and closed at one end—was filled with mercury, the open end was closed with the thumb, and the tube inverted, so that when the thumb was removed the open end of the tube was immersed in mercury, Fig. 7. No air was allowed to enter the tube during the operations. Instead of mercury remaining in the tube, as would have been the case with water, the column of mercury fell to such an extent that its height above the surface of the mercury in the dish was nearly 30 inches, or 760 millimetres.

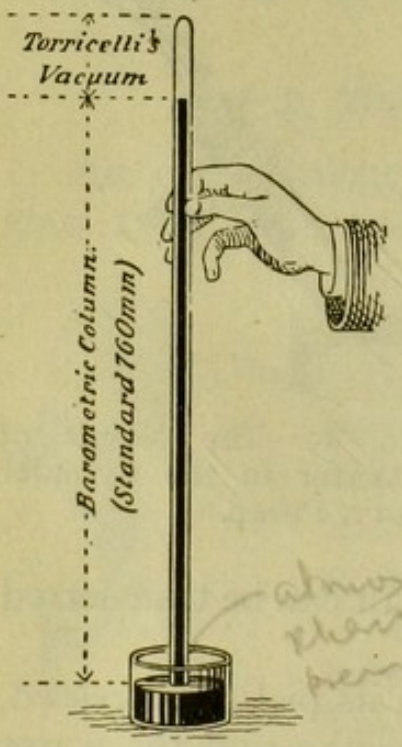


FIG. 7.—Torricelli's Experiment.—The Barometer.

Here, again, Nature's horror of a vacuum at the top of the tube only extends to the equivalent of 30 inches of mercury. Accordingly, Torricelli rejected the hypothesis that the mercury refused to rise higher than 30 inches in the tube out of respect for this particular whim on the part of Nature; and he argued, rightly enough, that the column of mercury was maintained by the air pressing on the surface of the mercury in the outer vessel.

B. Pascal here reasoned that since mercury is nearly 13½ times as heavy as water, if Torricelli's hypothesis be correct,

a 30-inch column of mercury will be equivalent to a $30 \times 13\frac{1}{2} = 405$ inches, or $33\frac{3}{4}$ feet column of water. Accordingly, Pascal repeated the experiment of Torricelli with a tube about 40 feet long, using water in place of mercury, and he found that the pressure of the atmosphere, as he predicted, supported a column of water nearly 34 feet long. Hence he inferred that **the height of the column of mercury is a measure of the pressure of the atmosphere,** and that fluctuations in the pressure of the air are accompanied by a corresponding rise or fall of the column of mercury in Torricelli's instrument. R. Boyle (1665) happily applied the term **barometer** to Torricelli's instrument from Greek words meaning "a weight-measurer."

In a posthumous work published in 1663, Pascal summarized the arguments for and against Torricelli's hypothesis, and the result conclusively showed that **all those effects, previously attributed to Nature's horror of a vacuum, are really produced by the pressure, that is, by the weight of the air.**—Thus perished the hypothesis: Nature abhors a vacuum—ÆTAT 2000.

The pressure and weight of air.—The pressure of the air in any given locality, as represented by fluctuations of the barometer, varies within comparatively narrow limits. The **normal or standard pressure of the atmosphere** is equal to the weight of a column of mercury of unit area and 760 mm. high. This pressure is sometimes called "one atmosphere." It is merely necessary to know the height of the barometric column to know the weight or pressure of the air per unit cross-sectional area. The standard corresponds with a weight of 1033·3 grms. per square centimetre, or 14·7 lbs. per square inch—the word "pressure" is generally used here in preference to "weight."

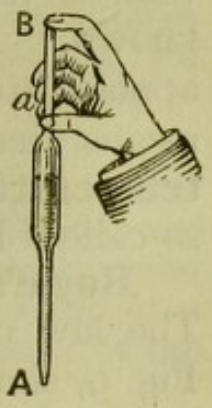


FIG. 8.—The Pipette.

The pipette.—The pressure of the air is neatly illustrated by the pipette used for measuring definite volumes of liquid—5 c.c., 10 c.c., etc. The end *A*, Fig. 8, is dipped in the liquid, and suction applied with the mouth at *B*. When the liquid has risen to the mark *a*, the finger is applied as shown in the diagram, and

the liquid can be then transferred where desired, for the orifice at *A* is too narrow to allow air to enter when a liquid is in the tube, and no liquid will run out. The pipette is emptied by releasing the pressure of the finger at *B*. The pipette shown in Fig. 8 has been nearly half emptied.

§ 7. The Influence of Pressure on the Volume of Gases —Boyle's Law.

The air-pump was discovered about the time Pascal and Torricelli demonstrated the weight and pressure of the atmosphere. The new instrument attracted much attention, and the effect of the " vacuum " [1] on all kinds of animate and inanimate objects was tried. Robert Boyle placed a partially inflated lamb's bladder in the " vacuum " produced by the air-pump, and noticed that the bladder became fully distended ; when air was readmitted, the bladder contracted to its former size. This experiment established the important fact that " the greater the amount of pressure removed from a given volume of air, the more does it expand."

In 1661, Boyle continued his work on the elasticity or " spring " of the atmosphere, and found " the pressures and expansions," as he expressed it, " to be in reciprocal proportion." When this fact was discovered, air was the only gas known. It was subsequently found that what applies to air applies to other gases, and accordingly Boyle's discovery means that **the volume of a gas kept at one uniform temperature varies inversely as the pressure.** This is the so-called **Boyle's law.**

Boyle's law for pressures greater than atmospheric.— The law can be tested in a bent U-tube of uniform bore, Fig. 9, similar to that used by Boyle himself.

The shorter leg is hermetically sealed at one end, and the end of the longer leg is open. The tube is fixed to a board as shown in Fig. 9. The tube can be graduated by fixing bits of gummed paper at definite distances apart. Mercury is poured into the

[1] The term " vacuum " is often employed when " reduced pressure " is meant.

longer leg so as to fill the bend and reach to the same height in both legs. It may be necessary to tilt the apparatus a little to expel a few bubbles of air from the shorter leg. Read the volume of gas confined in the shorter leg. Since the level of the mercury is the same in both limbs, it is assumed that the pressure on the surface of the mercury on both sides of the U-tube is the same. There is a pressure of one atmosphere on the mercury in the open leg, hence also there is an equivalent pressure of one atmosphere on the mercury in the closed leg. A pressure of one atmosphere is equivalent to about 30 inches of mercury, or 760 mm. of mercury. In reality the pressure is equivalent to the height of the mercury barometer at the time of the experiment. Pour a little mercury into the open leg. The gas confined in the shorter leg diminishes in volume. It is easy to prove that no gas has escaped from the shorter leg, and consequently, the gas in the shorter leg has been compressed. In other words, the concentration of the gas per unit volume is increased by the pressure. The difference in the levels of the mercury in the two legs plus the pressure of the atmosphere represents the pressure on the gas in the short leg. More mercury may be poured in the longer leg, and thus a series of numbers are obtained representing the pressure and the volume of the gas in the closed limb. When Boyle had poured sufficient mercury in the longer leg to reduce the volume of the gas in the shorter leg one-half, he said, "When we cast our eye on the longer leg, we observed, not without delight and satisfaction, that the quicksilver in the longer part was 29 inches higher than in the other." In other words, the volume was diminished one-half when the pressure was doubled by superposing on to the ordinary pressure of the atmosphere, the pressure of a column of mercury 29 inches long and equal to the pressure of the atmosphere at the time of the experiment.

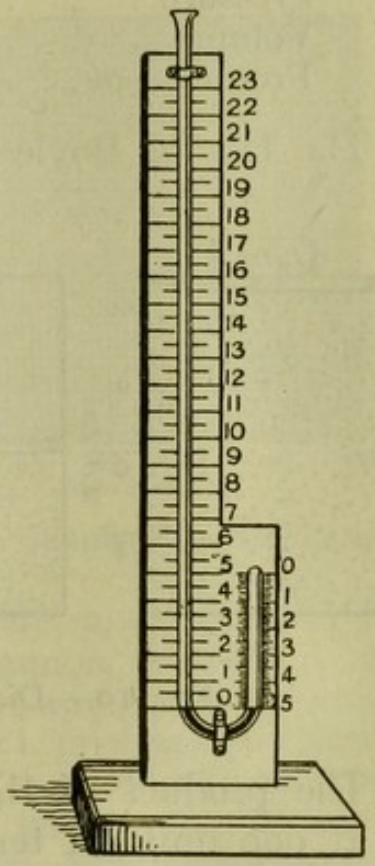


FIG. 9.—Boyle's Law —High Pressures.

To illustrate Boyle's important generalization, imagine 12 litres of a gas confined in a cylinder closed by a gas-tight piston free to slide up and down the cylinder without friction. Suppose further that the gas supports a weight of one atmosphere on the piston, *A*, Fig. 10. If another equal weight be placed

upon the piston, *B*, Fig. 10, the gas will be compressed until it occupies a volume of six litres ; another atmosphere pressure, *C*, Fig. 10, will reduce the volume of the gas to 4 litres ; and still another atmosphere pressure, *D*, Fig. 10, will reduce the volume of the gas to 3 litres. Collecting all these results into one table, we see that :

Pressure . . .	1,	2,	3,	4,	6 atmospheres
Volume . . .	12,	6,	4,	3,	2 litres
Product—pv . .	12,	12,	12,	12,	12

The law of Boyle may therefore be expressed another way :

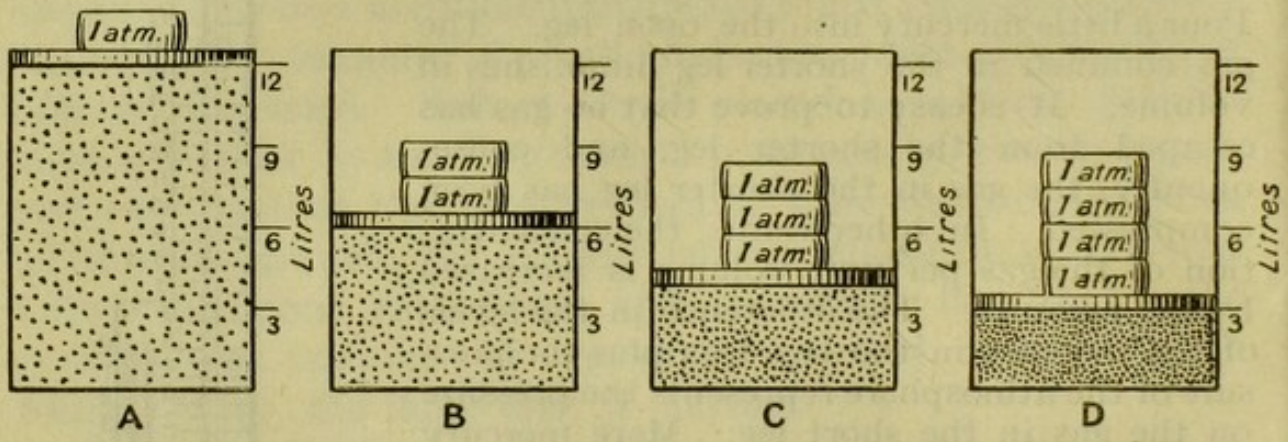


FIG. 10.—Diagrammatic Illustration of Boyle's Law.

The product of the pressure and the volume of a gas kept at one uniform temperature is always the same. Or,

$$pv = \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

All possible measurements of the relation between the volume and pressure of air are summarized in this simple statement. The numerical value of the constant, of course, depends upon what units are selected for representing the pressures and volumes. Pressures may be expressed in atmospheres, millimetres of mercury, pounds per square inch, etc. ; and the volumes in litres, cubic centimetres, cubic feet, etc.

By plotting the equation $pv = 100$ on squared paper, as is done in Fig. 11, the whole history of the change is brought vividly before the mind, for the relation between pressure and volume of a gas is then exhibited in the form of a picture, and the meaning of the law is seen at a glance. If the law correctly

describes the volume of a gas under different pressures, then no pressure, however great, can reduce the volume of a gas to zero. This is illustrated by the very very gradual approach of the curve to the line representing zero volume.

Boyle's law assumes yet another guise. If p_1 be the pressure of a gas occupying a volume v_1; and p the pressure when the volume is v, then, since the products p_1v_1 and pv are equal to the same constant, they are equal to one another. Consequently,

$$pv = p_1v_1 \quad . \quad . \quad . \quad (2)$$

If any three of these magnitudes be known, the fourth can be calculated directly.

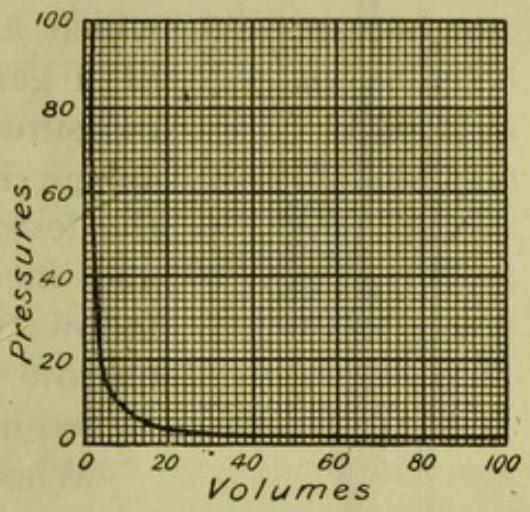


FIG. 11.—Graph of Boyle's Law.

EXAMPLE.—A vessel holds 4·5 litres of gas when the barometer reads 755 mm. What will be the volume of the same body of gas when the barometer stands at 760 mm. ? Here, $p_1=755$, $v_1=4{\cdot}5$, $p=760$; hence $v=4{\cdot}47$ litres. The most common problem is to calculate—" reduce "—the volume of a gas at any observed pressure to the corresponding volume at normal pressure 760 mm. Given 4·5 litres of gas at 755 mm. pressure, there is no need for any formula to calculate the corresponding volume at 760 mm. The pressure, 760 mm., is greater than 755 mm., hence the volume will be less, hence multiply 4·5 by the fraction $\frac{755}{760}$ and the result is 4·47 litres.

Boyle's law for pressures less than atmospheric.—Boyle showed that the law holds good at pressures less than atmospheric. Boyle used an arrangement similar in principle to that illustrated in Fig. 12. Some mercury is poured into a narrow tube which is closed at one end and open at the other. The open end is closed by the thumb and inverted in the tall cylinder of mercury. The narrow tube is raised or lowered, and the volume of gas confined in the narrow tube as well as the difference in the levels of the mercury in the narrow and in the wider tube read at the same time. We can recognize the principle of the U-tube, Fig. 9, in this apparatus,

Fig. 12. The pressure on the mercury in the wide cylinder is one atmosphere, and the pressure of the gas in the narrow tube is one atmosphere less the pressure of a column of mercury equal to the difference in the level of the mercury in the two tubes.

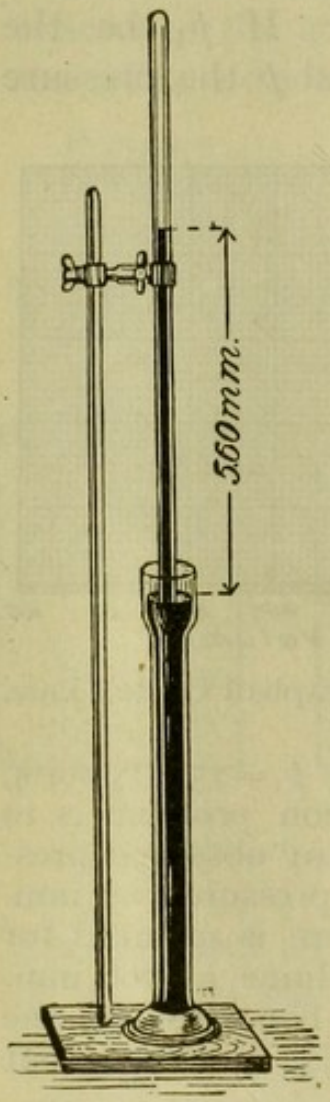


FIG. 12.—Apparatus to illustrate Boyle's Law — Low Pressures.

Measuring the volumes of gases.— The last experiment illustrates a problem which arises very often when the volume of a gas, collected over mercury, is to be measured. If the pressure of the atmosphere is 760 mm., and the difference in the levels of the mercury in the gas jar and in the pneumatic trough is 56 cm., it follows that the pressure of the gas in the narrow tube is 760 mm. less 560 mm. = 200 mm.

Whenever practicable, of course, the mercury inside and outside is brought to the same level before the gas is measured.

Suppose that the confining liquid is water, not mercury. Water is frequently used when the gases are not appreciably soluble in that liquid. Suppose that the external pressure is 760 mm. (barometer), and there is a difference of 10 cm. between the level of the water confining the gas, and the level of the water exposed to the air. The weight of 10 cm. of water is not the same as the weight of 10 cm. of mercury. Mercury is 13·55 times as heavy as water, hence a 10-cm. column of water is equivalent to the weight of a column of mercury $\frac{10}{13 \cdot 55}$ or 0·74 cm. or 7·4 mm. high. The pressure of the gas is therefore

$$760 - 7 \cdot 4 = 752 \cdot 6 \text{ mm.}^1$$

[1] The water vapour exerts a definite pressure, and a still further reduction must be made if we want the pressure actually due to the gas and not to the mixture of water vapour and gas. This will be investigated later.

§ 8. The Methods of Science.

Facts are the body of science, and the idea of those facts is its spirit.—S. BROWN.

Hypothesis is the general, and experiments are the soldiers.—LEONARDO DA VINCI.

The first aim of science is to collect facts. Science can do nothing without facts. They are the foundation and the building stones of the whole superstructure. The edifice is alone stable when it is founded on the immutability of facts. The accumulation of facts, however, is not the only purpose of the man of science, but, whatever be his secondary intentions, his prime object is the discovery of new facts. It is conceivable that a student might be able to memorize every fact which has been recorded in chemical encyclopædias, and yet know little or nothing of the *science* of chemistry. Such a student would be overwhelmed and dazed by a chaos of facts crowded in prodigious variety.

The higher purpose of science is to show that, amid wild and terrible disorder, order and law reign supreme. The man of science seeks a refuge from the bewildering complexity in unifying principles by which the facts can be grouped and classified into systems. As he gazes into nature, the man of science must be quick to discern hidden resemblances among a thousand-fold differences; he must be quick to disentangle natural relations from a medley of detail; and quick to detect dissemblances amidst alluring similarities.

Notice how Boyle's law was discovered. The facts were first garnered; these were then arranged in columns to show the volumes occupied by air at different pressures. The unifying principle showing the relation between the volume and pressure of the air then became clear—volume varies inversely as the pressure. The law thus summarizes in a concise form an indefinite number of measurements of the volume occupied by air at different pressures. The law was thus deduced from the facts. This method of investigation is called the **deductive method**, from a Latin verb *deducere*, meaning "to draw from or out of."

The pressure of the air was discovered in quite a different way. Certain phenomena were explained by guessing that "Nature abhorred a vacuum." Supposing that this conjecture be true, it followed that (1) Nature's horror of a vacuum must be greater at sea-level than on the top of a hill, because the mercury of the barometer always stands at a lower level on a hill-top than in the valley lower down ; and (2) that Nature's repugnance is equivalent to a mercury column about 30 inches high, or to a water column nearly 34 feet high. It did not seem probable that Nature should have a particular whim of this character, and Torricelli's rival hypothesis—the barometric column is supported by the pressure of the air—proved quite adequate. Every logical deduction from Torricelli's hypothesis has been abundantly confirmed when confronted with facts.

The purpose of an hypothesis is to give coherency to ascertained facts, and to serve as a starting-point for further inquiry. Thus, Torricelli's hypothesis rendered all the facts known in his time comprehensible to the understanding, and it served as a point of departure for new observations. A successful hypothesis will be strengthened by the testimony furnished by diverse facts, and the more numerous and significant the particular instances embraced by the hypothesis, the more nearly will their joint testimony "mount to the altitude of proof." It is absolutely necessary to submit all conjectures to the incorruptible test of fact in order to avoid being seduced by immaterial creations of the imagination. Faith without facts availeth nothing. The test must be made with unremitting diligence, rigorously and impartially, without conscious bias. Trial by a combat of wits in disputations has no attractions for the seeker after truth ; to him, the appeal to experience is the last and only test of the merit of an opinion, conjecture, or hypothesis.

In the deductive method laws are deduced from the facts ; in the second method, hypotheses are invented to explain the facts, and the logical consequences of each hypothesis are tested by comparison with other facts. Every hypothesis must be rejected or modified if it fails when treated in this manner. The second method of investigation is called the **inductive method,**

from the Latin verb *inducere*, meaning "to lead into"; the idea is that hypotheses prompt new experiments and thus lead to the discovery of new facts and new laws. Hypotheses have been compared with the scaffolds and ladders used in the erection of a building, and they are to be removed when the building is completed. Consequently, hypotheses are temporary auxiliaries erected to assist in building the temple of truth.

When a hypothesis gives promise of ripening into a law, it is called a **theory**. There is thus no well-defined difference between a hypothesis and a theory; both are more or less speculative and probably tentative, whereas a **law** or a **law of nature** is a condensed description or summary of observed facts. **An hypothesis is supposed to be established when it, and it alone, is in harmony with known facts.** The hypothesis then ranks as a theory or law. Laws, theories, and hypotheses are all on probation. However successful a theory or law may have been in the past, directly it fails to interpret new discoveries, its work is finished, and it must be discarded or modified. On account of the "unproved assumption" embodied in all hypotheses, they are of necessity transient, fleeting, and less stable than theories; and theories, in turn, are less stable than laws. A theory believed to-day may be abandoned to-morrow. Hypotheses and theories are continually changing. Science in making is "a battlefield of competing theories," the path of progress is strewn with dying and dead hypotheses.

§ 9. The Influence of Temperature on the Volumes of Gases—Charles' Law.

In 1790, Joseph Priestley concluded "from a very coarse experiment" that "fixed and common air expanded alike with the same degree of heat"; and J. Dalton, in 1801, as a result of some experiments on this subject, stated: "Upon the whole, I see no sufficient reason why we may not conclude that all elastic fluids, under the same pressure, expand alike equally by heat." J. L. Gay-Lussac also, in 1802, quoted some experiments in support of the view: **The same rise of temperature produces in all gases the same increase in**

volume, provided the pressure be kept constant. This law is designated **Charles' law,** in honour of J. A. C. Charles, who, according to Gay-Lussac, made some crude experiments on the subject fifteen years before Gay-Lussac's publication.

The relation between the temperature and the volume of a gas can be illustrated in the laboratory by means of a tube (Fig. 13) with a bead of mercury, and graduated as shown in the diagram. The end of the tube is fitted by means of a bored cork with a short piece of glass tube packed with fragments of calcium chloride and glass wool in order to protect the interior of the tube from moisture.[1] The tube is supported horizontally in a bath kept at, say, the melting point of ice, 0°, and the position of the bead of mercury noted. The temperature of the bath is then raised, and both the temperature and the position of the mercury bead noted. A

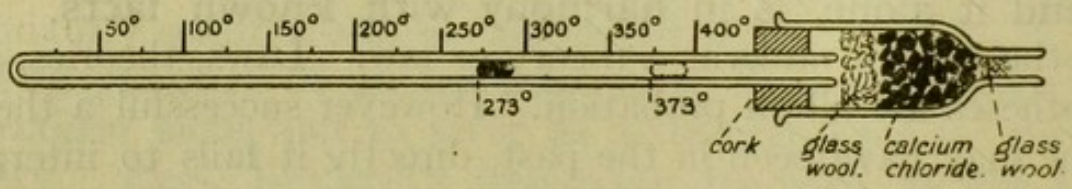


FIG. 13.—Apparatus to illustrate Charles' Law.

series of numbers can thus be obtained showing the relation between the volume of the air confined in the tube by the bead of mercury and the temperature.

The increase in volume which occurs when one volume of gas at 0° is heated under conditions where *exact* measurements can be made are indicated in the following table :—

Temperature, $t°$.	Volume, v litres.	Expansion per litre per degree.
0	1·00000	
1	1·00368	0·00368
2	1·00736	0·00368
3	1·01104	0·00368
4	1·01472	0·00368

[1] Fused calcium chloride rapidly absorbs moisture from the atmosphere. This is easily shown by placing a few pieces on a watch-glass. The object of the glass wool is to keep the calcium chloride in place. The calcium chloride tube is often omitted, but students do not then get such good results in the laboratory, perhaps because films of moisture condense on the cold glass, and vaporize when the glass is warmed. The experimental error is about one-fifth per cent.

The numbers in the last column are all the same. If the measurements had included another significant figure, the differences in the third column would have been affected by experimental errors. Instead of 0·00368, numbers varying from 0·003678 to 0·003676 were actually observed. The number 0·00368 is the so-called **coefficient of thermal expansion**; it means that the volume, v litres of air when heated through $t°$, can be represented very closely by the expression :

$$v = 1 + 0{\cdot}00368t \text{ litres.}$$

In other words, air increases 0·00368, or very nearly $\frac{1}{273}$rd part of its volume at 0° for every degree rise of temperature. More

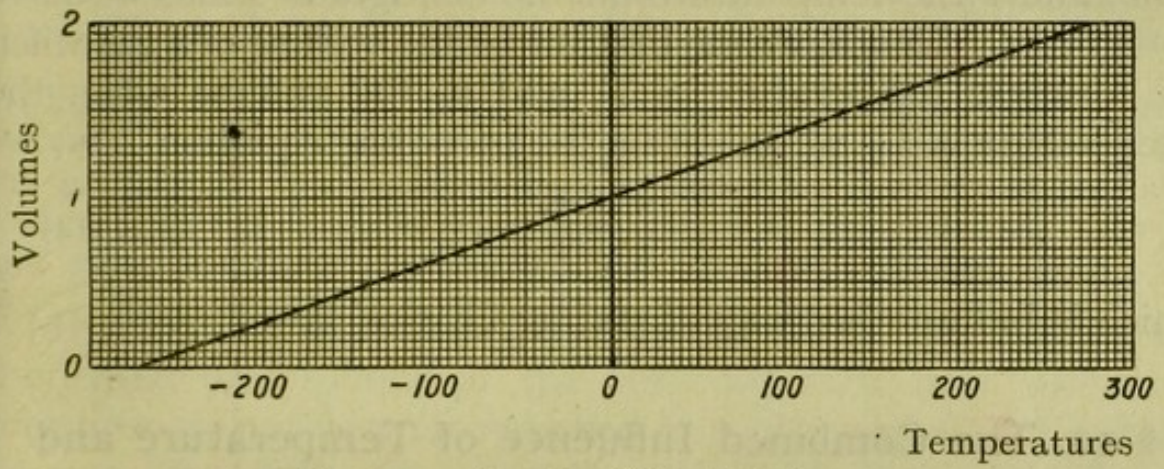


FIG. 14.—Graph of Charles' Law.

generally, if v_0 be used to denote the volume of a gas at 0°, we have, instead of the preceding expression :

$$v = v_0\left(1 + \frac{t}{273}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This is very nearly true for most of the common gases. By plotting the above equation, we get the curve shown in Fig. 14. If the temperature be less than −273°, the gas would have a negative volume, that is a volume less than nothing ! If the temperature be −273°, the gas would occupy no volume ! It is impossible to imagine a substance occupying no space, but such is a logical conclusion from Charles' law. Where is the fallacy ? Whenever a natural process is represented by mathematical symbols, it is well to remember that the artificial

statement often expresses more than actually obtains in nature, because, in the physical world, only changes of a certain kind occur. We must therefore limit the generality of the mathematical expression, for the gas would liquefy before the temperature $-273°$ was attained, and the simple gas law of Charles would not then be applicable.

The temperature $-273°$ C. is supposed to be a limiting temperature—the nadir or lowest possible temperature. Hence, it is sometimes called the **absolute zero**; and temperatures reckoned from this zero are called **absolute temperatures**. On the absolute scale of temperatures, o° C. will be $273°$ abs. If T be employed to denote the temperature on the absolute scale, and t the temperature on the Centigrade scale, we have $T = 273 + t$. Hence, we see that if v be the volume of a gas when the absolute temperature is T, and v_1 the volume when the temperature is T_1, we get, from the preceding equation,

$$\frac{v}{T} = \frac{v_1}{T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is but another way of stating Charles' law.

§ 10. The Combined Influence of Temperature and Pressure on the Volume of a Gas.

According to Boyle's law, the volume of a gas varies inversely as the pressure, and if a gas at a pressure p_1 and volume v_1 changes to a volume x under a pressure p_2, then, from equation (2), page 13, $p_1 v_1 = p_2 x$; again, according to Charles' law, the volume varies directly as the absolute temperature, so that if a gas whose volume is x at a temperature T_1 changes to a volume v_2 when the temperature rises to T_2, we have, from equation (4), $xT_2 = v_2 T_1$. On substituting the value of x from the preceding equation, we get the relation :

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If p_2, v_2, and T_2 respectively denote the pressure, volume, and temperature of a gas under standard conditions, the fraction on the right of equation (5) will have a constant value, say R,

and it follows at once that when both temperature and pressure vary, the effect on the volume of the gas will be represented by the equation :

$$p_1 v_1 = RT_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where R is the constant of proportion, generally called the **gas constant.**

These formulæ are used a great deal in calculations involving the variations in the volumes of gases owing to variations in temperature and pressure. For instance, in reducing the volume of a gas at any observed temperature and pressure to the corresponding volume at **normal temperature and pressure**—0° C. and 760 mm. pressure—often represented by " n.p.t.", or " N.P.T.", or " S.T.P.", or " S.T., S.P."

EXAMPLE.—If a gas measures 170 c.c. at a pressure of 735 mm. mercury, and a temperature of 15°, what is the volume of the gas at normal temperature and pressure ? Here it is required to find v_1 in the formula when $p_1 = 760$, $T = 273$, $T_1 = 288$, $v_2 = 170$, and $p_2 = 735$; hence $v_1 = \frac{273}{288} \times \frac{735}{760} \times 170 = 155{\cdot}8$ c.c.

It might be added that the laws of Boyle and Charles are condensed descriptions of the observed facts only when the pressures are not very far removed from the normal atmospheric pressure, for, if the pressures be very large, these laws do not describe the facts very accurately.

Questions.

1. The following numbers give the volume of a gas at different pressures. Plot a curve from them in which the volume is taken as abscissa, and the pressure as ordinate :—

Volume, c.c.	Pressure, mm.	Volume, c.c.	Pressure, mm.
110	909	183	546
123	813	191	524
131	763	204	490
145	690	212	472
157	637	220	455
169	592		

Panjab Univ. (modified).

2. In the experiment on page 4, if the temperature at the time the gas was weighed was 11° and the barometric pressure 758 mm., what correction would be necessary for the weight, under standard conditions, of 1000 c.c. of air —1·26 grms. ? Hint : From formula (5), $1000 \times \frac{758}{284} = v_2 \times \frac{760}{273}$, or $v_2 = 960$ c.c. If 960 c.c. weigh 1·26 grms., 1000 c.c. will weigh 1·301 grms. at 0° and 760 mm. pressure.

3. Suppose a gas occupies 50 c.c. when confined under normal atmospheric pressure in the measuring vessel *A*, Fig. 15, with the mercury at the same level inside and outside the measuring vessel, what pressure will be exerted upon the confined gas when the measuring vessel is raised so that the mercury inside is (1) 20 cm. *above* the level outside the cylinder, *B*, Fig. 15 ; and (2) 20 cm. *below* the outside level of the mercury, *C*, Fig. 15 ? What will be the volume of the confined gas in each case ? Hint : The pressure of the gas in the tube *B* will be equivalent to a column of mercury 76 less 20 = 56 cm., and in the tube *C* to 76 plus 20 = 96 cm. In the former case, therefore, the gas will have a volume of $50 \times \frac{76}{56} = 67{\cdot}9$ c.c. ; and in the latter case $50 \times \frac{76}{96} = 39{\cdot}6$ c.c.

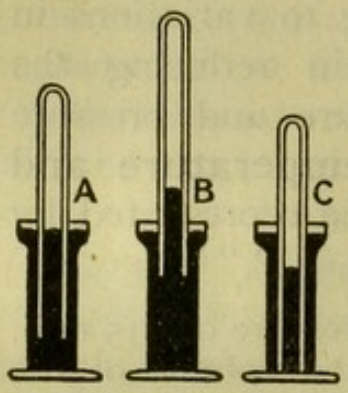


FIG. 15.

4. What changes do you think would be observed in the height of the barometer if the instrument were taken down to the bottom of a mine and back again ?

5. How high would the columns of a water and of a glycerol barometer stand at the time a mercurial barometer registered 30 inches when the specific gravity of mercury is $13\frac{1}{2}$, and glycerol $1\frac{1}{4}$? Hint : Since mercury is $13\frac{1}{2}$ times as heavy as water, the water barometer must have a column of $13\frac{1}{2} \times 30 = 405$ inches, or $33\frac{3}{4}$ feet high ; and the glycerol barometer will stand $\frac{4}{5}$ of 405 = 324 inches, or 27 feet high.

6. If a tumbler quite full of water is covered with a card and inverted, the card apparently clings to the rim of the glass and supports the water : give a precise explanation of this fact.—*Sydney Univ. Public Exam.*

7. A bulb 150 c.c. capacity is evacuated and weighed. It is then filled with a gas under 740 mm. pressure at 17°. On weighing again, it is found to be 0·3072 grms. heavier than before. What is the weight of a litre of the gas ?

8. If there are 5800 cubic feet of air in a room, and if its temperature is 0° and the mercury barometer reads 30 ins., by how much will the air originally in the room expand if the barometer should fall to 29 ins. without any change occurring in the temperature ?—*Cape Univ.*

9. A dirigible balloon contains 1000 cubic metres of gas when resting in its shed with the barometer standing at 760 mm. If the balloon rises until the barometer stands at 500 mm., what will be the effect on the gaseous contents of the balloon ?

10. A litre of gas is measured at 15° and 750 mm. pressure. What will be the volume of the gas at n.p.t. ?

11. A room has a capacity of 500 cubic metres. What volume of air will escape from the room, supposing it is warmed from 14° to 18°, while the barometer remains unchanged ?

12. State the laws relating to the change of volume of a quantity of gas due to change of pressure and of temperature.—*Calcutta Univ. Prelim.*

13. If you are provided with a glass tube and some mercury, how would you construct a barometer ? How would the length of a barometer column be affected (*a*) if the barometer were carried up a mountain, and (*b*) if a hole were drilled in the upper part of the tube ?—*Staffs. Minor. Schol.*

CHAPTER II

The Chemical Nature of Air

§ 1. The Roasting of Metals in Air.

The facts.—Some metals, like gold and silver, are apparently unaffected when heated in air ; whilst others seem to lose their metallic character, and form white or coloured calces (plural of calx) or ashes. For instance, tin, zinc, and magnesium change to white powders ; copper becomes dark brown ; lead, yellow or orange ; iron, reddish-brown ; mercury, red ; etc. The old chemists used to call those metals which altered in this way **base metals**, in order to distinguish them from the **noble metals**, which are not affected when roasted in air.

Attempt at an explanation—The phlogiston hypothesis.—Just as coal or charcoal, when heated, burns to a residual ash, so it was once inferred, by analogy, that the base metals, when roasted in air, lose something and leave behind residual ashes. In order to fix the idea, it was said that during these changes the base metals lost the " principle of combustion " which was supposed to be normally associated with these metals, and with combustible substances generally ; this principle was later on called **phlogiston**, from a Greek word meaning combustible. This seems to be a plausible explanation of the action. All combustible substances possess this principle in common ; during combustion the phlogiston escapes, and an ash remains behind. The noble metals have their phlogiston so firmly fixed that nothing can take it from them. While the base metals are turned into calces when roasted in air, the royal metals remain intact during the fiercest trial.

A confirmatory experiment.—Suppose the ash obtained

by the calcination of one of the above metals be heated with powdered charcoal, which is presumably very rich in phlogiston because it burns so readily and leaves so little ash, then, some phlogiston seems to pass from the charcoal and unite with the calx, for the original metal is restored. The experiment is conveniently illustrated by mixing the ash from lead with charcoal, and heating the mixture in a crucible to redness. On cooling, a button of the metal will be found at the bottom of the crucible. This result fits in very well with our provisional explanation. Let us put the symbol → for "produce" or "produces," and + for "together with"; the changes just indicated can then be symbolized:

Combustion of charcoal:
Charcoal → Phlogiston + Ash.
Roasting metallic tin:
Metallic tin → Phlogiston + Ash.
Heating tin calx with charcoal:
Ash from tin + Phlogiston → Metallic tin.

§ 2. An Attempt to find the Properties of Phlogiston.

Observe that we have not yet proved that phlogiston really exists; we have simply pretended that there is a principle of combustion, and christened the imaginary substance with a name. We therefore provisionally accept this hypothesis as a guide to further experiment until we have established either its truth or falsity. We must accordingly try to find out more about this phlogiston. Let us first inquire:

What weight of phlogiston is lost per gram of metal during the roasting? The experiment is conveniently done in the laboratory with the apparatus illustrated in Fig. 16, where a shallow porcelain dish or

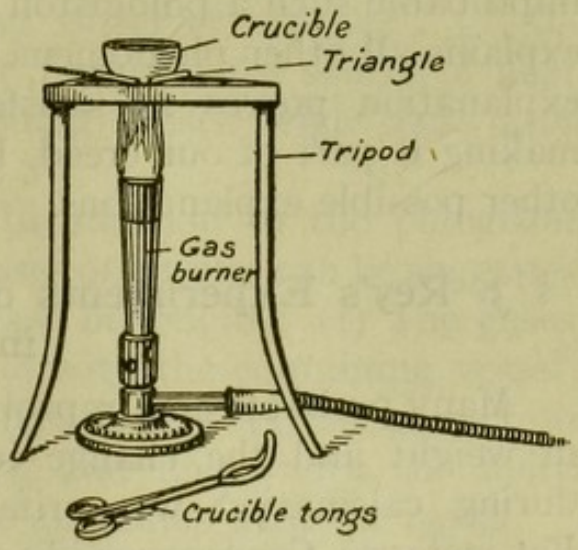


FIG. 16.—The Calcination of Metals in Air.

crucible with about a gram of tin is supported on a triangle which in turn rests on a tripod. The heating is done by means of a gas-burner. An experiment from a student's notebook shows that :

Metallic tin before roasting	1·000 gram.
Ash or calx produced	1·269 ,,
Gain in weight	0·269 ,,

The ash thus weighs more, not less, than the metal from which it has been produced ! This also in spite of the fact that the metal has presumably *lost* phlogiston during the calcination. This fact was known in the eighth century. The result does not fit in with our provisional explanation unless we also assume that *phlogiston is not a form of matter, but rather an imponderable which weighs less than nothing !* No form of matter weighing less than nothing is known, and accordingly, it might appear, at first sight, that our phlogiston is nothing but a chimera—a product of the imagination—with no real existence. On the other hand, there is just a possibility believed by the chemists of the eighteenth century that when phlogiston unites with a calx to produce a metal, the metal is buoyed up, so to speak, by the phlogiston. It therefore remains to examine the properties of a phlogiston weighing less than nothing. However improbable such a phlogiston might appear, if it harmoniously explains all other phenomena we might discover, and no other explanation proves so satisfactory, we shall be justified in making it part of our creed, but it is our duty to first test all other possible explanations.

§ 3. Rey's Experiments on the Calcination of Metals in Air.

Many probable and improbable explanations of the increase in weight and the change in the appearance of the metals during calcination were rife during the sixteenth century. For instance, Cardanus said :

"The metal during calcination dies, for the celestial heat which gave it life and rendered it light, is dissipated, and it consequently becomes heavier."

Terms like *caput mortuum* (dead head) and *terra damnata* (condemned earth) were accordingly applied to the metallic calces. The former of these terms persists to-day for the calx of iron. It was apparently implied that during calcination the "spirit" departed from the metal, and the "body" alone remained behind. This is obviously the phlogiston hypothesis in a more fanciful dress.

Several workers suggested that the cause of the increase in weight was due to the fixation or assimilation of the "ponderous parts of flame," "the igneous corpuscles," or "the vapours of charcoal" by the roasting metal. Robert Boyle (1661), for instance, heated tin and lead in hermetically sealed vessels, that is, in glass vessels with the opening sealed or fused so as to shut off the interior from the external air. The metals suffered partial calcination, and hence Boyle inferred that "glass is pervious to the ponderous parts of flame." Jean Rey appears to have been the first to critically examine the different hypotheses by an appeal to experiment. A description of Rey's work was published in an obscure pamphlet, in 1630, and it does not appear to have been known at the time to those interested in the subject.

The facts.—In order to clarify the mind, let us review the facts. Four things are present during the calcination of the metal in air: (1) The containing vessel or crucible; (2) the metal being calcined; (3) the air; and (4) the source of heat. Again, the metal and the containing vessel weigh more after the calcination than before.

Guessing at the cause.—In addition to the phlogiston hypothesis, four plausible hypotheses or guesses can be suggested to explain the cause of the increase in weight: (1) The gases, etc., from the source of heat unite with the containing vessel; (2) the air unites with the containing vessel; (3) the gases from the flame penetrate the crucible, and unite with the metal (Boyle's hypothesis); and (4) the air unites with the metal.

Testing the hypotheses by experiment.—By heating the crucible alone without the metal, no change in weight occurs. This blank, control, or dummy experiment, shows that neither the first nor the second hypothesis will account for the

increase in the weight of the metal. The third hypothesis can be tested by heating the crucible and the metal out of contact with the air. There is, then, no change in the weight of the metal. The third hypothesis is therefore untenable. This method was not practicable for the early chemists, and hence Rey employed a less decisive test. It might be expected that if the result depended upon the absorption of the flame gases, different results must be obtained by using different sources of heat—sun-glass, etc.—but the same results are obtained in every case, and accordingly the third hypothesis is probably wrong.

Conclusion.—Rey examined all the explanations of the phenomenon which had been previously suggested and rejected them one by one. The only unchallenged factor is air. **The sole invariable antecedent of a phenomenon is probably its cause.** Hence, unless something has been overlooked, we conclude that **when metals are heated in air, the increase in weight is due to the fixation of air by the metal**, and not to the absorption of furnace gases, nor to variations in the weight of the vessel in which the calcination is made.

§ 4. Lavoisier's Experiments on the Calcination of Metals in Air.

Lavoisier made some very interesting observations about 1774. Lavoisier modified Boyle's experiment, for he roasted some metallic tin with air in an hermetically sealed flask until no further change was observed. Part and only part of the metal could be converted into calx or ash. When cold, the vessel and contents were weighed. Neglecting decimals, the result was :

Flask and contents before roasting . .	7628 grains
Flask and contents after roasting . .	7628 ,,
Change in weight	nil

No change in weight thus occurred during the roasting. Presumably, the phlogiston, which is supposed to have escaped from that part of the tin which has been converted into ash, still

remains in the flask, and it will rush out when the flask is opened. On opening the flask there was a rush of air *inwards!* The vessel and its contents were now heavier than before :

Flask and contents before opening . . .	7628 grains
Flask opened	7631 ,,
Gain in weight	3 ,,

This inrush of air makes it appear that **when the metal is converted into a calx it absorbs some air.** The inrush of air, which occurred in Lavoisier's experiment when the flask was opened, must have been due to outside air taking the place of the absorbed air, for we have scarcely sufficient imagination to invest the imaginary phlogiston with a volume less than nothing. Lavoisier's explanation was confirmed by also weighing the tin itself before and after the calcination in the flask. It was found to have increased in weight 3 grains. Hence the amount of air fixed by the tin was virtually equal to the air withdrawn from the flask. The phlogiston hypothesis now seems so improbably an explanation of the above experiment that we will now try how the alternative hypothesis fits the facts, and assume with Rey and Lavoisier that the formation of an ash or calx when a metal is calcined in air is due to the fixation of air by the hot metal.

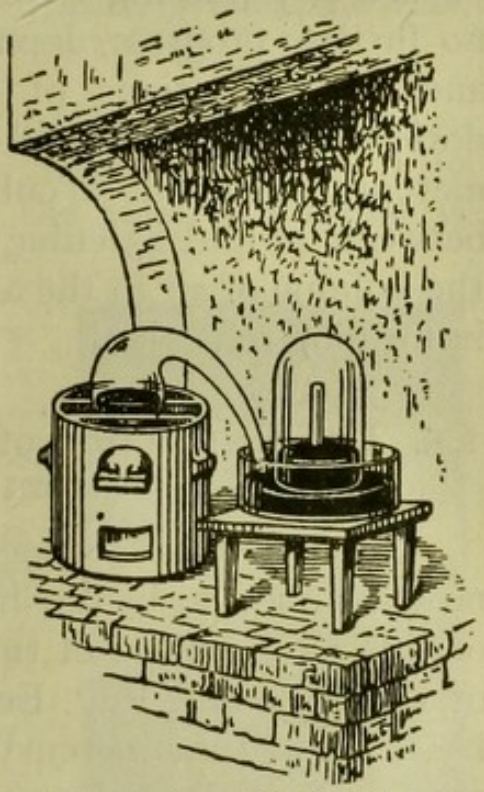


FIG. 17.—Lavoisier's Experiment on the Calcination of Mercury in Air.

The metal during calcination can absorb only part of the air.—Lavoisier continued his interesting study with mercury in place of tin. Mercury forms a red calx when roasted in air at a comparatively low temperature. Lavoisier confined some mercury in a glass retort with an S-shaped neck which dipped under a bell-jar containing air as shown on the right of Fig. 17 ; the retort rested on a charcoal furnace, so that it

could be heated as shown on the left of the diagram. The air in the retort was put in communication with that in the bell-jar. The mercury in the bell-jar was adjusted at a convenient level, and its position "very carefully marked with a strip of gummed paper." The charcoal furnace was lighted and the mercury in the retort heated—not quite to its boiling-point. Lavoisier said, "Nothing of note occurred during the first day. The second day I saw little red particles swimming over the surface of the mercury, and these increased in number and volume during four or five days; they then stopped increasing, and remained in the same condition. At the expiration of twelve days, seeing that the calcination of the mercury made no further progress, I put the fire out." After making allowance for variations of temperature and pressure, Lavoisier noticed that the original volume of the air in contact with the mercury was about 50 cubic "inches," and after the experiment, between 42 and 43 cubic "inches," hence, about one-sixth [1] of the volume of air in the apparatus was absorbed by the mercury in forming red calx.

§ 5. The Extraction of the "Spirit" or "Air" or "Gas" from Mercury Calx.

The red calx obtained when mercury is calcined in air is now assumed to be a compound of mercury with air; the calx of tin, a compound of tin with air, etc. Long before the time of Lavoisier and Rey, Eck de Sulzbach, in 1489, is reported to have found that mercury increases in weight when calcined in air, owing to the union of a "spirit" with the mercury, and the resulting red calx, when heated to a higher temperature disengages the "spirit"; and J. Priestley, in ignorance of the work of Eck de Sulzbach, extracted an "air" from mercury calx on August 14th, 1774. Priestley noticed that a candle burned in the extracted "air" with a remarkably brilliant flame.

The extraction of the absorbed air from mercury calx.—The apparatus used by Priestley is illustrated in Fig. 49. With more modern apparatus, the "spirit," "air," or "gas" from the

[1] One-fifth would be nearer what we get when the experiment is repeated under conditions better suited for exact measurement.

calx of mercury can be extracted in the following manner : The calx is placed in a hard glass tube *A*, Fig. 18, bent as shown in the diagram, and fitted with a cork *B* and bent glass tube, called the **delivery tube.** The tube *A* is clamped to a retort stand so that the end of the delivery tube dips in a trough of mercury. The **mercury gas trough** or the **mercury pneumatic trough** illustrated in the diagram can be worked with about 5 lbs. of mercury, and it is convenient for collecting small quantities of gas when it is desirable to keep the gas from contact with water. The temperature of the tube containing the mercury calx is gradually raised by means of the Bunsen's gas burner. The hot air in the tube is allowed to bubble from the end of the delivery tube and escape into the air. A gas-jar is filled with mercury and inverted in the mercury trough so that the mouth of the gas-jar is kept below the surface of the mercury in the trough, Fig. 18. The gas-jar is rested on a shelf beneath the surface of the mercury, so that the mouth of the gas-jar is over a small hole in the submerged shelf. Globules of mercury begin to collect in the upper part of the tube *E*, and the gas, travelling along the delivery tube, bubbles through the hole in the perforated shelf, rises in the gas-jar, and displaces the mercury. In this particular case the gas-jar is best clamped to a retort stand to prevent its tilting over.

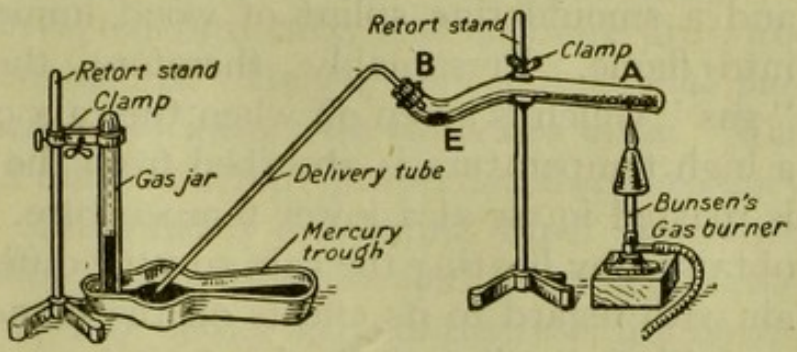


FIG. 18.—The Extraction of the Spirit from Mercury Calx.



FIG. 19.—Testing the Properties of the Spirit from Mercury Calx.

Testing the air extracted from mercury calx.—When a jar full of gas has been collected, a plate is placed under its mouth, and the jar removed from the trough in order that its contents may be examined. A small lighted taper or a glowing splint of wood may be plunged in the gas as illustrated in Fig. 19. The wire holding the taper passes through a piece of cardboard which forms a loose-fitting cover for the gas-jar while the taper is inside.

Lavoisier, having heard of Priestley's observations on the action of heat on mercury calx, repeated the experiment, and confirmed Priestley's statements. Lavoisier found that the candle burned in the gas with a flame of "blinding brilliance," and a smouldering splint of wood immersed in the gas burst into flame. Presumably, therefore, the "spirit," "air," or "gas" which is given off when the calx of mercury is heated to a high temperature is absorbed from the air when the mercury is roasted in air at a lower temperature. If so, why is the gas obtained by heating the calx so very different from atmospheric air with regard to its effects on the flame of a candle and on a smouldering splint of wood?

There seems to be a flaw in our second attempt to find a satisfactory explanation of the increase in weight which occurs during the roasting of metals in air, owing to the union of the air with the heated metal. We must be careful not to reject the provisional explanation too hastily, because it may be possible to remove the blemish by a simple modification of the hypothesis. In other words, it is possible that even now we have won part of the truth from Nature, but not the whole truth.

§ 6. The Active and Inactive Constituents of Air.

The facts.—Let us review our position. It has been proved experimentally that when metals are calcined in air confined in a closed vessel—

(1) The gain in weight of the metal is equal to the loss in weight suffered by the air.

(2) The air diminishes—about one-fifth—in volume during the calcination, and a volume of gas equal to that which disappears can be recovered from the metallic calx.

(3) The residual air which remains after the metal has absorbed what it can, and the air which is recovered from the calx, each has different properties from the original air.

An hypothesis.—These facts can be satisfactorily explained by assuming that *air is a composite substance compounded of at least two distinct gases each of which has its own characteristic properties.*

Testing the hypothesis.—Let us return to the heating of metallic tin in a closed vessel, and to Lavoisier's experiment on mercury, illustrated in Fig. 17. However long the two metals be heated under the conditions of the experiments, no more metal can be converted into calx, and no more air "absorbed" by the heated metals. Hence, *only a fractional part of the air—about one-fifth—can unite with the heated metal.* The residual four-fifths has quite different properties from ordinary air. The residual air extinguishes a burning taper immersed in the gas; and a mouse is quickly suffocated, for when placed in the gas, the mouse at once shows signs of distress, lies down, gives a few spasmodic kicks, and is dead. Hence, Lavoisier called the residual air **azote,** "from the *a* privative of the Greeks, and ζωὴ, life." That part of the air which was removed by the heated mercury and afterwards evolved when the resulting calx was heated to a still higher temperature, as indicated above, was first called **vital air.** Both gases are present in ordinary air, and hot mercury furnishes a convenient means of separation. *Artificial air, indistinguishable from normal air, can be made by mixing together in the right proportions the two gases obtained from air.*

Azote is now called **nitrogen,** and vital air is called **oxygen.** The calces or compounds formed by the union of the oxygen of the air with the metals are called **oxides.** Thus, tin furnishes **tin oxide**; mercury, **mercury oxide**; etc. The phenomenon which occurs when oxygen unites with a substance to form a calx or an oxide is called **oxidation.**

§ 7. Summary.

It is now possible to make some important statements:

(1) Atmospheric air contains at least two gases with different properties—one is called oxygen and the other nitrogen.

(2) Atmospheric air contains about one-fifth of its volume of oxygen and four-fifths of its volume of nitrogen.

(3) When some metals are calcined in air, they unite with the oxygen to form metallic oxides.

(4) The increase in weight which occurs when the metals are calcined in air is due to the union of the metal with the oxygen of the air.

The roasting of a metal in air can now be represented by the scheme :

Metal + Oxygen → Metallic oxide.

The decomposition of mercury oxide by heat :

Mercury oxide → Mercury + Oxygen.

And, adds Lavoisier : Phlogiston is a " hypothetical being, a gratuitous assumption." The hypothesis which has just been developed is " more probable, more conformable with facts, and involves less strained explanations, and fewer contradictions," and " it becomes exceedingly probable that **phlogiston does not exist.**"

Here, then, the student has received in a couple of lessons the result of over a thousand years of thought and labour on the nature of atmospheric air !

Difficulties which confronted the early investigation of air.—It seems curious that such a long period of time should have been required to work from the facts known in the eighth century that " metals increase in weight when calcined in air," to Lavoisier's proof in the eighteenth century that " the increase in weight is due to the absorption of oxygen from the air." This will occasion no surprise when we remember the difference between the properties of air which cannot be seen, and the properties of solids and liquids which can be readily seen and handled. As G. F. Rodwell has pointed out, the most obvious property of matter is its visibility, and the conception of matter divested of this quality is no small effort to a mind untutored in physical thought, for the inquiry into the nature of an intangible, invisible body, which exercises no apparent effect on surrounding objects, belongs to an advanced order of experimental philosophy. There were no means of recognizing even the more salient properties of air at the disposal of the chemists until a comparatively late period, and the earlier chemists, accordingly, believed air to be intrinsically different in its essence from more familiar visible substances.

§ 8. The Law of Constant Composition.

Attention must now be directed to the singular observation made by Jean Rey, in 1630 (page 27), that during the calcination of a metal in air, " the weight of the metal increased from the beginning to the end, but when the metal is saturated, it can take up no more air. Do not continue the calcination in this hope : you would lose your labour. Nature, in her inscrutable wisdom, has set limits which she does not overstep." In other words, **however long a metal may be heated in air, a definite weight of each metal can combine with only a definite maximum amount of air.** Students to-day regularly repeat Rey's experiments on the metals—under various guises —as class exercises. The following table is taken from students' laboratory notebooks :—

TABLE I.—ACTION OF AIR ON THE CALCINATION OF THE METALS.

Metal.	Weight of metal. Gram.	Weight of calx. Gram.	Increase in weight. Gram.	Ratio. Weight air absorbed : Metal used.
Magnesium . .	1	1·658	0·658	1 : 1·52
Zinc	1	1·246	0·246	1 : 4·06
Aluminium . .	1	1·890	0·890	1 : 1·12
Copper . . .	1	1·252	0·252	1 : 3·97
Tin	1	1·269	0·269	1 : 3·72

Hence, one gram of the absorbed air is respectively equivalent to

(Absorbed air).	Magnesium.	Zinc.	Aluminium.	Copper.	Tin.
1	1·52	4·06	1·12	3·97	3·72 grms.

One gram, and only one gram, of air is absorbed by definite amounts of the given metals under the conditions of the experiment ; and Lavoisier's work proves that the *oxygen* of the air is alone absorbed. Accordingly, one part by weight of oxygen is equivalent to

Oxygen.	Magnesium.	Zinc.	Aluminium.	Copper.	Tin.
1	1·52	4·06	1·12	3·97	3·72

Instead of making the weight of oxygen unity, it will be more convenient, later on, and also more in accord with general usage, to make oxygen 8 instead of unity. Hence, multiplying the preceding numbers by 8, we obtain :

Oxygen.	Magnesium.	Zinc.	Aluminium.	Copper.	Tin.
8	12·16	32·48	8·96	31·76	29·76

When magnesium is calcined in the presence of oxygen, or air, the metal always unites with the oxygen in the proportion of one part of oxygen per 1·52 parts of magnesium, or 8 parts by weight of oxygen per 12·16 parts by weight of magnesium. The same principle obtains when magnesium oxide is made in several different ways ; and likewise with the other metallic oxides. Hence, as P. G. Hartog puts it : **two like portions of matter have the same composition.** The converse of this statement is not necessarily true, for two portions of matter with the same composition are not necessarily alike.

The composition of a definite chemical compound appears to be independent of its mode of formation, and therefore it is inferred that substances always combine in definite proportions. If an excess of one substance be present, the amount in excess remains uncombined. Thus, if 12·16 grms. of magnesium be heated with 9 grms. of oxygen, 20·16 grms. of magnesium oxide will be formed, and one gram of oxygen will remain in excess ; similarly, if 13·16 grms. of magnesium be heated with 8 grms. of oxygen, 20·16 grms. of magnesium oxide will be formed and one gram of magnesium will remain in excess. This deduction from the observed facts is called **the law of definite proportions,** or **the law of constant composition ; a particular chemical compound always contains the same elements united together in the same proportions.** Probably no generalization in chemistry is more firmly established than this. It was not discovered by any particular man, but gradually grew among the doctrines of chemistry. The law was tacitly accepted by many before it was overtly enunciated. The validity of the law was the subject of an interesting controversy during the years between 1800 and 1808. J. L. Proust maintained that constant composition is the invariable rule ; C. L. Berthollet maintained that constant composition is the

exception, variable composition the rule. Proust's words are worth quoting :

> According to my view, a compound is a privileged product to which Nature has assigned a fixed composition. Nature never produces a compound, even through the agency of man, other than balance in hand, *pondere et messura*. Between pole and pole compounds are identical in composition. Their appearance may vary owing to their aggregation, but their properties never. No differences have yet been observed between the oxides of iron from the South and those from the North ; the cinnabar of Japan has the same composition as the cinnabar of Spain ; silver chloride is identically the same whether obtained from Peru or from Siberia ; in all the world there is but one sodium chloride ; one saltpetre ; one calcium sulphate ; and one barium sulphate. Analysis confirms these facts at every step.

So great is the faith of chemists in the truth of this generalization that a few accurate and careful experiments are considered sufficient to settle, once for all, the composition of a substance. For instance, if a substance possessing all the properties of magnesium oxide be given to a chemist, without taking any more trouble, he knows that it will contain 12·16 parts of magnesium for every 8 parts of oxygen.

§ 9. What is an Element ?

We have just seen that air can be resolved into two gases—oxygen and nitrogen. It is further possible to resolve all known substances—air, mercuric oxide, etc.—into about eighty distinct, elemental, or primitive forms of matter. Mercury and oxygen, for example, can be obtained from mercuric oxide ; but no chemist, however, has ever separated from oxygen anything but oxygen ; from nitrogen, anything but nitrogen ; nor from mercury, anything but mercury. Hence, oxygen, nitrogen, and mercury are said to be elements. We can combine mercury, oxygen, and nitrogen in many different ways, and then decompose the resulting compounds ; but we can get nothing more from the compounds than the three elements—mercury, nitrogen, and oxygen—used at the commencement. But we are not yet prepared with a definition of the term " element."

We are indebted to Robert Boyle (1678) and to A. L. Lavoisier (1789) for the modern conception of the word. Lavoisier, quite logically, considered lime, magnesia, baryta, and alumina to be elements. We now know that these "elements" of Lavoisier are compounds of oxygen with calcium, magnesium, barium, and aluminium respectively. Lavoisier apparently foresaw some such possibility, for he stated: "We are certainly authorized to consider them simple bodies until by new discoveries their constituent elements have been ascertained." It is not possible to improve upon Lavoisier's conception of an element, and I feel compelled to quote his words, although written before 1789:

> If we apply the term elements or principles to bodies to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all substances into which we are able to reduce bodies by decomposition. Not that we are entitled to affirm that these substances which we consider as simple, may not themselves be compounded of two, or even of a greater number of more simple principles; but since these principles cannot be separated, or rather, since we have not hitherto discovered the means of separating them, they are, with regard to us, as simple substances, and we ought never to suppose them compounded until experiment and observation have proved them to be so.

In fine, "element" is a conventional term employed to represent the limit of present-day methods of analysis or decomposition. We may therefore summarize these ideas in the definition: **An element is a substance which, so far as we know, contains only one kind of matter.** The moment Auer von Welsbach (1885) proved that what was considered to be elementary didymium was really a mixture of two new elements—praseodymium and neodymium—one element ceased to exist, and two elements were born.

Questions.

1. Robert Boyle concluded that the increase in weight which copper undergoes when heated over a flame proved that the increase was due to particles of fire uniting with the copper. What experiments show that this conclusion is erroneous? Whence the increase in weight?

2. Illustrate the meaning of the terms "deduction" and "induction" with reference to the discovery that the increase in weight which occurs when tin is calcined in air is due to the fixation of air by the metal, and to the discovery of Charles' law.

3. What do you understand by the density of a gas? The volume of a given weight of a gas has to be calculated at the standard temperature and pressure. What does this mean?—*Science and Art Dept.*

4. If 100 c.c. of air contains 30 grms. of oxygen, and 70 grms. of nitrogen, what volume of air will be required to oxidize 100 grms. of metallic tin?

5. Purified atmospheric air is passed slowly over metallic copper heated to redness. Supposing the copper to increase 2·99 grms. in weight, what weight of nitrogen would remain unabsorbed?—*Oxford Senr. Locals.* (Given the fact that the atmospheric air contains 23 per cent. of oxygen, and 77 per cent. of nitrogen by weight.)

6. What occurs when the following substances are heated in air:—platinum, magnesium, mercuric oxide, magnesium oxide, and sulphur?—*Staffs. Minor Schol.*

7. A certain substance when heated in a crucible lost weight. What does such a result show? Suggest any experiments you would make to find out the reason for such a loss.—*Staffs. Intermediate Schol.*

8. Give details of an experiment with heated mercury to show the composition of air.—*Cape Univ.*

9. Give an account of the theory of phlogiston, stating the chemical facts on which it was based, as well as those which finally led to its overthrow.—*Calcutta Univ.*

10. Lavoisier recovered 41·5 grains of mercury when he had heated 45 grains of mercury calx. The difference represented oxygen gas. Hence calculate the percentage composition of mercuric oxide.

CHAPTER III

Ice, Water, and Steam

§ 1. The Three States of Water—Solid, Liquid, and Gaseous.

It is well enough known that water can exist in a solid condition as **ice** when the temperature is below 0° ; and as a vapour or gas—**steam**—when the temperature is above 100°. **Most substances, like water, can exist in all three conditions—solid, liquid, and gaseous.** The addition or abstraction of heat enables a liquid to pass from one state to another. For water, 0° is the freezing or melting-point, that is, the transition point from the solid to the liquid condition, and conversely ; and 100° is the boiling-point, or the transition point from the liquid to the gaseous condition, and conversely. These facts are symbolized thus :

$$\text{Water}_{\text{ice}} \overset{0^\circ}{\rightleftharpoons} \text{Water}_{\text{liquid}} \overset{100^\circ}{\rightleftharpoons} \text{Water}_{\text{steam}}$$

Investigators who have special facilities for working at high temperatures, report that gold has a melting-point, 1062°, and a boiling-point, 2530°, or :

$$\text{Gold}_{\text{solid}} \overset{1062^\circ}{\rightleftharpoons} \text{Gold}_{\text{liquid}} \overset{2530^\circ}{\rightleftharpoons} \text{Gold}_{\text{gas}}$$

Again, men working in laboratories specially equipped for work at low temperatures report that oxygen has a melting-point, −227°, and a boiling-point, −182·5°, or :

$$\text{Oxygen}_{\text{solid}} \overset{-227^\circ}{\rightleftharpoons} \text{Oxygen}_{\text{liquid}} \overset{-182{\cdot}5^\circ}{\rightleftharpoons} \text{Oxygen}_{\text{gas}}$$

Ice.—*Liquid water* freezes at 0° into crystalline ice, while *water vapour* freezes directly into hoar frost and snow. The

crystals of ice are extremely rare, and difficult to measure. The crystals can often be seen when a piece of ice is examined with a lens while a beam of bright light is passed through it. Snow crystals are common. They appear in the form of an hexagonal (six-sided) nucleus or six-rayed star with the rays developed in bewildering complexity. No two seem alike. Ice appears to be colourless or white when pure, but it is pale blue when seen in large masses.

The relation between the volume and temperature of water.—By plotting the volume of a given mass of water at different temperatures, we get a curve similar to that illustrated in Fig. 20. This curve, at temperatures above 4°, shows that water, like most liquids, expands when heated, and contracts when cooled down to 4°; but the curve below 4° is abnormal. It shows that water expands when cooled below, and contracts when heated up to 4°. If the specific gravity of water at 4° be taken as unity, it follows that water becomes specifically lighter when the temperature is raised or lowered beyond this point. The specific gravity of water at the **temperature of maximum density**, 4°, is often taken as a standard of reference for specific gravities, etc.

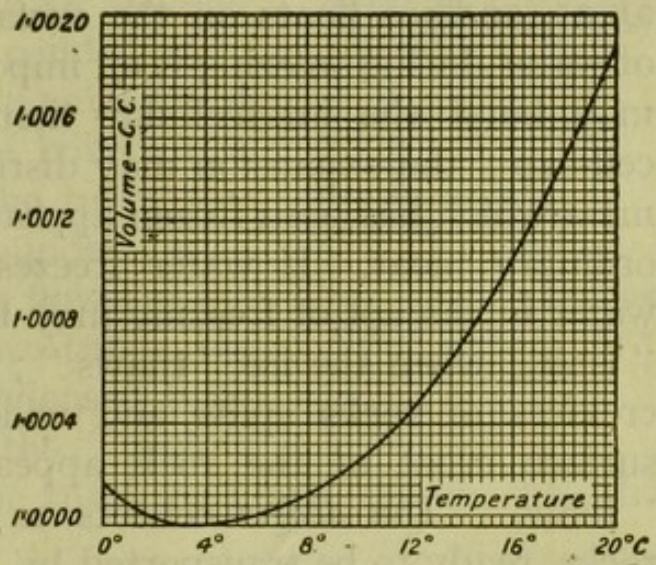


FIG. 20.—Relations between the Volume and Temperature of Water.

The expansion of water when cooled from 4° to 0° is very small, but that minute quantity has a very important bearing in nature. When the water on the surface of, say, a lake is cooled, it contracts. The heavier cold water sinks, and the warm water rises. This circulation cools the temperature of the whole body of water down to 4°; any further cooling results in the formation of specifically lighter water. Accordingly, this remains on the surface, and circulation ceases. Finally, as

a result of this remarkable and abnormal property, when the temperature of the atmosphere falls to 0°, a surface film of ice is formed. If the water did not expand in this way, as the temperature fell to 0°, the whole body of water would freeze from below upwards and produce profound climatic changes, since the larger amount of ice formed in winter would materially affect the temperature for the rest of the year.

The volume changes of water when it freezes.—In the act of freezing, water expands so that 100 c.c. of liquid water at 0° gives approximately 110 c.c. of ice at the same temperature. Accordingly, water at 0° is denser than ice at 0°, and ice floats on the surface of water. The expansion of water during freezing is an important factor. The expansion may burst the intercellular tissue of plants by freezing the cell-sap ; the expansion may disrupt the fibres of flesh, so that meat which has been frozen appears rather more " pulpy " than ordinary meat. If water freezes in pipes, the expansion of water in the act of freezing may burst the pipe, and water will " leak " when the ice " thaws " ; water freezing in the surface crevices of rocks splits and widens the fissures so that the surface crust of the rock appears to disintegrate during a " thaw." The *débris* collects as " talus " at the foot of the rocks, ready to be transported by water to lower levels. Hence this simple force plays an important part in the weathering and decay of rocks, building stones, etc., in countries exposed to alternate frost and thaw ; and J. Tyndall adds : " The records of geology are mainly the history of the work of water."

Review.—To summarize the action of heat on water, start with ice at some temperature below zero. Ice expands as its temperature rises up to 0° ; at 0° it contracts so that one volume of ice furnishes nearly $\frac{9}{10}$ths of a volume of water ; from 0° to 4° the water contracts ; and from 4° to 100° it expands ; at 100° a cubic inch of water changes into nearly a cubic foot of steam at 100°, that is, one volume of the liquid at 100° becomes 1700 volumes of steam at 100° ; and the steam then behaves as if it were a gas, since its volume changes with rise of temperature very nearly as described by Charles' law.

§ 2. Distillation.

The gradual evaporation of water in a dish exposed to the air shows that liquid water is continually being changed into an invisible gas which diffuses into the atmosphere. The evaporation proceeds more quickly if the vessel of water be warmed; and if the water be boiled, the change is rapid and vigorous. The vapour which rises from the water is colourless and invisible, as is illustrated by the interior of the flask, Fig. 21, which contains boiling water and steam. On meeting the cold air outside the flask, the invisible steam condenses to a cloud or mist of innumerable particles of liquid water. If the water be boiled in a retort, *A*, Fig. 22, so that the tube conveying the steam is surrounded with another tube, and cold water flows in the annular space between the two tubes, the steam from the **boiler** is condensed back to the liquid condition in the "cooling tube" or **condenser,** and the resulting liquid trickles into the **receiver.** The operation is called **distillation**, and the water which collects in the receiver is called the **distillate**—in the present case, **distilled water**.

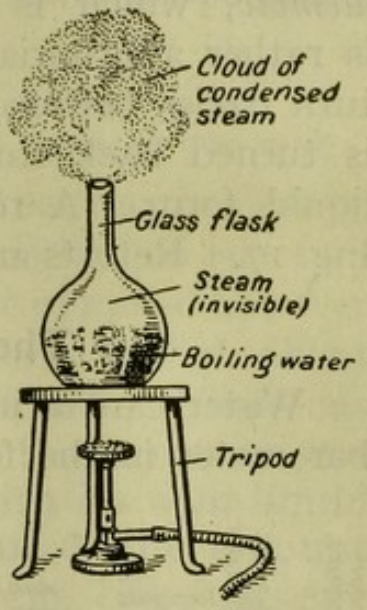


FIG. 21. — Boiling Water so as to show the Invisibility of Steam.

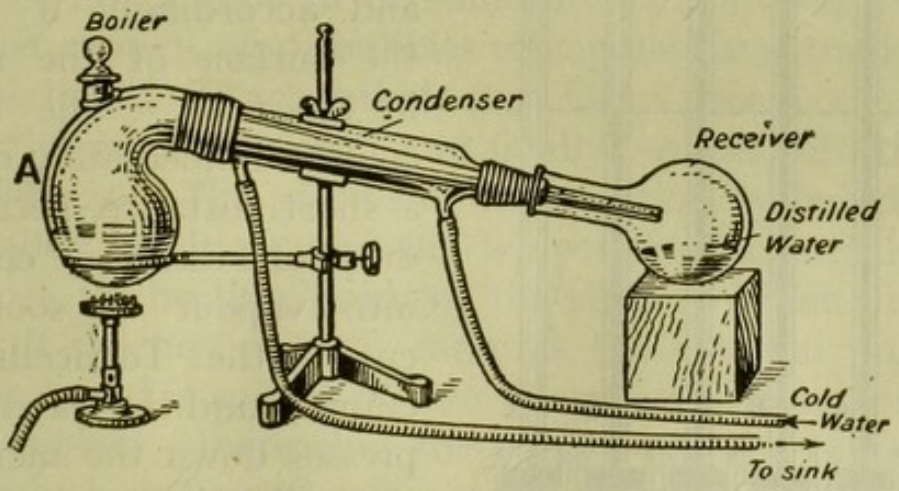


FIG. 22.—The Distillation of Water.

There are many modifications of the principle. To economize space, the " cooling tube " is usually coiled in the form of a spiral—called the " worm "—and kept in a tank through which cold water flows. In Fig. 22, a retort is used as a boiler. The **retort** is an improved, more modern form of the older *alembic*, which is now almost obsolete. The name retort is rather appropriate. It comes from the Latin *retorqueo* (to turn back), because the liquid which is undergoing distillation is turned back from the gaseous condition into its original liquid form. A retort with an S-shaped neck, is shown in Fig. 17. Retorts are used for other purposes besides distillation.

§ 3. The Vapour Pressure of Water.

Water can be introduced into the Torricellian vacuum of a barometer in the following manner: Suck a little water into a pipette, Fig. 8; place the tip of the pipette below the open end of the barometer tube (Fig. 23, *A*), and blow a drop of water out of the pipette, but be careful to allow no air to pass. The water is lighter than mercury, and accordingly it rises to the surface of the mercury in the tube. The mercury column immediately descends a short distance, because the drop of water is converted into vapour as soon as it enters the Torricellian vacuum; and the water vapour presses down the mercury in the tube just as would be the case if a bubble of air entered. Another drop of water is introduced, and the mercury descends a little further; finally, when a drop of

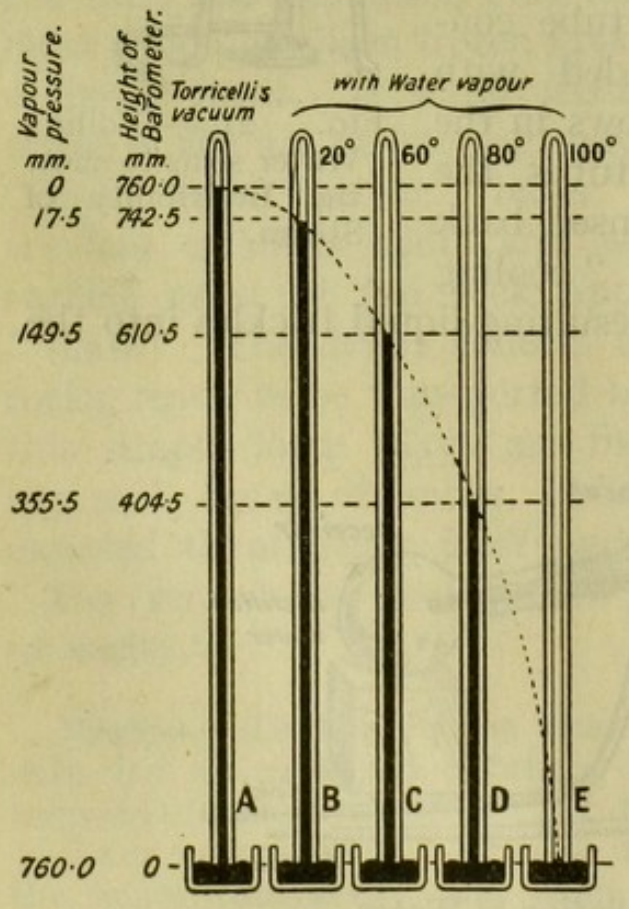


FIG. 23.—Effect of Water Vapour at Different Temperatures on the Height of the Barometer.

water *remains as liquid* above the mercury, the mercury falls no more, because the space above the mercury can hold no more water vapour, in other words, the space is saturated with water vapour, Fig. 23, *B*. If the experiment be conducted at a higher temperature more water will be vaporized in the space before it is saturated than is the case at a lower temperature, Fig. 23, *C*, *D*, *E*. For instance, at

Temperature . . .	0°	20°	40°	60°	80°	100°
Mercury column falls	4·6	17·5	55·3	149·5	355·5	760 mm.

These same measurements are expressed another way in Fig. 23. Raising the temperature of Torricelli's vacuum has no effect on the barometric column. The same results are obtained however wide the barometer tube; and what has been stated about water applies, *mutatis mutandis*, to other liquids. Numerous experiments have proved that **at a given temperature the vapour pressure of a liquid in contact with its own liquid is a constant quantity, and is independent of the amount of vapour or liquid present in the system.** The pressure of water vapour in contact with its liquid is expressed in the table books in millimetres of mercury.

Boiling, or ebullition.—The raising of the temperature of an evaporating liquid increases the rate of evaporation. When the temperature is high enough, the exposed surface of the liquid does not appear to be sufficient to allow the vapour to escape fast enough, since bubbles of vapour are actually formed *within* the liquid. Each bubble as it forms rises to the surface; increases in size as it rises; and finally escapes into the atmosphere, Fig. 21. The process of vaporization by bubble formation is called **boiling**; and the temperature at which boiling commences, the **boiling-point** of the liquid. When the vapour pressure of the liquid is the same as the external pressure to which the liquid is subjected, the temperature does not usually rise any higher. Increasing the supply of heat increases the rate at which evaporation proceeds or at which bubbles are formed. Hence it is sometimes convenient to define: **The boiling-point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the external pressure exerted at any point on the liquid surface.** This

external pressure may be exerted by the atmospheric air, by vapour and air, and by other gases. Hence a table of the vapour pressures of a liquid at different temperatures also shows the boiling-points of that liquid under different pressures. Thus water at a pressure of 4·6 mm. of mercury boils at 0°, and at 60° when the pressure is 149·46 mm. Water boils at 100° and 760 mm. pressure. The greater the pressure, the higher the boiling-point; and conversely, the less the pressure, the lower the boiling-point. These phenomena occur with liquids generally, and it is therefore necessary to state the pressure when giving the boiling-point of a liquid, although if no pressure is stated, 760 mm. is understood. Thus, at Quito (9350 feet above sea-level), with the barometer at an average height 525·4 mm., water boils at 90·1°; and on the top of Mount Everest (29,002 feet), barometer at 255·3 mm., water would boil at 72°. Liquids which decompose at their boiling-point under ordinary atmospheric pressure can frequently be distilled without decomposition at the lower boiling temperature obtained by reducing the pressure. Hence the so-called process of **distillation under reduced pressure,** or, as it is sometimes less accurately styled, **distillation in vacuo.**

§ 4. Measuring the Volume of Moist Gases.

We have discussed evaporation in an evacuated space. In 1802, John Dalton showed that **the mass of vapour required to saturate a given space at a given temperature, and consequently also the vapour pressure of a given liquid, is the same whether the vapour be by itself, or associated with other gases upon which it has no chemical action.** In other words, the total pressure of a mixture of gases and vapour is the sum of the partial pressures of each constituent. This is **Dalton's law of partial pressures.** In the case of air, the total barometric pressure is the sum of the partial pressure of the oxygen, of the nitrogen, and of the water vapour.

When a gas is confined over water, the observed volume of the gas is determined by the temperature and pressure of the

barometer. By Dalton's law the total pressure of the gas is the joint effect of two partial pressures : (1) the partial pressure of the water vapour at the observed temperature ; and (2) the partial pressure of the gas under observation. Hence the barometer reading does not represent the pressure of the gas alone, but rather the pressure of the gas plus the pressure of the water vapour. To find the latter, note the temperature, and a " Table of Vapour Pressures of Water in Millimetres of Mercury," in most " Table Books," will furnish the desired datum. This must be subtracted from the observed pressure (barometer) in order to find the pressure of the gas at the temperature in question.

EXAMPLE.—What is the volume of $4\frac{1}{2}$ litres of a gas at 0°, 760 mm., when it is measured in contact with water at 15°, and the barometer reads 767·7 mm. ? From the " Table of Vapour Pressures," the vapour pressure of water at 15° is 12·7 mm. Hence the gas is really under a partial pressure of $767-12{\cdot}7=755$ mm. of mercury. The problem is now solved by the same method as the example on p. 21. The answer is 4·24 litres.

§ 5. The Water Vapour always present in Atmospheric Air.

Owing to evaporation from every surface of water exposed to the atmosphere—ocean or lake, river or stream—there must always be some water vapour in the air.* The amount must be greater on warm days, because, the hotter the air, the greater the amount of water vapour it can carry before it is saturated. If some pieces of ice be placed in a glass vessel, clean and dry on the outside, the outer surface will soon become covered with moisture. The water vapour in the air is condensed to liquid water on the cold surface of glass. As far back as 1667 it was proposed, by the Florentine Academy, to determine the amount of water vapour in air by collecting and weighing the amount of moisture collected in this way during a given time.

Alumina which has been calcined to about 600° increases in weight when exposed to the atmosphere. The increase in weight is due to the absorption of moisture, for if the " exposed "

alumina be heated in a test tube, *a*, Fig. 24, while the test tube is gripped by a piece of wet paper as shown in the diagram, the original weight of alumina is restored, and moisture collects in the cooler part of the tube. The water can also be collected and weighed. It will be found equivalent to the gain in the original weight of the alumina. Calcium chloride, concentrated sulphuric acid, quicklime, phosphorus pentoxide, potassium hydroxide, etc., all absorb moisture from the air rather quickly, and in virtue of this property they are said to be **hygroscopic**; and if the solids absorb sufficient moisture to dissolve them or make them become wet, they are said to be **deliquescent.** These substances are used for drying gases provided the gas

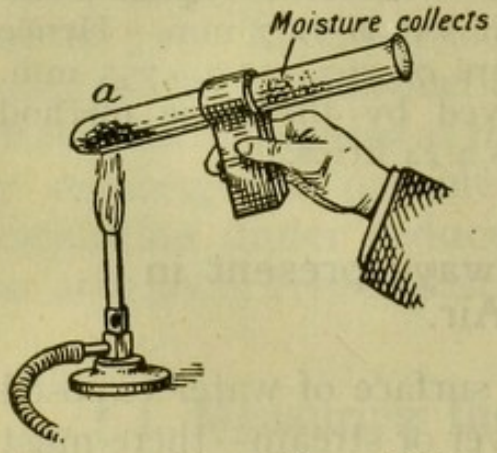


FIG. 24.—Expulsion of Water from Alumina which has been exposed to the Air.

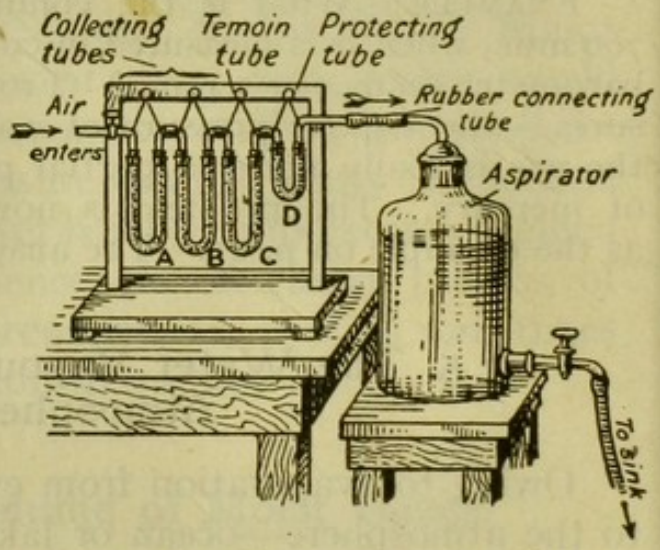


FIG. 25.—Determination of the Amount of Moisture in Air.

exerts no other action on the desiccating agent. A little dry potassium carbonate placed on a watch glass and exposed to the air will give a good idea of the phenomenon of deliquescence.

Determination of the amount of water vapour in air.—To determine the amount of moisture in a given volume of air fit up an apparatus similar to that illustrated in Fig. 25. Four U-tubes are charged with pieces of calcium chloride and connected with a large bottle of water, as shown in the diagram. The U-tubes *A* and *B* are weighed together, and *C* is weighed alone. The temperature is read on a thermometer. Open the stopcock of the water-bottle, water runs out, and air

is aspirated through the U-tubes. Hence, the water bottle is here called an **aspirator.** When 10 litres of water have run from the aspirator, close the stopcock *a* ; detach and weigh the first two tubes *A* and *B* ; also weigh the tube *C*. The increase in weight of *A* and *B* represents the amount of moisture absorbed from the ten litres of air aspirated through the train of U-tubes :

Calcium chloride tubes *A* and *B*, before . .	142·797 grams
The same tubes afterwards	142·847 ,,
Moisture in 10 litres of air . . .	0·050 ,,

Hence, the air contains 0·005 grm. of moisture per litre.

The object of the tube *D* is to prevent an error which would occur if water vapour from the aspirator entered the collecting tubes by a back pressure. The purpose of *C* is to enable an answer to be returned to the question : Has all the water vapour been absorbed from the air which passed through the tubes *A* and *B* ? If *C* has the same weight before and after the experiment, it is inferred that the drying tubes *A* and *B* have done their work satisfactorily. Hence the U-tube *C* is called a **temoin tube** (French *temoin*, a witness), because it can be used as evidence to show whether or not the air which passed through was freed from water vapour.

One objection to the experiment might be raised. The increase in weight may be due not only to the absorption of water vapour, but also to the arresting of some particles of dust from the air. This error can be eliminated by interposing another U-tube packed with cotton wool beyond *A* in order to cut off the dust from the air before it enters *A*. It has also been proved by numerous workers that the other constituents of air are not absorbed to an appreciable extent under the conditions of the experiment.

§ 6. The Alleged Transmutation of Water into Air, and into Earth.

The belief that water, air, and earth are mutually convertible one into another dates from very early times. For instance, Anaximenes of Miletus, about 500 B.C., and Aristotle, about 350 B.C., taught that air could be condensed into water,

and that water, in turn, could be converted into earth and stones. This belief pervaded philosophy some 2500 years before it was finally abandoned. The condensation of air into water seemed to be proved daily by falling dew. Very few writers before the seventeenth century appear to have had any doubts about the dogma. Early in that century, J. B. van Helmont dissented in these words : " If air could be converted into water by cooling, it would certainly become water in cold weather " ; and added further, " If a known weight of water be distilled, the same weight of water will be found in the receiver at the end of the operation, for the water is retorted or struck back into its own form again." Van Helmont knew well enough that water evaporates at ordinary temperatures, and it is said that he invented the word " gas " in order to distinguish between the vapour of water from air proper. Curiously enough, van Helmont accepted the view that all metals and rocks could be resolved into water, and conversely.

Very exact experiments show that when water is distilled in glass vessels, the distillate, no matter how often it has been previously distilled, leaves a small earthy residue when it is evaporated. H. Boerhaave concluded that the earthy deposit is derived from particles of atmospheric dust settling on the water before it enters the distilling vessel. This idea was disproved by redistilling water in hermetically sealed vessels so that it was not exposed to the atmosphere. These facts were taken to strengthen the belief that water can be transformed into earthy matter. Lavoisier doubted the truth of the inference, and published the results of some test experiments made in 1770 to decide if water can really be changed into earth.

1. The facts.—An earthy residue is obtained when the purest obtainable water is distilled in hermetically sealed glass vessels. It is obvious that if the earth be derived from something outside the vessels, the weight of the vessel and its contents should *increase* during the experiment. On trial, the weight of the vessel and its contents were found to remain unchanged, and accordingly *the earth must originate in the vessel and its contents.*

2. Guessing at the cause.—There remain three possible

sources of the earth: (1) The earth comes from the vessel alone; if so, the vessel should lose weight, and the loss should be exactly equal to the weight of the earth formed. (2) The earth comes from the water alone; if so, the weight of the vessel should not change during an experiment. (3) The earth comes from both the vessel and the water; if so, the vessel should lose weight, but not to the same extent as the weight of the earth formed.

3. Testing the guesses.—Water was heated in a glass pelican, Fig. 26, for 100 days. The pelican is an instrument now obsolete. The larger bulb, *A*, contained the water being heated, the vapours condensed in the smaller bulb, *B*, in the upper part of the vessel, and returned to the main liquid in *A*. The pelican had an opening, *C*, for charging it with liquid; and handles *HH*. In Lavoisier's experiment the opening *C* was hermetically sealed. The weight lost by the pelican was virtually equal to the residue obtained when the water was afterwards evaporated to dryness.

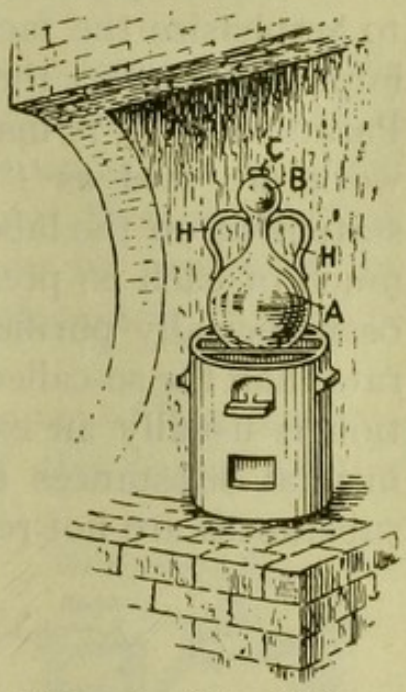


FIG. 26.—The Pelican—an Obsolete Instrument.

4. The conclusion.—Lavoisier therefore concluded that "the greater part, possibly the whole, of the earth separated from rain water by evaporation is due to the solution of the vessels in which it has been collected and evaporated."

In the light of what has been learned since Lavoisier's time it would have been easier to test the "guesses" by comparing the amount of residue obtained when the water is boiled in metal—gold or platinum—vessels. To avoid the contamination of distilled water by its solvent action on glass, block tin condensers are preferred to glass when making distilled water for laboratory use, since the water acts very much more vigorously on glass than it does on tin. Distilled water which has been kept some time in a glass bottle is sure to be contaminated.

Pure and impure substances.—The experiments of Lavoisier are important because they show how substances thought to be pure can be contaminated with impurities in devious and subtle ways. It is easy to understand how the idea that water could be changed into an earth could flourish in ignorance of the solvent action of water on glass. A compound can be contaminated with impurities in many ways—from the raw materials used in preparing the compound; from the vessels in which it was prepared; by exposure to the atmosphere; by the decomposition of part of the substance, etc.

The term **pure** is applied to a substance when it is desired to emphasize the fact that it is not contaminated with sufficient impurity to affect the most exact work for which it is employed. Paradoxical as it may seem, the substances used in analytical work are sold as "chemically pure," and yet they have a statement on the labels indicating what impurities are, and how much of each is, present. "Commercial" materials have not been specially purified, and they are usually sold at a cheaper rate than the so-called "chemically pure" substances. Purification is usually an expensive operation, and the cheaper commercial substances are used whenever the specially purified substances are not required.

§ 7. Solutions.

When sodium chloride—*i.e.* common salt—is added to water, kept at a constant temperature, the salt is gradually dissolved, and the process of solution continues until a definite amount has dissolved. The amount of solid remaining in excess of this will remain an indefinite time without further change, provided the temperature remains constant and no solvent is lost by evaporation. The solid and solution are then in equilibrium, and the solution is said to be **saturated** with the salt at the temperature of experiment. **The weight of salt dissolved by 100 grms. of the solvent so as to make a saturated solution at any assigned temperature is called the solubility of the salt.** Thus 100 grms. of water at 20° will dissolve 26·5 grams of sodium chloride, and accordingly, 26·5 is the

solubility of sodium chloride in water at 20°. **Accordingly, solutions have been defined as homogeneous mixtures of two or more substances whose composition can vary within certain definite limits.** The **concentration** of a solution is determined by the relative amount of solute in solution. If but a small proportion is present, the solution is said to be *weak* or *dilute ;* if a relatively large amount of solute is dissolved, the solution is said to be *strong* or *concentrated.* For convenience the dissolved substance is often called the **solute,** and the liquid in which the solute is dissolved the **solvent.** The solution generally acquires some of the properties of the dissolved substance—taste, colour, etc.

The particles of a true solution do not settle when the mixture stands, and the solution, whether coloured or not, is *clear* in transmitted light. Particles suspended in a liquid make the liquid *turbid ;* the particles are not then in solution. Particles suspended in a liquid can usually be separated by filtration, but when a substance is in solution it cannot be separated from the solvent by filtration.

In the laboratory, an open-textured paper—**filter paper**—is used for filtration. Solids remain on the paper, soluble matters run through. The operation is conducted as follows : A circular piece of filter paper is folded four-ply so as to form the quadrant of a circle ; the quadrant is opened to form a hollow cone—Fig. 27 ; and placed in a **glass funnel.** The paper is wetted and carefully bedded close to the glass. The paper should not come within a centimetre from the top rim of the funnel. The funnel is placed in a **filter stand,** and a beaker or flask is placed below the funnel as shown in Fig. 27. A glass rod held in one hand is pressed against the edge of the beaker containing the liquid to be filtered, and part of the contents of the beaker are poured into

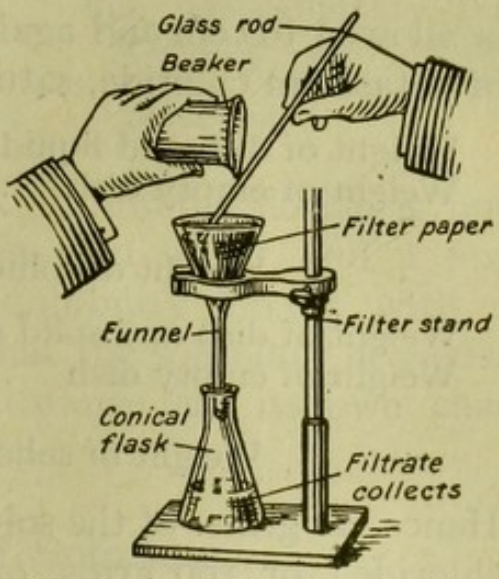


FIG. 27.—Filtration in the Laboratory.

the filter paper so that the liquid runs down the glass rod. There will then be no splashing, and with a little practice the pouring can be done without any liquid running down the outside of the beaker. The filtered liquid—called the **filtrate**—collects in the vessel below the funnel. The solid matter on the funnel can be washed free from the solution by running more of the solvent—water—through the paper and its contents until the liquid which passes through is free from solute.

How to determine the solubility of a solid.—A porcelain dish is weighed first empty, and then partially filled with a clear saturated solution of, say, potassium chloride, and again weighed. The liquid is then evaporated to dryness. One way of conducting the evaporation is illustrated in Fig. 28. The liquid to be evaporated is placed in the **evaporating basin,** which is supported on a **retort ring**, which in turn is clamped to a **retort stand**. A gas burner is lighted and placed below the basin. The flame of the burner must not be too high or some liquid may be lost from the basin by spurting. The dish is allowed to cool and again weighed. Suppose with a solution of potassium chloride, saturated at 15°, we obtain :

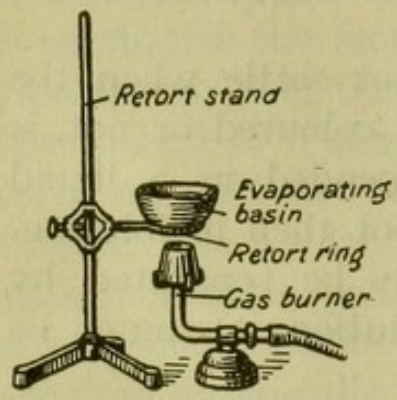


FIG. 28.—Evaporation.

Weight of dish and liquid	72·7	grms.
Weight of empty dish	52·7	,,
Weight of solution	20·0	,,
Weight of dish and solid residue	57·6	,,
Weight of empty dish	52·7	,,
Weight of solid	4·9	,,

Hence, 20 grms. of the solution dissolve 4·9 grms. of potassium chloride ; or 100 grms. of the solution contain 24·5 grms. of solid matter ; or 100 — 24·5 grms. of water dissolve 24·5 grms. of solid ; or 100 grms. of water at 15° dissolve 32·4 grms. of potassium chloride, and this number—32·4—is the solubility of this substance in water at 15°.

The influence of temperature.—The solubility of most substances increases with the temperature; the higher the temperature, the greater the solubility. The relation between the solubility of solids and temperature is usually plotted in the form of curves called **solubility curves.** The solubility curve presents a graphic picture which enables the relation between solubility and temperature to be seen at a glance. In illustration, Fig. 29 shows solubility curves of potassium chloride, chlorate, and perchlorate. The upward left-to-right slope of the curves shows that the solubility of these salts

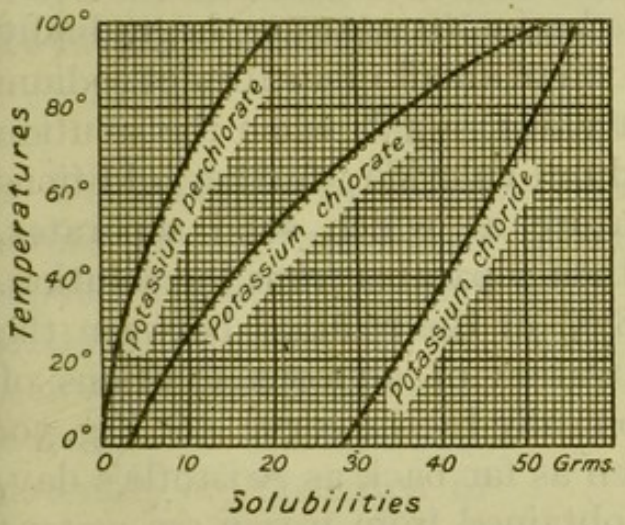


FIG. 29.—Solubility Curves of Potassium Chloride, Chlorate, and Perchlorate.

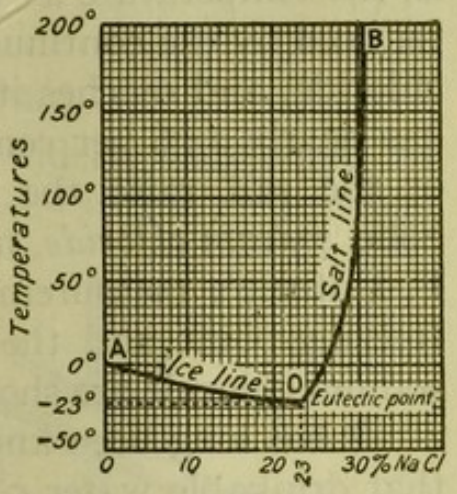


FIG. 30.—Solubility and Freezing Curves of Sodium Chloride : Water Solutions.

increases with a rise of temperature. Sodium chloride is but slightly more soluble in hot than in cold water, and a few substances—*e.g.* slaked lime—give solubility curves with a right-to-left upward slope, showing that the solubility *decreases* with rising temperatures. Each substance has its own characteristic solubility curve.

§ 8. The Freezing of Solutions.

The curve *OB*, Fig. 30, represents the solubility of sodium chloride at temperatures ranging from −23° to +200°; the observation cannot be continued below −23° because the whole mass freezes; the upward curve would probably stop only at

the melting-point of sodium chloride, 801°, if it were not for the volatilization of the water. Hence, to determine the solubility at high temperatures, the pressure would have to be very great to prevent the water volatilizing.

The freezing temperature of a solution is generally lower than that of the pure solvent. More than a century ago, C. Blagden (1788) cited a number of observations which led him to the belief that **the lowering of the freezing-point is proportional to the amount of substance in solution.** This generalization is sometimes called **Blagden's law.** The freezing-point of an aqueous solution of sodium chloride, that is, the temperature at which *ice* begins to separate, is gradually reduced by the continued addition of small quantities of sodium chloride, and reaches its lowest value, −23°, when the solution has nearly 23·6 per cent. of sodium chloride ; further additions of the salt raise the temperature at which solid separates. Solid *sodium chloride*, not ice, then separates from the solution. F. Guthrie's measurements (1875) of the relation between the freezing-point and the concentration of aqueous solutions of sodium chloride are shown graphically by the curve *AO*, Fig. 30.

It has long been known, even as far back as Aristotle's day, that drinkable water could be obtained from frozen sea-water ; and that if an aqueous solution of salt be gradually cooled, comparatively pure ice first separates from the solution. Imagine a 5 per cent. solution of salt subjected to a gradually diminishing temperature. Start at 0°. When the temperature reaches, say, −3·4°, ice separates from the solution. The mother liquid remaining has therefore more than 5 per cent. of salt in solution ; as the temperature falls, more ice separates. The further concentration of the mother liquid and the separation of ice continue until the mother liquid has about 23·6 per cent. of salt, when the whole remaining liquid freezes *en bloc* at −23°. Quite an analogous sequence of changes occurs if solutions containing more than 23·6 per cent. of salt be gradually cooled. This time, however, instead of pure ice, pure salt separates until the residual liquid has 23·6 per cent. of salt. The whole solidifies *en masse* at −23°. If the cooling solution has just 23·6 per cent. of salt, neither ice nor salt

separates, until the temperature has fallen to −23°, when the whole freezes to a solid mass. No other mixture of water and salt freezes at a lower temperature than this. No matter what the composition of the original solution, the last fraction to solidify always has the same composition. Hence a solution containing 23·6 per cent. of salt is called a **eutectic mixture**; and −23° the **eutectic temperature**—from a Greek word meaning easily fused. Eutectic mixtures have these important characteristics: (1) They have a definite composition; (2) a definite melting-point; and (3) they are heterogeneous mixtures of solvent and solute, as can usually be seen when the mixtures are examined under the microscope.

§ 9. Natural Waters.

Occurrence of water.—Water is widely distributed in nature in its three states of aggregation—steam or aqueous vapour, liquid water, and solid ice and snow. It has been estimated that three-fourths of the surface materials on the crust of the earth is water. A large amount of water can be obtained by burning animal or vegetable matter—*e.g.* fish yield the equivalent of about 80 per cent. of water; beef, 60–62 per cent.; the human body, 70 per cent.; aquatic plants between 95–99 per cent.; and ordinary land plants, 50–75 per cent. Similarly, a great many rocks yield water when they are calcined—thus, china clay, thoroughly dried at 100°, when heated in a porcelain or fireclay retort, Fig. 31, by means of a blast burner, yields liquid water which can be collected in the receiver. Every 100 grams of china clay will give between 10 and 14 grams of water.

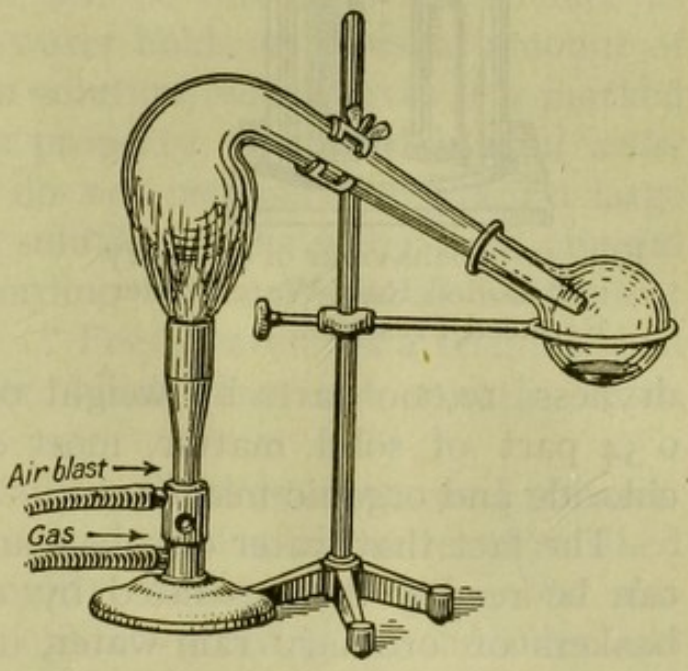


FIG. 31.—Action of Heat on Clay.

Rain-water.—Rain, in its journey through the air, dissolves a little oxygen, and nitrogen, and several other substances which might be present in the atmosphere ; it also carries down dust—organic and inorganic. Rain-water, particularly if collected near the sea in high winds, contains sodium chloride ; and if collected near towns, sulphur compounds derived from the products of combustion of coal. The rain which falls at the end of a shower is more pure than that which falls at the beginning, because the atmosphere is washed, so to speak, during the earlier part of the shower. When evaporated to

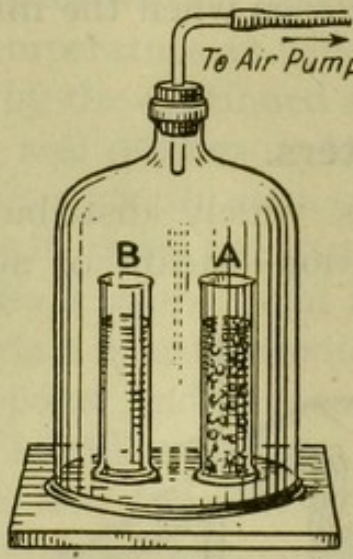


FIG. 32.—Behaviour of Ordinary and Boiled Rain Water under Reduced Pressure.

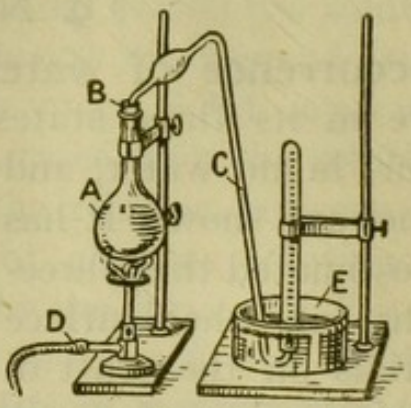


FIG. 33.—Driving the Dissolved Air from Water.

dryness, 10,000 parts by weight of rain-water will give about 0·34 part of solid matter, most of this consisting of sodium chloride and organic matter.

The fact that water dissolves an appreciable quantity of air can be readily demonstrated by comparing the behaviour of beakers of ordinary rain-water, *A*, Fig. 32, and of recently boiled water, *B*, Fig. 32, under an evacuated bell-jar. Air bubbles develop in the former and rise to the surface, and not in the latter. Again, by fitting up an apparatus like that shown in Fig. 33, where a glass flask *A* is fitted with a one-hole stopper, *B*, and a glass delivery tube, *C*, bent as shown in the diagram. The flask is filled with the water under examination and the stopper with its tube pressed into position. As a result the flask and delivery tube will be filled quite full of water.

The flask is supported so that the delivery tube dips in a basin of water. A graduated gas tube, *E*, full, say, of water, is clamped over the end of the delivery tube in the dish of water *E*. The water is then boiled, and the gas dissolved in the water is driven out of the flask to collect in the gas jar. When exact results are required, mercury is used in place of water for collecting the gas.

Spring and mineral water.—Directly the rain-water strikes the ground, it begins to attack and dissolve various rocks, decaying organic tissue, etc., forming *surface and ground water*. It is estimated that between 25 and 40 per cent. of the rainfall, in temperate regions, soaks into the ground. In its journey underground—*underground water*—the percolating water loses most of its organic matter and dissolves more or less mineral matters—compounds of calcium, magnesium, and sodium, carbon dioxide, etc. Sooner or later the water which has percolated underground will be forced to the surface as *spring-water*. If the spring-water holds an unusual amount of some particular substance in solution, which gives it a marked taste or some other specific property, the term *mineral water* is applied. Mineral waters do not necessarily contain a large excess of mineral matters in solution. The water from mineral springs is often named according to some special constituent or the locality of the spring. " Fresh water " is a term applied vaguely to a natural water which does not contain much dissolved impurity.

River-water.—Spring-water collects in rivers and streams. Rivers contain not only the solvent and solid matters furnished by spring-waters and the country which they drain, but also organic matter derived from plants growing on the sides and bottom of the river, and also drainage from the villages and towns through which the river passes. The river, in virtue of its greater volume and force, also carries along a considerable amount of suspended solids.

Sea-water.—Just as spring-water flows into the rivers, the rivers flow into the sea, carrying their dissolved salts, and suspended matters which have not been deposited in transit. The vapour which rises from the sea by evaporation is almost

pure water; hence, unless the dissolved matters are continuously removed, sea-water must be gradually getting more and more "salty." Sea-water contains a relatively large proportion of soluble salts—about 3·5 per cent. of solids in solution. Where the evaporation is greatest we naturally expect to find the greatest proportion of salts in solution. Thus the Mediterranean contains about 3·4 per cent. of solids in solution; whereas the Baltic, with its numerous tributaries and less evaporation, contains between 0·3 and 0·8 per cent. of solids in solution. Salts accumulate in land-locked seas and lakes much faster than in the sea. In illustration, the Dead Sea contains 22·8 per cent. of solids in solution; the Great Salt Lake (Utah), 23 per cent.; and the Elton Lake (Russia), 27 per cent. These masses of water behave as if they were exposed in a large evaporating basin, for the salts accumulate in the water and are deposited in crystalline masses on the shores of the lakes as the water evaporates.

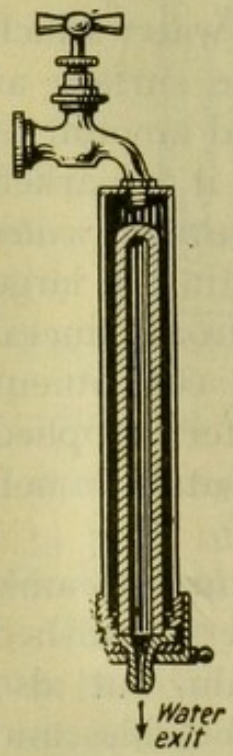


FIG. 34.—Pressure Filter for removing Bacteria from Water.

Potable and drinking water.—The inorganic or mineral matters usually found in solution in natural water are not directly injurious to health. The purification of water for towns and cities is a very important practical problem for the chemist. Water should be free from pathogenic (disease-producing) bacteria, and from suspended impurities. This is generally done by filtration through large filter beds made from layers of sand and gravel, extending in some cases over an acre of ground. A Pasteur-Chamberlain's filter made of unglazed porous earthenware, and shaped like a hollow candle, is arranged to be screwed on to the water tap, Fig. 34. The water is forced through the earthenware by the pressure of the main, and "filtered water" trickles through the aperture below. A slimy mass of bacteria, organic matter, etc., collects on the inside.

The circulation of water in nature—the water cycle.—

The water on the earth passes through a remarkable cycle of changes. The heat of the sun leads to the evaporation of water from the seas, etc. ; water vapour is only 0·62 times as heavy as an equal volume of air, and consequently it rises into the upper regions of the atmosphere. The temperature of the ascending vapour gradually decreases, and consequently a plane must be reached where the air is saturated with moisture. The vapour will then condense in the form of fine drops of water—mist or clouds. The fine drops coalesce into larger drops. Ultimately, the condensed water must descend again to the earth as rain, snow, etc. The wind distributes the vapour. The heat given up during the condensation of the vapour is distributed or carried from the hotter regions—where evaporation is fastest—to the colder regions—where the vapour is condensed—thus helping to "stretch" the temperate regions nearer to the poles. The water which is sprayed, as rain, etc., on the surface of the globe, does a certain amount of physical and chemical work. On the chemical side, water helps in the decomposition and weathering of rocks ; and on the physical side it transports matter in suspension from the higher to the lower levels. The soluble matters ultimately collect in the seas.

Thus the water cycle involves : (1) evaporation from the oceans, seas, lakes, etc. ; (2) condensation in the upper regions of the atmosphere as a fine mist of distilled water, where it collects as clouds ; (3) further condensation is followed by rain ; (4) the rain-water percolates through the soil and collects on an impervious bed of rock, whence it is forced to the surface, as spring water, by the pressure of the superincumbent water ; and (5) the spring-water is collected by the streams and rivers and forwarded to the sea, to commence anew the never-ending cycle. The poet P. B. Shelley has described these phenomena in a charming manner. "The Cloud" speaks :

"I am the daughter of the Earth and Water,
And the nursling of the Sky :
I pass through the pores of the ocean and shores ;
I change, but I cannot die.
For after the rain—when with never a stain
The pavilion of heaven is bare,

And the wind and sunbeams, with their convex gleams,
Build up the blue dome of air—
I silently laugh at my own cenotaph,
And out of the caverns of rain,
Like a child from the womb, like a ghost from the tomb,
I rise and unbuild it again."

§ 10. The Properties of Water.

The substance we call water has its own specific properties, but sea-water, spring-water, rain-water, and distilled water show certain differences in their properties. The differences, however, are not due to the water, but to the substances—impurities—which the water has dissolved from its surroundings. For instance, if the less pure natural waters be distilled, the "impurities" remain behind in the retort, and fairly pure water collects as distillate. At ordinary temperatures, such water is a tasteless and odourless liquid; it is colourless in moderately thin layers, but it appears greenish-blue when viewed in thick layers. The freezing-point, 0°, and boiling-point, 100°, are characteristic, and distinguish water from all other liquids.

We have seen that air, and gases generally, are highly compressible; liquids are but slightly compressible in comparison. Thus, if 1000 c.c. of water be subjected to a pressure of two atmospheres the volume will be reduced by 0·05 c.c. According to P. G. Tait, this very small compressibility means that if sea-water were quite incompressible, the average level of the sea would be raised 116 feet higher than it is to-day, and 4 per cent. of the present land surface would be submerged.

Non-metallic liquids are bad conductors of heat; water is one of the best of liquids for conducting heat (mercury excepted), but even then, the thermal conductivity is small. Witness, a piece of weighted ice at the bottom of a test tube of cold water, when, if the test tube be held obliquely and heated by a Bunsen's burner near the surface, the water at the surface will boil, but the ice at the bottom will remain unmelted.

Questions.

1. 10 c.c. of a solution of Epsom salts in water at 20° weighed 13·7 grms. After evaporation, 3·6 grms. of the salt remained. Calculate the solubility of Epsom salts in water at this temperature, and plot a solubility curve for Epsom salts from the following data :

Temperature . .	0°,	20°,	40°,	60°,	80°,	100°
Solubility . . .	26·9,	36·2,	45·6,	55·0,	64·2,	73·8

2. How would you prepare pure water and common salt from sea-water ?—*London Univ. Matric.*

3. State the chemical differences between rain-water, river-water, spring-water, and sea-water, and describe experiments which illustrate these differences.—*London Univ. Matric.*

4. Describe as many experiments as you can which would exhibit the difference between sea and fresh water respectively.—*Staffs. Agric. Schol.*

5. How would you obtain perfectly pure water from a very dirty sample ? Sketch any apparatus you would require, and explain the use of each part of it.—*Oxford Junr. Locals.*

6. If heat were applied to a cubic foot of ice at the melting temperature, explain the changes of temperature and volume it undergoes ? Why do water pipes frequently burst during a severe frost ?—*Staffs. Minor Schol.*

7. It is desired to infer from a volume measurement of a quantity of air confined in a graduated tube over water. What observations must be made ?—*Oxford Junr. Locals.*

8. Explain the meaning of the terms: solution, saturated solution, and crystallization. Show how it can be proved experimentally that hot water is generally a better solvent than cold water.—*Cape Univ.*

9. You are provided with some sea-water containing some mud or sand in suspension. Describe how you would prepare from this, pure water, and also dry samples of the dissolved salt, and the suspended matter.—*Staffs. Minor Schol.*

10. Sketch the apparatus you would use for one of the following purposes, and describe how you would use it. (*a*) To show that a gas expands when heated. (*b*) That heat is absorbed when a liquid evaporates rapidly. (*c*) That the atmosphere exerts pressure. —*Staffs. Minor Schol.* Hint: To answer (*b*), every minute, plot on squared paper the temperature indicated by a thermometer immersed in the liquid being heated, and interpret the resulting curve; or place a little ether in a beaker which rests on a block of wood with a film of water between. Blow air through the beaker,

The evaporating ether absorbs so much heat that the water is frozen.

11. On squared paper plot curves to represent the following tabulated quantities : —

GRAINS OF SOLID DISSOLVED IN 100 GRAMS OF WATER

Temperature.	Sodium sulphate.	Potash alum.
0°	5·0	3·9
10°	9·0	9·5
20°	19·4	15·1
30°	40·0	22·0
40°	48·8	30·9
50°	46·7	44·1
60°	45·3	66·6
70°	44·4	90·7
80°	43·7	134·5
90°	43·1	209·3
100°	42·5	357·5

Answer by reference to your diagram : (*a*) Equal volumes of two solutions on evaporation yielded 26·5 grms. of sodium sulphate and potash alum respectively. At what temperatures were the two solutions made up ? (*b*) A saturated solution of potash alum was made at 64° and another of sodium sulphate at 72°. If both were cooled to 15°, how many more grams of potash alum would separate out than of sodium sulphate ?—*Staffs. Intermediate Schol.*

12. If you wished to evaporate a liquid quickly what shaped vessel would you prefer, and why ? Indicate what conditions you think would favour and what conditions would retard rapid evaporation ?

13. A few cubic centimetres of a clear colourless liquid are given to you. How would you find if it is water ; and if it be water, how would you find if it is *pure* water ?

14. After heating a gram of gypsum in a crucible to a dull red heat, the cooled residue weighed 0·791 grm. How would you proceed to show that water is given off when gypsum is treated in this way ; and, from the data just indicated, compute the percentage amount of water lost.

15. Describe and explain a method of determining the amount of aqueous vapour in air.—*Science and Art Dept.*

CHAPTER IV

Mixtures and Compounds

§ 1. Physical and Chemical Changes.

One element or compound is distinguished from all other elements or compounds in possessing certain specific and characteristic properties. First and foremost, a chemical compound has a fixed and definite composition ; then again, it melts and boils at definite temperatures ; its specific gravity, specific heat, colour, odour, behaviour when in contact with other substances, etc., are characteristic of one particular chemical compound. When the melting-point of, say, pure silver chloride has been once accurately determined, it follows that all other samples of pure silver chloride will melt at the same temperature under the same conditions. The more salient characteristic properties of a compound are employed as **tests** for its identification—that is, for distinguishing it from all other known compounds. Thus a student would be probably correct in stating that given liquid was water if it boiled at 100°, froze at 0°, and was colourless, tasteless, and odourless.

Physical changes.—When liquid water becomes ice or steam there is no change in the *chemical* nature of the substance, for the matter which makes steam and ice is the same in kind as that of liquid water. A substance can generally change its state, as when liquid water becomes steam or ice. The idea is further emphasized by the fact that in most cases a substance is called by the same name, whether it be in the solid, liquid, or gaseous state of aggregation, *e.g.* we speak of " liquid " oxygen, " liquid " air, " molten " silver chloride, etc. Again, matter

may change its *volume* by expansion or contraction ; it may change its *texture*, as when a porous solid is compressed to a compact mass ; it may change its *form*, as when matter in bulk is ground to powder ; it may change its *magnetic qualities*, as when a piece of soft iron in contact with a magnet attracts other pieces of iron, etc. It is conventionally agreed to say that in none of these cases of physical change is there any evidence of the formation of a new substance ; and that the matter does not lose or change those properties which distinguish it from other forms of matter. **A physical change involves an alteration in the properties of a substance without the formation of a new substance.**

Chemical changes.—When magnesium metal is heated in air, a white powder is formed, and when red mercury oxide is

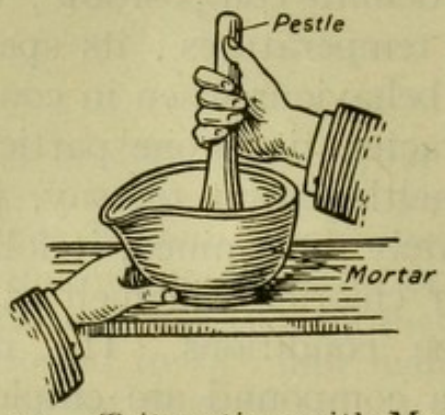


FIG. 35.—Trituration with Mortar and Pestle.

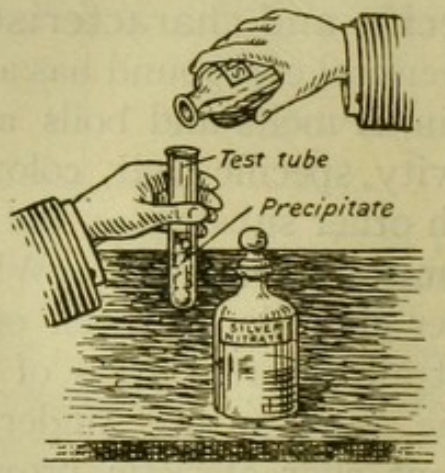


FIG. 36.—Precipitation from Mixed Solutions: Silver Nitrate and Salt.

similarly treated, metallic mercury and gaseous oxygen are obtained. The action of heat in both cases furnishes forms of matter with very different specific properties from those forms of matter employed at the start. **A chemical change involves the formation of a fresh substance or substances, with different specific properties from the original substance or substances.** Two more examples might be given. (1) Rub together white potassium iodide with white mercuric chloride by means of a pestle and mortar, Fig. 35. A scarlet powder is obtained ; (2) mix together a few cubic centimetres of colourless solutions of silver nitrate and common salt, and dense white precipitate appears, Fig. 36. The red powder and

the white precipitate are so different from their constituents that it is inferred that the substances have united chemically. In both chemical and physical changes, as we shall soon find, the total mass of matter before and after the change remains constant, but in chemical changes alone the *kind* of matter changes.

It is not always easy to distinguish between physical and chemical changes, because the only real distinction between the two turns on the question : Is there any evidence of the formation of a new substance during the change ?

§ 2. Compounds and Mixtures.

1. The constituents of a compound are combined in definite proportions.—The law of constant proportions is of fundamental importance in forming a conception of the meaning of the term " chemical compound." If a substance produced in different ways be not constant in composition, it is not considered to be a chemical compound, but rather a mixture. R. Bunsen (1846), for example, showed that the proportion of oxygen to nitrogen in atmospheric air is not constant, because the oxygen varies from 20·97 to 20·84 per cent. by volume, by methods of measurement with an error not exceeding 0·03 per cent. Hence, the oxygen and nitrogen in atmospheric air are said to be simply mixed together, and not combined chemically. We shall soon see, however, that substances with a definite composition are usually, but not always, chemical compounds.

2. Compounds are homogeneous, mixtures are usually heterogeneous.—It is comparatively easy to detect particles of sugar and sand in a mixture of the two ; and a simple inspection of a piece of Cornish granite will show that it is a mixture of at least four constituents—silvery flakes of mica ; black patches of schörl ; whitish crystals of felspar ; and clear glassy crystals of quartz. A photograph of a thin slice of this rock, as it appears under the microscope magnified about 50 diameters, is shown in Fig. 37. Very frequently, the constituents of a mixture are too small to be distinguished by

simple inspection, and the body appears homogeneous. A microscopic examination may reveal the heterogeneous character of the substance. Blood and milk, for instance, appear to be homogeneous fluids, but under the microscope (magnified, say, 600 diameters) the former appears as a colourless fluid with red corpuscles in suspension, Fig. 38; and milk appears as a transparent liquid containing innumerable white globules (fat), Fig. 39. Naturally, too, the stronger the magnification, the greater the probability of detecting whether the body is homogeneous or not. Sometimes the microscope fails to detect non-homogeneity under conditions where other tests indicate heterogeneity.

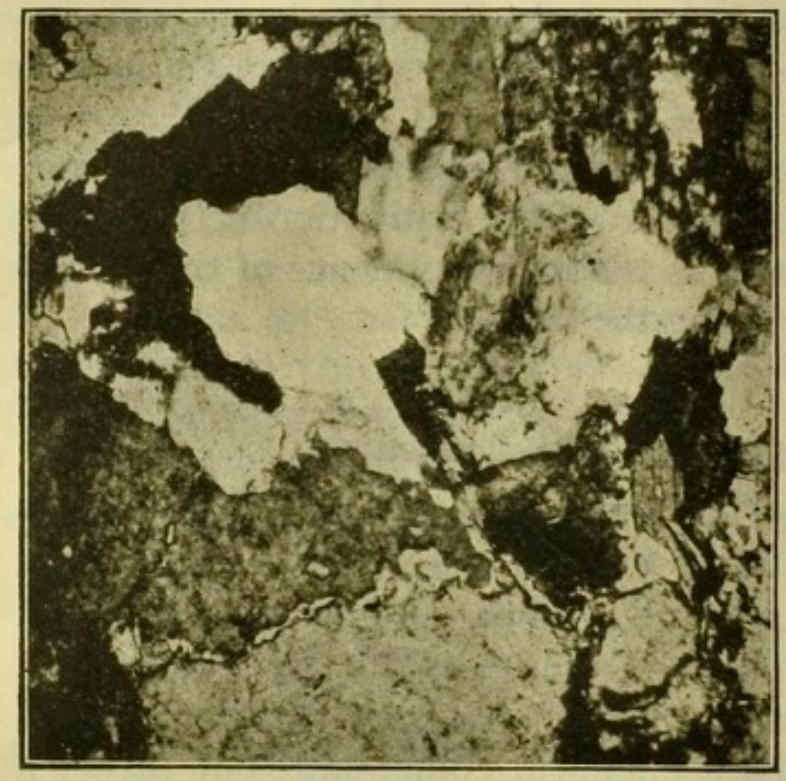


FIG. 37.—Cornish Granite (×50).

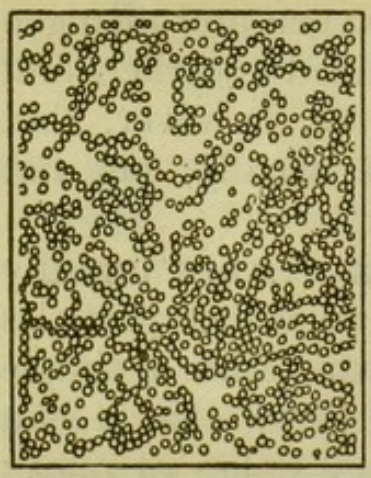


FIG. 38.—Microscopic Appearance of Blood (× 600).

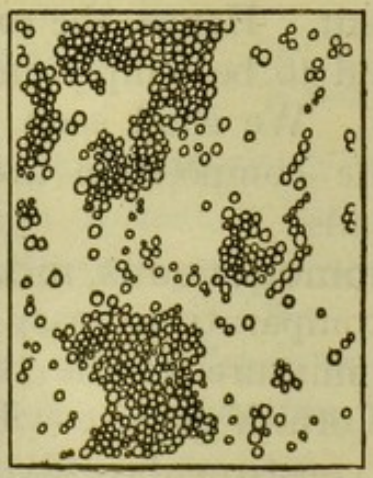


FIG. 39.—Microscopic Appearance of Milk (× 600).

Before constant composition can be accepted as a proof of chemical combination, it must also be shown that the substance is homogeneous. **A homogeneous substance is one in which every part of the substance has exactly the same composition and properties as every other part.** A substance may have a fixed and constant composition

and yet not be homogeneous—*e.g.* eutectic mixtures described on p. 57. A substance may be homogeneous, for all we can tell to the contrary, and yet not have a constant composition—*e.g.* atmospheric air ; a solution of sugar in water, etc. This simply means that *all chemical compounds are homogeneous, but all homogeneous substances are not chemical compounds.* Indeed, it is sometimes quite impossible to tell by any single test whether a given substance is a mixture or a true chemical compound.

3. The constituents of a mixture can usually be separated by mechanical processes.—The properties of a mixture of finely-powdered iron and sulphur have been used in chemical text-books since 1823 to illustrate the difference between mixtures and compounds. It would be difficult to find a better example. Rub together a mixture containing, say, 6 grams of iron and 4 grams of sulphur in a mortar, and note that : (1) the colour of the mixture is intermediate between the colour of the iron and of the sulphur ; (2) the particles of iron and sulphur can be readily distinguished under the microscope ; (3) some of the iron can be removed without difficulty by means of a magnet ; and (4) the two can be separated quite readily by washing the mixture on a dry filter paper by means of carbon disulphide, Fig. 28. The sulphur dissolves in the carbon disulphide ; the solution can be collected in a dish placed below the filter paper ; and the sulphur can be recovered by allowing the carbon disulphide to evaporate from the dish by placing the dish over a vessel of hot water with no flame in the vicinity (carbon disulphide vapour ignites very easily). Sulphur remains behind as a crystalline residue, Fig. 142. The metallic iron remains on the filter paper. Here, then, the constituents of the mixture have been separated by the mechanical processes —magneting, and the action of solvents. It is not always possible to apply these tests. Solvents, as we shall find later, sometimes decompose a compound into its constituents, or conversely, " cause " the constituents of a mixture to combine.

4. A mixture usually possesses the common specific properties of its constituents ; the properties of a compound are usually characteristic of itself alone.—

The properties of a mixture are nearly always additive, *i.e.* the resultant of the properties of the constituents of the mixture. For instance, a mixture of equal parts of a white and black powder will be grey. The specific gravity [1] of a mixture of equal volumes of two substances of specific gravity 3 and 5 will be 4, because if one c.c. of water weighs one gram, there will be a mixture of 0·5 c.c. weighing 1·5 grams of one substance ; 0·5 c.c. of the other substance weighing 2·5 grams and $1·5 + 2·5 = 4$ grams per c.c. It must be added that such properties of compounds are additive, for they are the sum of the properties of their constituents.

EXAMPLE.—What is the specific gravity of air containing a mixture of one volume of oxygen and four volumes of nitrogen when the specific gravity of oxygen is 16, and the specific gravity of nitrogen, 14·01 ? One-fifth volume of oxygen weighs 3·2 units, and four-fifths volume of nitrogen weighs 11·2 units. Hence one volume of the mixture will weigh 14·4 units when one volume of oxygen weighs 16 units.

If a portion of the mixture of sulphur and iron indicated above be placed in a hard glass test tube, and warmed over the Bunsen's flame, the contents of the tube begins to glow, and a kind of combustion spreads throughout the whole mass. When cold, break the test tube, and note that (1) the porous black mass formed during the action is quite different from the original mixture ; (2) the microscope shows that the powdered mass is homogeneous ; (3) it is not magnetic like iron ; [2] and (4) it gives up no sulphur when digested with carbon disulphide.[3]

[1] SPECIFIC GRAVITY.—The student is supposed to know that *specific gravity is a number which expresses how much heavier a given substance is than an equal volume of water taken at a standard temperature and pressure.* In the case of gases, either air = unity, oxygen = 16, hydrogen = 1, or hydrogen = 2 is usually taken as standard ; and in the case of liquids and solids, water at + 4° is taken as unity. Specific gravity may thus be regarded as the weight of unit volume if the standard water = 1 be taken, and the weights are reckoned in grams, and volumes in cubic centimetres. The great value of specific gravity data lies in the fact that *specific gravity is a number which enables volume measurements to be converted into weights, and weight measurements to be converted into volumes.*

[2] This provided the iron was not in excess.

[3] This provided the sulphur was not in excess, but the excess of sulphur, if present, can often be driven off as vapour.

These facts lead to the assumption that there has been a chemical reaction between the sulphur and the iron. **When chemical combination occurs, the reacting constituents appear to lose their individuality or identity more or less completely, and each new substance which is formed has its own distinctive properties.**

5. **Thermal, actinic (light), or electrical phenomena usually occur during chemical changes.**—Attention must be directed to the fact that a great deal of heat was developed during the combination of the iron and sulphur. The heat required to start the reaction does not account for the amount of heat developed during the reaction. This point is perhaps better emphasized (1) by placing an intimate mixture of powdered sulphur and zinc on a stone slab. After the flame of a Bunsen's burner has been allowed to play on a portion of the mixture for a short time to start the reaction, the zinc and sulphur combine with almost explosive violence ; (2) zinc "wool" oxidizes with a brilliant incandescence when it is ignited in air, forming dense white clouds of zinc oxide ; (3) with magnesium "wool" the change is explosively violent ; (4) sprinkle a few pieces of the element iodine on some yellow phosphorus, the two combine and ignite spontaneously ; and (5) when powdered tartaric acid and sodium bicarbonate are intimately mixed together, the mixture appears homogeneous until it is examined under the microscope, when the two constituents can be readily distinguished. On stirring up the mixture with water, effervescence occurs, and a gas is evolved. The crystals obtained by evaporating the remaining solution are quite different from either of the original components. In the first four cases, a large amount of heat and light is developed during the reactions.

If a plate of commercial zinc be placed in dilute sulphuric acid, bubbles of gas are copiously evolved, and if a thermometer be placed in the vessel, the rise of temperature shows that heat is generated during the chemical action. If the zinc be pure, very little if any gas is developed. It makes no difference if a plate of platinum be dipped in the same vessel as the zinc, provided the plates are not allowed to come into contact with

one another. If the two plates are connected by a piece of copper wire, a rapid stream of gas bubbles arises from the surface of the platinum plate, and some gas also comes from the zinc plate. The platinum is not attacked by the acid in any way, but the zinc is rapidly dissolved. If a voltmeter be interposed in the circuit between the two plates —Fig. 40—the deflection of the needle shows that an electric current passes from the platinum to the zinc, as represented by the arrows. *The electric current is generated by the chemical reaction between the zinc and the acid, which results in the formation of zinc sulphate and a gas.* The action will continue until all the acid or the zinc is used up.

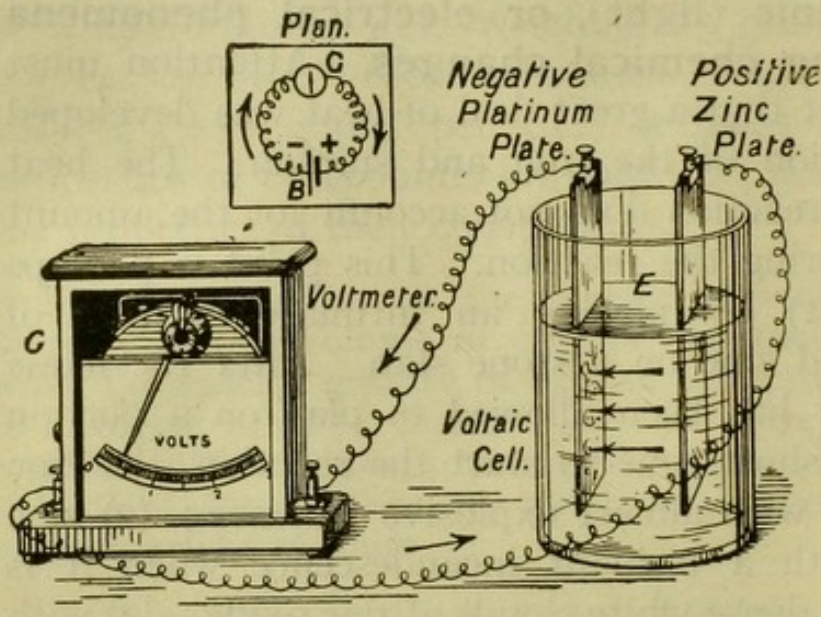


FIG. 40.—Electricity by Chemical Action—Voltaic Cell.

Nomenclature.—The **zinc or positive or + plate** of the cell *B* is often represented by a short thick line, and the **platinum or negative or – plate** by a longer thinner line as illustrated by the plan, Fig. 40. Hence the platinum in this simple cell is called the negative plate ; and the zinc is the positive plate. Here *G* represents the voltmeter or galvanometer. The vessel of acid with its two plates is called a **voltaic cell,** and this particular combination can be symbolized :—

Platinum | Dilute sulphuric acid | Zinc.

The chemical reaction just indicated is far from being the most economical mode of generating electricity, but all the different forms of voltaic cell on the market agree in this : **Electricity is generated during chemical action.**

The development of heat, light, or electrification are common concomitants of chemical action. The absence of such phenomena when substances are simply mixed together is usually

taken as one sign that chemical action has not taken place. When nitrogen and oxygen are mixed together in suitable proportions to make atmospheric air, there is no sign of chemical action, and this fact is sometimes cited among the proofs that air is a mixture. The argument is not always conclusive, because the condensation of steam and the freezing of water are usually called physical changes, though heat is evolved during both transformations.

Summary.—The tests for distinguishing chemical compounds from mixtures involve answers to the following questions :—

1. Are the different constituents united in definite and constant proportions ?
2. Is the substance homogeneous ?
3. Are the properties of the substance additive ?
4. Were thermal, actinic, or electrical phenomena developed when the substance was compounded ?
5. Can the constituents be separated by mechanical processes ?

Mechanical processes of separation.—The so-called mechanical processes of separation usually include : (1) Magneting, hand-picking, sieving, etc. (2) Elutriation, or washing in currents of air or water of different velocities. The densest particles are least affected, the lightest are carried furthest. (3) If some mixtures be placed in liquids of the right specific gravity, the lighter constituents will float, and the heavier constituents will sink. (4) Differences in the solubilities of the constituents in suitable solvents. (5) Distillation, freezing, etc.

§ 3. Circumstantial and Cumulative Evidence.

The student can consider himself as the judge in a lawsuit to decide whether a given substance is a chemical compound or a mixture. One witness asserts that the substance is a chemical compound because it appears to be homogeneous. The next witness asserts that it is a chemical compound because it has a fixed definite composition. The second witness is thus

in agreement with the first, and their joint testimony gives a very much more probable conclusion than either alone. By piling up the evidence in this manner, for or against our suspicion, we can make a chain of circumstantial evidence which enables highly probable conclusions to be drawn. Each bit of evidence taken by itself is not of much value, but all the evidence taken collectively has tremendous weight. It is easy to see, too, that the probability of the truth of an hypothesis becomes less as the number of unproved assumptions on which it is based becomes greater. **Every bit of additional evidence in favour of a conclusion multiplies the probability of its being correct in an emphatic manner; and evidence against a conclusion acts similarly in the converse way.** Huxley has stated that one of the tragedies in science is the slaughter of a beautiful hypothesis by one *incongruent fact;* a conclusion based solely upon circumstantial evidence is always in danger of this Damoclean sword.

A writer has said: "When two facts seem to be in conflict, we may be driven to decide which is the more credible of the two." This statement may give rise to a misunderstanding. We cannot admit the possibility of two contradictory facts. Facts can, and often do, contradict hypotheses. Again, a fact is a fact, and cannot be disputed. If there be any doubt about the truth of an alleged fact, something is wrong. **He who doubts should inquire.** The laboratory, not the study, is the place to decide if the alleged fact is the result of an incomplete or of a mal-observation. Facts *quâ* facts cannot be graded in degrees of probability or credibility.

§ 4. Analysis and Synthesis.

The term **synthesis**—from Greek words meaning "to place together"—is employed for the operations involved in making a particular compound from its constituents. *E.g.* methods for the synthesis of ferrous sulphide, and also for the synthesis of various oxides, were described in preceding sections. The term **analysis**—from Greek words meaning "to unloosen"—is employed for the process of separating the constituents of a compound or mixture. Thus mercuric oxide is broken down

into its constituents when heated. The object of the analysis may be to answer the question : What are the constituents of the mixture or compound ? The analysis is then said to be **qualitative**. If the relative quantities of the different constituents are to be determined, the analysis is said to be **quantitative**. For instance, if a weighed portion of a mixture of sulphur and iron be treated with carbon disulphide as described above, and the separated sulphur and iron be weighed, the two weights should be nearly equal to the weight of the original mixture taken for the analysis. The numbers so obtained express the result of a quantitative analysis of the mixture.

Analysis of gunpowder.—Gunpowder is a mixture of nitre (soluble in water), sulphur (soluble in carbon disulphide), and carbon (insoluble in both the solvents just mentioned). Hence, gunpowder can be analyzed by first washing a weighed quantity of the powder on a filter paper with warm water, Fig. 27 ; and collecting and evaporating the filtered solution to dryness in a weighed dish, Fig. 28. The increase in the weight of the dish with its contents represents the amount of nitre. The insoluble residue is dried and treated in a similar manner with carbon disulphide, and the amount of sulphur determined as in the case of the mixture of iron and sulphur. The dried carbon is then weighed. The result of a quantitative analysis of a sample of gunpowder, expressed in percentage numbers, is : nitre, 78 per cent. ; sulphur, 12 per cent. ; charcoal, 10 per cent. For the appearance of the residual nitre (potassium nitrate) left on evaporating the aqueous solution, see Fig. 154 (left) ; and for the sulphur residue, Fig. 142.

The analysis of aqueous solutions of zinc sulphate by the electric current.—In the experiment illustrated by Fig. 40 an electric current was developed during the reaction between dilute sulphuric acid and metallic zinc which resulted in the formation of zinc sulphate. Fit up a similar arrangement as before, but place two platinum plates, *E*, and pure distilled water in the clean glass jar, which will now be called the " electrolytic cell." Connect the two platinum plates with an accumulator or secondary battery (which may be regarded as a machine

for generating electricity), and a voltmeter as indicated in Fig. 41. The object of the accumulator is to generate an electric current. If the water is pure, the needle of the voltmeter moves very little, if at all. Add a concentrated solution of zinc sulphate to the water in the glass jar. The jump of the needle of the voltmeter shows that a current of electricity is flowing through the circuit, and hence also through the solution of zinc sulphate. If chloroform, benzene, or an aqueous solution of cane sugar had been used in place of the solution of zinc sulphate in the electrolytic cell, no current would pass

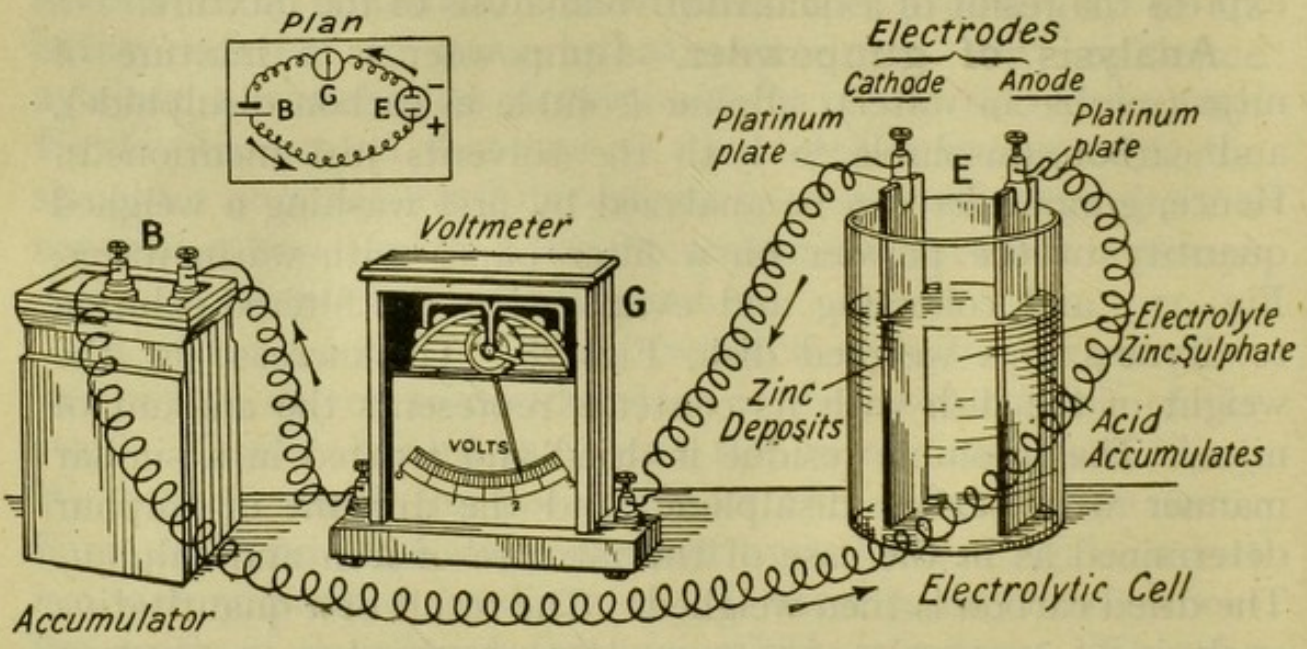


FIG. 41.—Chemical Action induced by Electric Current—Electrolysis.

through the circuit. Hence **liquids may be either conductors or non-conductors of electricity.** The current which passes through the solution of zinc sulphate produces some remarkable changes: (1) a spongy mass of metallic zinc accumulates about one of the platinum plates; (2) if the solution be tested, particularly in the neighbourhood of the other platinum plate, sulphuric acid will be found to be accumulating in the solution during the process of electrolysis; and (3) bubbles of oxygen gas, easily tested by collecting some in a test tube, rise from the same platinum plate about which the acid accumulates. If the experiment be continued long enough, and the products of the action be examined, we shall find that metallic zinc and sulphuric acid have been produced. If the

accumulator be disconnected, and the connections be made as indicated in Fig. 36, the zinc will redissolve in the acid, reproducing zinc sulphate ; and an electric current will be generated during the dissolution of the zinc.

Nomenclature.—The process of decomposition or analysis by the aid of the electric current is called **electrolysis.** The liquid which is decomposed is called the **electrolyte.** The passing of the electric current through the conducting copper wires, and through the conducting platinum plates, produces no change in these metals. Hence we recognize two kinds of conductivity—in one the conducting medium is decomposed by the current—electrolyte ; and in the other the conducting medium is not decomposed by the current—non-electrolyte. The plate at which the zinc collects is called the **cathode**—from the Greek κατά (kata), down ; ὁδός (odos), a path—and the other plate, about which the acid collects, is called the **anode**—from the Greek ἀνά (ana), up ; ὁδός (odos), a path. The anode and cathode together are called the **electrodes.** With the conventions indicated on p. 72 as to the direction of the electric current, the current is said to enter the electrolytic cell *viâ* the anode, and to leave the cell *viâ* the cathode. The two electrodes are thus " the doors or ways by which the current passes into or out of the decomposing body." It seems as if the electric current first splits the decomposing liquid into two parts which pass to the electrodes. The term **anions**—from the Greek ἴων (ion), traveller—is applied to those parts of the decomposing fluid which go to the anode ; and those passing to the cathode are called **cations,** and when reference is made to both the anions and cations, the term **ions** is employed. " Ions " is thus a general term for those bodies which pass to the electrodes during electrolysis. This notation was proposed by M. Faraday in 1834.

The principle of reversibility.—The experiments indicated above illustrate an important principle—the principle of reversibility : **If an antecedent event A produces an effect B, then an antecedent event B may reproduce the effect A.** Thus, chemical action can produce an electric current, Fig. 40, and conversely, an electric current can produce chemical action, Fig. 41. The one can undo the work of the other. Other examples of the principle will be found as we progress in our studies. Heat causes gases to expand ; conversely, if a gas expands by its own elastic force, the gas cools ;

a chemical reaction is attended by the evolution of heat, then heating the products of the reaction may reverse the reaction; etc.

§ 5. Chemical Affinity.

> There are agents in nature able to make the particles of bodies stick together by very strong attractions. And it is the business of experimental philosophy to find them out.—ISAAC NEWTON.

The word "cause" is usually applied to an event, action, or process which produces an effect. **There is no cause without an effect, and no effect without a cause.** The one presupposes and completes the other. When the cause of an event has been discovered, the event is said to be explained by the cause. We soon recognize, however, that the cause then becomes an effect which itself needs explaining by some ulterior cause, and so we can descend deeper, ever deeper, into what seems a bottomless pit.

It is related that a student of elementary chemistry, impressed with the ability of his teacher to explain natural phenomena, asked, "Teacher, why is gold yellow?" whereupon the teacher reverently answered, "Because God made it so." Had the answer been, "Because gold absorbs violet rays from composite white light, and reflects the yellow rays," the further question might have been asked, "But why does gold absorb violet light?" No real explanation can be given. Scientific explanations are much the same. We can go back and back until finally the only possible answer is that given by the teacher.

The cause of chemical action has mystified man from the earliest ages, and there is no prospect of an immediate solution. Matter appears to be endowed with properties in virtue of which two or more dissimilar substances, when brought into contact, give rise to other forms of matter possessing properties quite distinct from the original substances. The process of change is called a **chemical reaction.** At present, **chemical action can only be referred back to the presence of selective forces, indwelling in the different kinds of matter, which lead certain substances, under certain conditions, to undergo chemical change.** It almost seems as if the

elementary substances have their likes and dislikes; that they have a passionate desire for some, and are lukewarm towards others; that they break up ordinary friendships with some elements in order to attach themselves more tenaciously to others. This selective force is called "chemical affinity."

Chemists are chary about using the term "chemical affinity" because it suggests that elements, etc., combine or react because of a relationship, kinship, or family tie. The elements fluorine, chlorine, bromine, and iodine, for instance, are said to have a "family relationship" or "natural affinity" for each other, because their properties are so much alike. As a matter of fact, elements related in this sense do not usually form stable compounds. On general principles it is well to avoid terms which are not clear and precise in meaning, and which are liable to misunderstanding, because they are not always understood in the same way by everybody. In chemistry, however, the term "affinity" is reserved to connote not a "resemblance" but a tendency of the different kinds of matter to unite with one another. H. Boerhaave used the term in this sense in 1732, and he metaphorically compared the force of affinity with "love, if love be the desire for marriage." We must allow, said J. B. Dumas (1837), that "there is some truth in this poetic comparison." Hence the term "affinity" is used by chemists in a metaphorical sense for that peculiar force or form of energy which is the origin of all chemical changes.

Observe that **although we now say that chemical affinity is the cause of chemical action, we are quite unable to state the cause of chemical affinity.** When it is said, "Oxygen unites with tin or mercury because the one element has an affinity for the other," we have explained nothing, but simply restated the facts in different words. Many examples of similar pseudo-explanations might be given. *E.g.* "Hydrogen burns because it is combustible"; "Morphia induces sleep because of its soporific qualities"; etc. It would not be quite fair to say that the term "chemical affinity" veils our ignorance in obscure language because we quite recognize

that the term does not explain the phenomenon. "Affinity" is a conventional term for grouping a large number of phenomena into one class. To quote Thomas Hobbes: "Words are wise men's counters, they do but reckon with them; but they are the money of fools."

§ 6. The Laws of Nature.

> We must confess that physical laws have greatly fallen off in dignity. No long time ago they were quite commonly described as the Fixed Laws of Nature, and were supposed sufficient in themselves to govern the universe. Now we can only assign to them the humble rank of mere descriptions, often erroneous, of similarities which we believe we have discovered.—J. H. POYNTING.

This is a convenient place to emphasize the meaning of the term "law" in chemistry. It is, of course, absurd to say that Charles' law or Boyle's law *must* be obeyed, implying that these laws are commands imposed upon gases which they are compelled to obey. "Law" is a useful term which the careless sometimes personify. It is employed by scientific men, purely in a metaphorical sense. The term has led to some confusion, and it would be replaced by another word if we could think of a better. As indicated previously, the term "law of nature" is applied to a comprehensive generalization which "methodically and systematically describes certain natural phenomena." **The laws of chemical and physical phenomena are collocations of those circumstances which have been found by experiment and observation to accompany all chemical and physical changes included in the statement of the law.** The test of the "law" is that the statement holds good without exception. The common meaning attached to the saying, "The exception proves the rule," is wrong, and it is an instance of confusion arising from the double meaning of words. In the old Latin proverb: *Exceptio probat regulam*, the word "probat" means "tests," just as to-day, "proving cannon" means testing them. The proverb therefore meant that the apparent exception furnishes a means of trying, testing, or proving the rule, and if the

exception cannot be explained, then the rule breaks down, for **the exception disproves the rule.**

When the exact conditions are set up, the law describes the phenomenon without variableness or shadow of turning. The law is then regarded as an objective power. This power is called a force, and further, the force is said to be the **cause** of the phenomenon. Thus gravitation is regarded as an attractive force causing one particle to attract every other particle in the universe; chemical affinity is regarded, in this sense, as a selective force which causes certain substances when placed in contact to undergo chemical change. If therefore we find a gas deviating from Boyle's law, or from Charles' law, the alleged law may be a false, incomplete, or imperfect description, or some perturbing influence is at work which masks the simple phenomena described by the law.

Questions.

1. Two powders are given you: one is a mechanical mixture, the other a chemical combination of sulphur and iron. In what respects would the two powders differ, and by what chemical reactions could you distinguish the one from the other?—*London Univ. Matric.*

2. Describe and explain any two simple experiments which serve to illustrate the law of definite proportions.—*London Univ. Matric.*

3. By what experiment would you prove that the atmosphere invariably contains some water? What means would you employ to cause the air in a vessel to become quite dry?—*Science and Art Dept.*

4. Describe exactly any experiment you have witnessed on the decomposition of a chemical compound by the electric current. Make a rough sketch of the apparatus which was employed. Define the terms "electrolysis," "electrolyte," and "electrode."—*London Univ. Matric.*

5. It is known that heat is generally evolved when chemical combination takes place. How would you arrange an experiment to show this?—*London Univ. Matric.*

6. Describe exactly what you can observe when mercuric oxide is heated. What experiments would you make in order to show that of the two successive changes which are apparent, one is physical, and the other chemical?—*London Univ. Matric.*

7. Why is gunpowder considered to be a mechanical mixture of

saltpetre, charcoal, and sulphur, and not a chemical compound of these constituents ?—*London Univ.*

8. Illustrate, using two different examples from your experience, the statement that chemical change is always accompanied by physical change, describing all the physical changes which you recognise in each case.—*Worcester Polytechnic Inst., U.S.A.*

9. State six examples of common substances known to you which you consider are mixtures, and six compounds. Select your examples as far as you can from every-day life.

10. Describe any experiments you have performed which illustrate the law of constant composition by weight.

CHAPTER V

Three Gases—Hydrogen, Oxygen, and Nitrogen

§ 1. The Preparation of Hydrogen.

The attention of the early workers in chemistry was mainly directed to visible, tangible liquids and solids, while the "spirits," "fumes," "vapours," "gases," and "airs"—odorous or inodorous, coloured or colourless—which escaped when different substances reacted together were usually considered to be unwholesome effluvia best avoided. To-day, a great deal of a student's time is spent in studying the imperceptible intangible gases ignored by earlier workers. The three gases—hydrogen, oxygen, and nitrogen—first claim attention.

History.—A writer in the sixteenth century mentioned that when an acid acts upon iron, "an air rises which bursts forth like the wind"; it required something like another century for chemists to discover that the air is inflammable; and still another century to find that the inflammable air is a definite substance with characteristic properties of its own. This step was taken by H. Cavendish, in 1766, and A. L. Lavoisier christened the gas **hydrogen** about twenty years later.

The preparation of hydrogen in the laboratory.—Commercial iron furnishes a gas which is not very pure, for the hydrogen is contaminated with odorous and inodorous impurities which would have to be washed out before we could examine the properties of the gas reasonably free from impurities. Zinc or magnesium gives the same gas when dissolved in acids, and the gas is then reasonably pure.

Granulated zinc is placed in a two-necked Woulfe's bottle—

so named after its inventor, Peter Woulfe, 1784—shown at *A*, Fig. 42. One neck is closed air-tight by a one-hole rubber stopper fitted with a tube funnel, *B*, extending nearly to the bottom of the bottle; the other neck is fitted with a glass tube, *C*—**delivery tube**—bent as shown in the diagram. Make sure that all the joints are air-tight, and that no escape of gas is possible other than through the delivery tube. This is done by pinching the rubber connecting the delivery tube with the tube leading from the bottle, and blowing from the funnel tube. Another way of fitting up the hydrogen generating flask in place of the Woulfe's bottle is shown in Fig. 47.

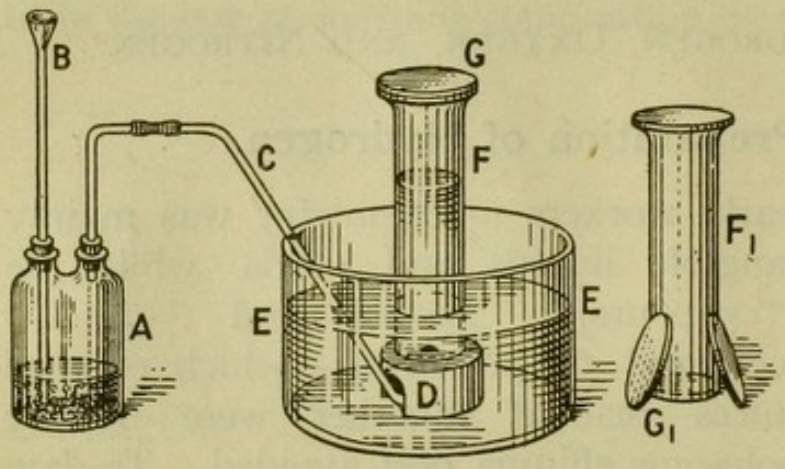


FIG. 42.—The Preparation of Hydrogen.

The delivery tube dips under a hollow earthenware cylinder with a perforated top, and side opening, called a **beehive**, shown at *D*. The beehive rests in a basin of water, *E*. The vessels *D* and *E* form a **collecting, gas, or pneumatic trough**. The tube funnel is sometimes called a **safety funnel**, because if the delivery tube gets choked in any way, the gas, instead of accumulating in the generating bottle under pressure, would force liquid out of the safety funnel and thus provide itself a means of relieving the pressure without bursting the bottle. The widened part of the funnel, *B*, Fig. 42, is sometimes shaped more or less like the typical "Scotch thistle," and the funnel is then called a **thistle-headed funnel**.

Pour some water through the funnel tube until the zinc is well covered. Pour concentrated sulphuric acid, a little at a time, through the funnel tube until the gas begins to come off vigorously. The mixture of air and hydrogen gas first issuing from the delivery tube is very explosive. It is therefore necessary to make sure that all the air has been expelled before the hydrogen is collected in the gas cylinders, or **gas jars**, *F*.

Hence, invert a test tube full of water over the hole in the upper floor of the "beehive." When the tube is full of gas, apply a lighted taper to the mouth of the test tube. If the gas detonates, repeat the trial until the gas burns quietly. *Always test hydrogen in this way before a light is applied.* Fill a gas jar full of water, cover it with a greased glass plate, *G*; turn the jar and cover upside down, and remove the plate while the mouth of the gas jar is below the surface of the water in the gas trough. Place the mouth of the jar over the hole in the floor of the "beehive." When the jar is full of gas, close the mouth of the jar with the glass plate, and remove the vessel from the gas collecting trough. Stand the jar mouth downwards, and collect several jars of the gas, for an examination of its properties.

By-product in the generating bottle.—The residue in the Woulfe's bottle can be examined at leisure. The solution is evaporated in a basin, Fig. 28, until a drop of the liquid when placed on a cold glass plate partly solidifies. Crystals of a substance called zinc sulphate are obtained if sulphuric acid be used in the preparation of the hydrogen; and zinc chloride, if hydrochloric acid be employed. A photograph of the zinc sulphate crystals is shown in Fig. 43. The outline drawing represents a perfect crystal. If iron had been used in place of zinc, pale green crystals of iron sulphate would have been produced.

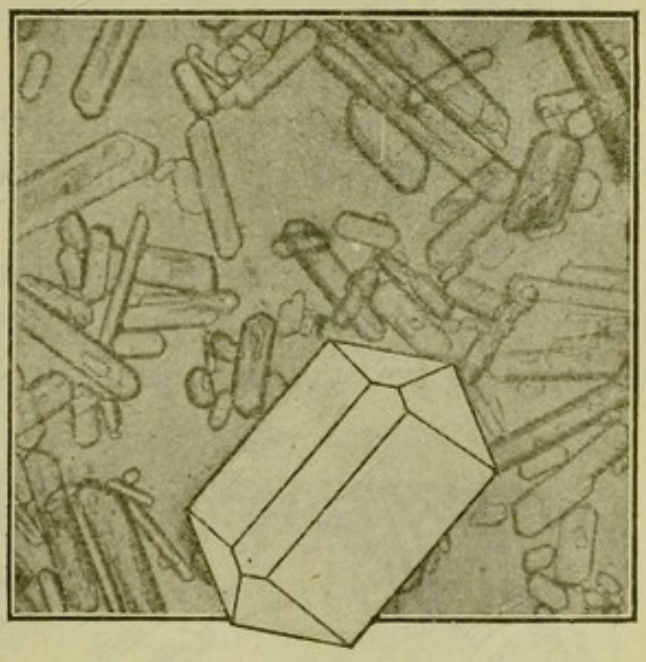


FIG. 43.—Crystals of Zinc Sulphate (×50).

§ 2. The Properties of Hydrogen.

At ordinary temperatures, hydrogen is a gas without colour, taste, or smell. It is so very sparingly soluble in water that it requires careful work with special instruments to detect its

solubility. The gas has been liquefied and even solidified by the application of very intense cold:

$$\text{Hydrogen}_{\text{solid}} \overset{-259^\circ}{\leftrightharpoons} \text{Hydrogen}_{\text{liquid}} \overset{-252^\circ}{\leftrightharpoons} \text{Hydrogen}_{\text{gas}}$$

At these low temperatures air itself freezes to a white crystalline solid. Pure hydrogen produces no injurious effects if inhaled for a moment, but it makes the voice squeaky and shrill. Suffocation follows in a very short time if, say, a mouse be placed in the gas.

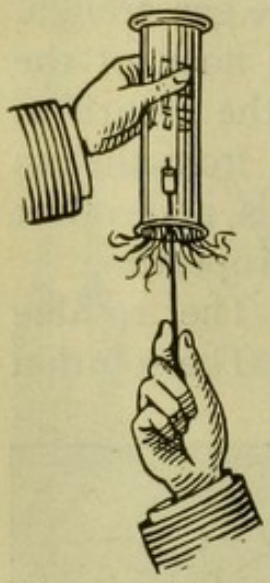


FIG. 44.—Combustibility of Hydrogen.

Plunge a lighted taper into one of the jars of gas while the jar is held mouth downwards as indicated in Fig. 44, the gas is combustible, for it burns with a scarcely visible blue flame at the mouth of the jar, and the taper is extinguished, showing that the gas does not support combustion. If the jar of hydrogen be held mouth upwards, Fig. 19, while the taper is plunged inside, the hydrogen burns so quickly that nothing but a long, roaring flame is obtained.

As indicated above, a mixture of hydrogen with oxygen or air is violently explosive. This can be illustrated by mixing two volumes of hydrogen gas with either one volume of oxygen or five volumes of air in a soda-water bottle. A lighted taper applied to the mouth of the bottle, Fig. 45, causes the gas to detonate violently. The combustion of the whole mass is almost instantaneous. The bottle is best wrapped in a towel before applying the light, in order to prevent an accident if the bottle should burst.

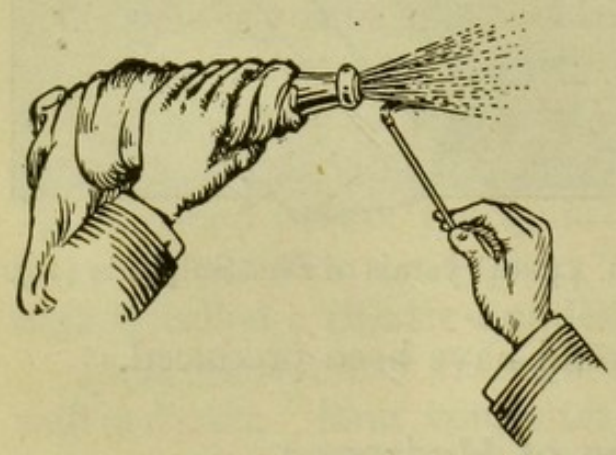


FIG. 45.—Explosion of a Mixture of Air and Hydrogen.

Hydrogen is the lightest substance known. A given volume of air at the same temperature and pressure is nearly 14·4 times

as heavy as an equal volume of hydrogen. Hence hydrogen is used for inflating balloons and air-ships. The lightness of hydrogen can be illustrated by pouring it upwards from one jar to another as illustrated in Fig. 46, and it can be proved that the hydrogen has left one jar and passed into the other by testing the contents of each jar with a lighted taper. For many purposes there is no need to use the pneumatic trough for collecting the gas. Bring the jar to be filled with gas over the delivery tube of the hydrogen generator as illustrated in Fig. 47. The hydrogen collects at the top of the jar and displaces the

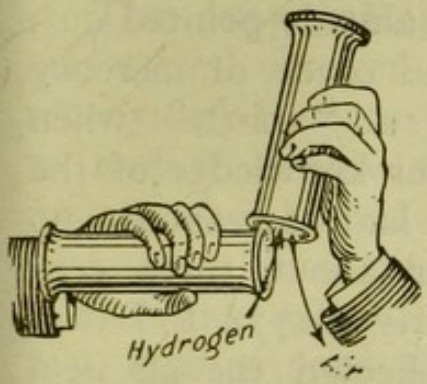


FIG. 46.—Pouring Hydrogen upwards.

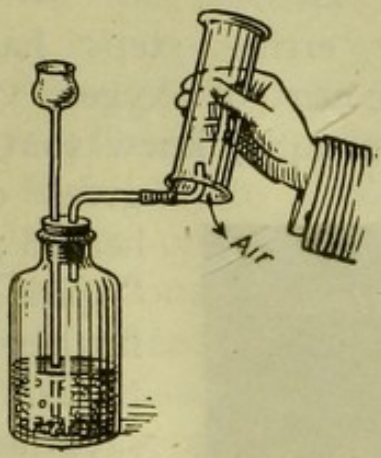


FIG. 47.—Collecting Hydrogen by the Downward Displacement of Air.

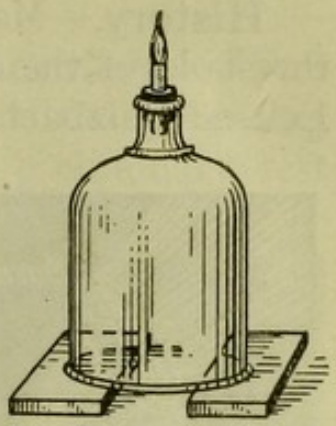


FIG. 48.—Explosibility of a Mixture of Air and Hydrogen.

air downwards—hence the term **collecting gases by the downward displacement of air.** The explosive character of a mixture of air and hydrogen, and the lightness of the gas, can be illustrated by fitting a stout bell-jar, Fig. 48, with a one-hole stopper and glass tube. The tube is plugged with a bit of rubber or cork, and filled with hydrogen. The jar of gas is placed on two pieces of wood, the plug removed, and the gas lighted as it escapes from the upper tube. The air flows in at the bottom, driving the hydrogen upwards, and at the same time air and hydrogen mix together. As soon as the mixture reaches the flame, a loud explosion results. No harm is done, because the open jar permits the free expansion of the hot gases.

Certain metals—palladium and platinum—absorb relatively large quantities of hydrogen. Heat is developed during the

absorption. If a jet of hydrogen be allowed to impinge on finely divided platinum in air, the heat may be great enough to ignite the gas. This is the principle of self-lighting gas-burners. Several substances unite with the gas, forming **hydrides,** *e.g.* potassium, sodium, calcium, etc. Calcium hydride has the commercial name *hydrolith,* it gives off hydrogen gas when brought into contact with water. The hydrides of carbon are called hydrocarbons.

§ 3. The Preparation of Oxygen.

History.—Many erring steps have stumbled on the threshold of the discovery of oxygen. As already pointed out, Eck de Sulzbach, in 1489, knew that red oxide of mercury gives off a "spirit" when heated; our knowledge of the "spirit" had advanced no further for about three centuries. Early in 1774, P. Bayen says he collected the air in a jar over water; but, like Eck de Sulzbach, Bayen did not pay much attention to the gas; in the same year (1st of August, 1774) Joseph Priestley heated red oxide of mercury confined with mercury in a cylinder, *A*, Fig. 49, by means of a sun glass or burning lens. He said: "An air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was that a candle burned in this air with a remarkable brilliant flame." Priestley also noticed several other peculiarities of the gas, and emphasized its individuality by calling it *dephlogisticated air;* the name was later on changed to *oxygen* by Lavoisier, and this is the name for the gas used to-day. The note-books of K. W. Scheele show

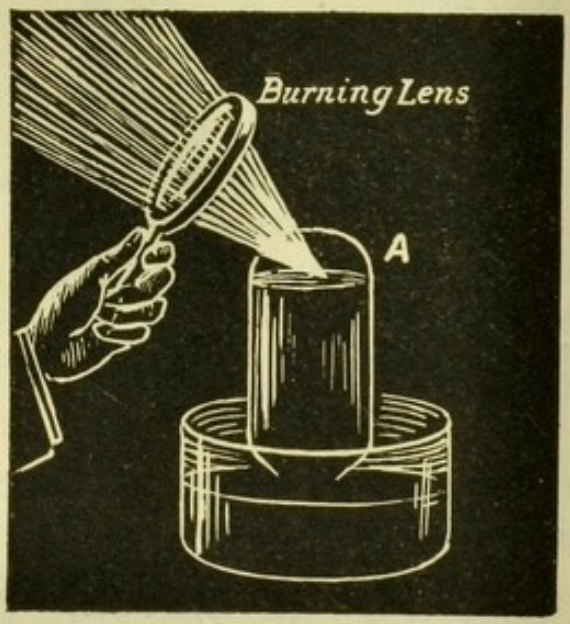


FIG. 49.—Priestley's Experiment.

that he also isolated the same gas in 1773, but he did not publish an account of his experiments until 1777. The man who deduces on good mental evidence, or even proves by actual experiment, the existence of something not known before is not always recognized as the discoverer; but rather is he hailed discoverer who proves by a conclusive series of experiments that the substance in question has properties distinct from all other substances. **He only discovers who proves.** Otherwise, Paracelsus would be called the discoverer of hydrogen, and Eck de Sulzbach of oxygen. For this reason Cavendish is generally credited with the discovery of hydrogen, and Priestley of oxygen.

The preparation of oxygen in the laboratory.—There are several cheaper ways of making oxygen than by heating red oxide of mercury. It is easy to make a preliminary test to find if a substance gives off oxygen when heated. This is done by heating the substance in a hard (*i.e.* fusing with difficulty) glass test tube gripped by wrapping a strip of paper round the tube, as indicated in Fig. 50, so as not to burn the fingers with the hot tube. Plunge a glowing splint of wood into the test tube now and again. If oxygen is given off, the glowing splint will burst into flame. Try red lead, and potassium chlorate in this way. When the potassium chlorate is heated, it melts to a clear liquid at about 350°, and when the temperature is a little higher, the molten liquid seems to boil, for bubbles of gas are freely given off; the test indicated in Fig. 50 shows that the escaping gas is oxygen. Potassium chlorate is a cheap and convenient source of small quantities for laboratory work. If the chlorate be mixed with some manganese dioxide, the oxygen

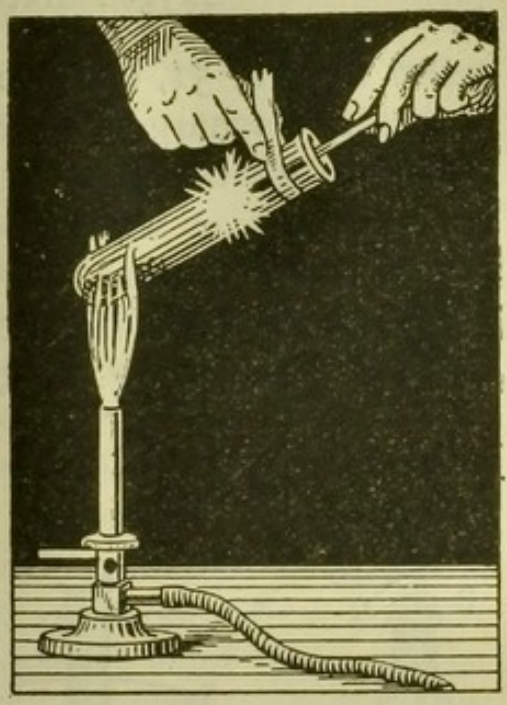


FIG. 50.—Testing for Oxygen by the Inflammation of a Glowing Splint.

is given off by the decomposition of the chlorate at a much lower temperature, and much more regularly. For experimental work, therefore, oxygen is prepared by heating the so-called *oxygen mixture*—that is a mixture of potassium chlorate (not powdered) with its own bulk of manganese dioxide—in a Florence flask, Fig. 51, or a retort, or a special copper "oxygen flask," fitted with a wide delivery tube, because the gas is liable to come off rapidly in rushes. The flask is best clamped while tilted slightly downward towards the mouth, as indicated in Fig. 51, because a considerable amount of moisture is usually discharged from the mixture, and there is a risk of the moisture trickling back and cracking the glass. The gas is collected over water as in the case of hydrogen. Ten grams of potassium chlorate give nearly $2\frac{3}{4}$ litres of oxygen.

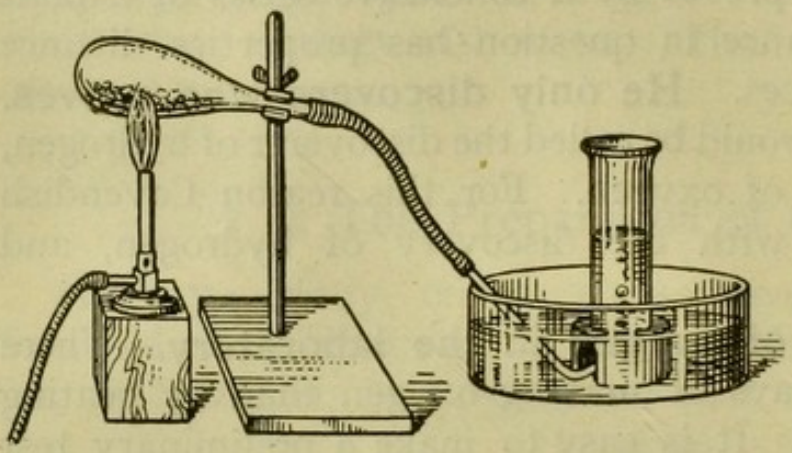


FIG. 51.—The Preparation of Oxygen from "Oxygen Mixture."

Sodium peroxide method of making oxygen.—Another method of preparing the gas depends upon the fact that sodium peroxide is decomposed by water, and oxygen gas escapes. Commercial brands of sodium peroxide are sold for the purpose under the names *oxone* and *oxolith*. Place about 10 grams of dry oxone in a dry 200 c.c. conical flask, *A*, Fig. 52. The flask is also fitted with a stopper, *B*, bored with two holes. One hole is fitted with a delivery tube, *C*, and the other hole with a stoppered funnel containing water. The water from the funnel is allowed to fall, drop by drop, on

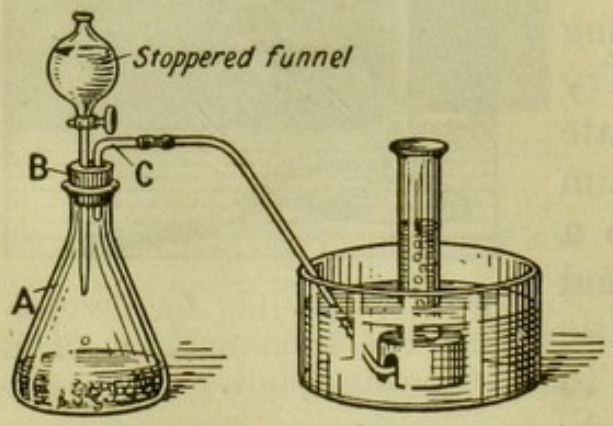


FIG. 52.—The Preparation of Oxygen from "Oxone."

to the peroxide. Each drop of water produces a definite amount of gas, so that the rate of evolution of the gas can be regulated by the rate at which water is allowed to drop from the funnel. No external application of heat is required. $6\frac{1}{4}$ grams of the peroxide give about a litre of oxygen.

Examination of the by-products.—If the contents of the flask containing the decomposed sodium peroxide be evaporated, a viscid or syrupy liquid will be obtained which feels soapy when a small drop is rubbed between the finger and thumb. It is **caustic soda,** a substance which will be studied in more detail later. Hence it is inferred that *when sodium peroxide is decomposed by water, caustic soda and oxygen are produced.* If the residue left after the mixture of potassium chlorate and manganese dioxide be boiled with water; filtered—Fig. 27; washed with hot water; and the filtrate and washings be evaporated—Fig. 28—cubical crystals of **potassium chloride** will be obtained. The crystals are like those illustrated in Fig. 85, and they will be studied in some detail later. The outline drawing represents a perfect crystal. As a result, it is inferred that *when heated, potassium chlorate decomposes into potassium chloride and oxygen.*

Catalysis.—The solid matter on the filter paper can be dried. It is manganese dioxide, and it can be used again in the preparation of oxygen; indeed, by washing out the potassium chloride after each preparation, the manganese dioxide can be used an indefinite number of times without deterioration. The action of the manganese dioxide in accelerating the rate of decomposition of the potassium chlorate is therefore very curious. We are not quite sure how it does its work, although we do know that when its work is done it is ready to start again without loss of vigour. We shall meet many other cases in our study of chemistry where the mere presence of a certain substance accelerates the rate of a chemical change without itself undergoing any perceptible alteration. It is convenient to have a name for this phenomenon. The word **catalysis** or **catalytic action** is in common use, and the substance is said to **act catalytically** and to be a **catalytic agent.**

Industrial preparation.—There are numerous other ways of preparing oxygen. The particular process to be employed must be determined by cost and convenience. If but a few litres of gas, not specially purified, are required, cost is not very serious, and convenience is perhaps the most important factor; if *pure* oxygen be required, a complicated apparatus may be needed, and neither cost nor labour must be spared. If large quantities of gas are needed, say for industrial purposes, the cost factor is of prime importance. Generally speaking, the success of industrial operations depends upon the ability of the chemist to manufacture his products cheaply. Oxygen is now made on a manufacturing scale from air which has been liquefied by intense cold. The liquid air contains oxygen and nitrogen. The former boils at $-182{\cdot}5°$, and the latter at $-195°$. Hence the nitrogen has a tendency to boil off before the oxygen, and this is made the basis of a method of separation by the repeated distillation of liquid air. Nearly all the oxygen on the market is now obtained by the liquid-air process. The oxygen is pumped into steel cylinders under a pressure of 100–150 atmospheres, and sold as "compressed oxygen." The gas may be obtained from the cylinders at any desired rate by opening the valve.

§ 4. The Properties of Oxygen.

At atmospheric temperatures, oxygen is a colourless, tasteless gas, without smell. Oxygen is very slightly heavier than air. It is rather more soluble in water than hydrogen, for 100 volumes of water at 20° will dissolve 1·8 volumes of hydrogen, and 3 volumes of oxygen, under normal atmospheric pressure. Oxygen has been liquefied by cooling it down to $-182{\cdot}5°$, and it solidifies at $-227°$. A mouse soon dies if placed in an atmosphere deprived of oxygen. Pure oxygen can be breathed for a short time without harm, and oxygen is used medicinally in artificial respiration in cases of suffocation, carbon monoxide poisoning, etc., where, owing to the enfeebled action of the lungs, the blood is not sufficiently aërated. The prolonged inhalation of oxygen soon raises the temperature of

the body dangerously high, and accordingly an animal placed in ordinary or in compressed oxygen soon dies.

We have already discovered that when a lighted taper is plunged into a jar of the gas, the gas does not itself burn, and it is therefore incombustible, but rather does the taper continue burning with increased brilliance, Fig. 19, and oxygen is therefore a vigorous supporter of combustion. This is exemplified by the fact that a glowing splint of wood immediately bursts into flame when plunged into a jar of the gas, Fig. 50.

The direct combination of oxygen with some of the elements can be illustrated by placing small dry pieces of carbon, sulphur, phosphorus in deflagrating spoons, heating them until combustion begins, and then plunging each into a jar of oxygen, Fig. 53. A glowing piece of **charcoal** burns very brightly and forms a colourless gaseous oxide, called *carbon dioxide*. If a little water be placed in the jar and shaken, the solution will redden blue litmus solution [1]; and it will give a turbidity with clear lime water—oxygen gas does neither. **Sulphur** burns with a lavender-blue flame, forming gaseous *sulphur dioxide*, which has the peculiar odour characteristic of burning sulphur. Sulphur dioxide is soluble in water, forming *sulphurous acid*, which reddens a solution of blue litmus. **Phosphorus** burns in oxygen vigorously and brilliantly, forming a white cloud of *phosphorus pentoxide*. Very great care must be taken in working with phosphorus. It must not be touched with the fingers, but a piece cut from the stick while it is under water.



FIG. 53.—Combustion in a Deflagrating Spoon in Oxygen.

[1] Litmus is a substance obtained by extracting a lichen with water. The solution is a purple colour which becomes red in presence of acids, and blue with alkalies. Several other substances will do as well. Red cabbage juice is red with acids (*e.g.* vinegar), and it becomes green with alkalies; violets also turn green with alkalies, and red with acids; an alcoholic extract of rose leaves is yellowish-brown, which is turned green with alkalies, and rose-red with acids; turmeric is turned reddish-brown with alkalies, yellow with acids.

The wet piece is dried on blotting-paper and lifted with a pair of forceps or tongs on to the dry spoon. The phosphorus pentoxide dissolves in water, forming *phosphoric acid*, which reddens blue litmus solution. Metallic **sodium** treated in a similar way (spoon perfectly dry) burns with a bright yellow flame and gives a white oxide which dissolves in water, forming a solution of *caustic soda*. The solution turns red litmus blue. **Calcium** behaves similarly, but it burns with an orange-red flame. A piece of burning **magnesium** ribbon plunged in oxygen burns with an exceptionally brilliant flame. The white solid obtained is slightly soluble in water, and the solution turns red litmus blue. These reactions will be studied in more detail when the elements in question receive individual treatment. In every case a compound with the element in question and oxygen is formed. We adopt Lavoisier's proposal (p. 33) and call such compounds **oxides.** Similar results would have been obtained had air instead of oxygen been in the gas-jar, only in that case the oxidation would not have been so vigorous.

To show the combustion of **iron** in oxygen gas, tie a tuft of " steel wool " to the end of a stout iron wire by means of a piece of steel wire. Heat the end of the wool in a Bunsen's flame, until incipient combustion begins, and quickly plunge it into a jar of oxygen on the bottom of which a layer of water, sand, or asbestos paper has been placed. The wool burns with dazzling scintillations, the produce of the reaction—iron oxide—falls to the bottom of the jar in fused globules. When cold, the oxide of iron resembles blacksmith's hammer scale, and, being feebly magnetic, it is called *magnetic oxide of iron*. It is insoluble in water, and it has no effect on red or blue litmus. A similar product is obtained as a calx when iron is heated in air. Hence the calces, or " ashes," obtained when metals are calcined in air are similar to those obtained by heating the metals in oxygen gas. We have the additional information that some elements give gaseous calces, so to speak, when heated in air or oxygen.

The facts are reviewed and summarized in Table II.

TABLE II.—THE COMBUSTION OF SOME ELEMENTS IN OXYGEN.

	Element.	Observations.	Product of oxidation.	Effect of water and litmus.
Non-metals	Carbon	Scintillating sparks	Colourless gaseous oxide—**carbon dioxide**	Soluble in water; reddens litmus
	Sulphur	Lavender flame	Cloudy gaseous oxide—**sulphur dioxide**	Soluble in water; reddens litmus
	Phosphorus	Bright white flame	White solid—**phosphorus pentoxide**	Soluble in water; reddens litmus
Metals	Sodium	Yellow flame	White solid—**sodium oxide**	Soluble in water; blues litmus
	Calcium	Brick-red flame	White solid—**calcium oxide**	Soluble in water; blues litmus
	Magnesium	Brilliant flame	White solid—**magnesium oxide**	Soluble in water; blues litmus
	Iron	Scintillating sparks	Greyish blue solid—**magnetic oxide of iron**	Insoluble in water; neutral to litmus

It may be added that oxygen combines directly with most of the other elements, particularly at elevated temperatures, forming **oxides.** Iodine, bromine, fluorine, gold, platinum, and argon do not combine *directly* with oxygen; but oxygen can be made to combine *indirectly* with all the elements excepting the argon group of elements, fluorine, and possibly bromine. If the metals be arranged in the order of their avidity or readiness to combine with oxygen, potassium and sodium will be found near one end of the series, while platinum will be found at the other end.

§ 5. The Preparation of Nitrogen.

In 1674, John Mayow burnt a candle under a jar of air, and noticed that the flame soon expired, from which he deduced the fact that air contains two substances, one of which supports the flame of a candle, and the other at once extinguishes the candle's flame. Nearly a century afterwards, D. Rutherford (1772) burnt phosphorus, charcoal, etc., in a confined space, and examined the properties of the residual air. Lavoisier called the residual gas "azote" (p. 33), and the name **nitrogen** was soon afterwards given to the gas. Rutherford is generally

credited with the discovery of nitrogen. His experiment is easily imitated, and it serves as a convenient method for preparing nitrogen for laboratory work. A lighted candle is floated on a cork and a bell-jar is placed over the candle in such a way that the stopper is placed *in situ* immediately the jar rests on a couple of glass rods on the bottom of the basin of water. The experiment can be repeated with a cup of burning phosphorus floating on a cork also in a basin of water, Fig. 54. The flame of phosphorus or candle expires in a short time. The gaseous oxides formed by the combustion of the candle or of the phosphorus are soon absorbed by the water in the basin, particularly if the water contains a little caustic soda in solution. In both experiments there is a contraction of about one-fifth in the gaseous contents of the bell-jar, and the residual four-fifths is largely nitrogen. This may be used for tests with a lighted taper, etc. The experiment is more easily controlled by using a tube divided into five equal divisions reckoned from the place where the levels of the water inside and outside are the same. A stick of clean phosphorus is mounted on a piece of wire and fixed inside the tube as shown in Fig. 55. The phosphorus slowly oxidizes, and in a few hours the water will have contracted one division.

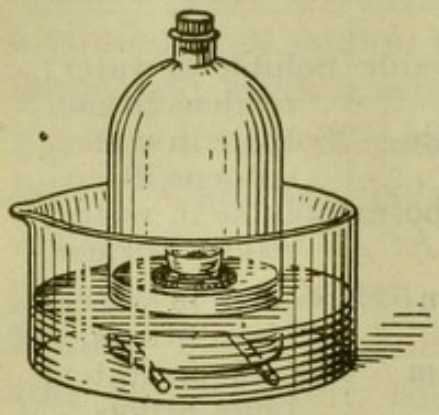


FIG. 54.—Preparation of Nitrogen by the Combustion of Phosphorus in Air.

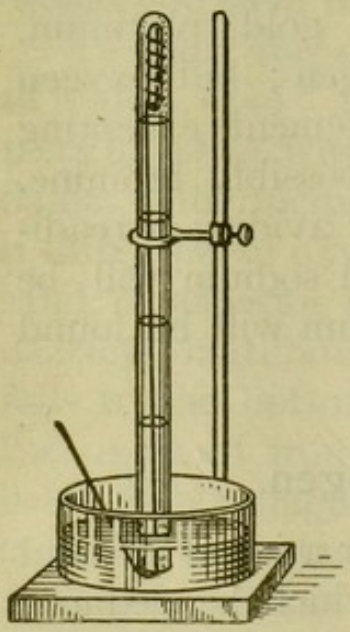


FIG. 55.—The Amount of Nitrogen in Air.

Air can also be freed from oxygen by passing it through a tube containing copper turnings heated red hot, Fig. 56. The air can be cleaned free from moisture, etc., by passing it first through a bottle, *A*, containing caustic soda solution, and then through another bottle, *B*, containing concentrated sulphuric acid, then passed through a red-hot tube containing copper

turnings. The copper removes the oxygen and forms copper oxide. The nitrogen passes on to be collected in a gas jar, or

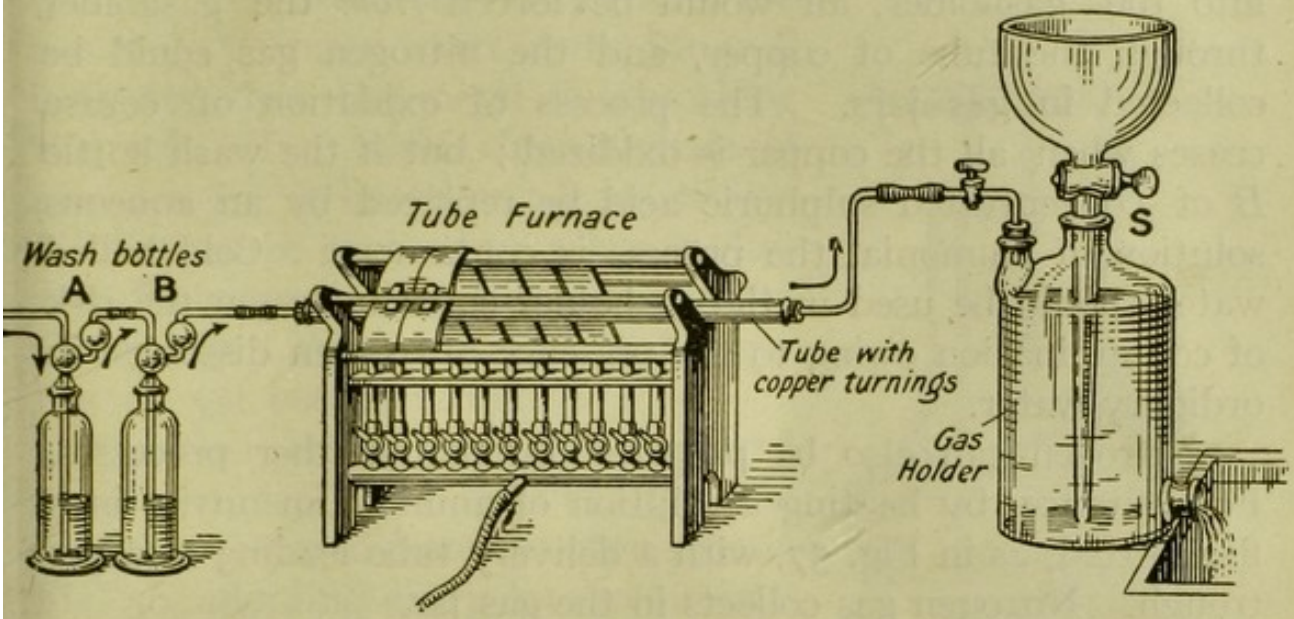


FIG. 56.—The Preparation of Nitrogen from Air.

gasholder, etc. In the diagram, the air is supposed to be drawn over the copper as water runs out from the lower opening

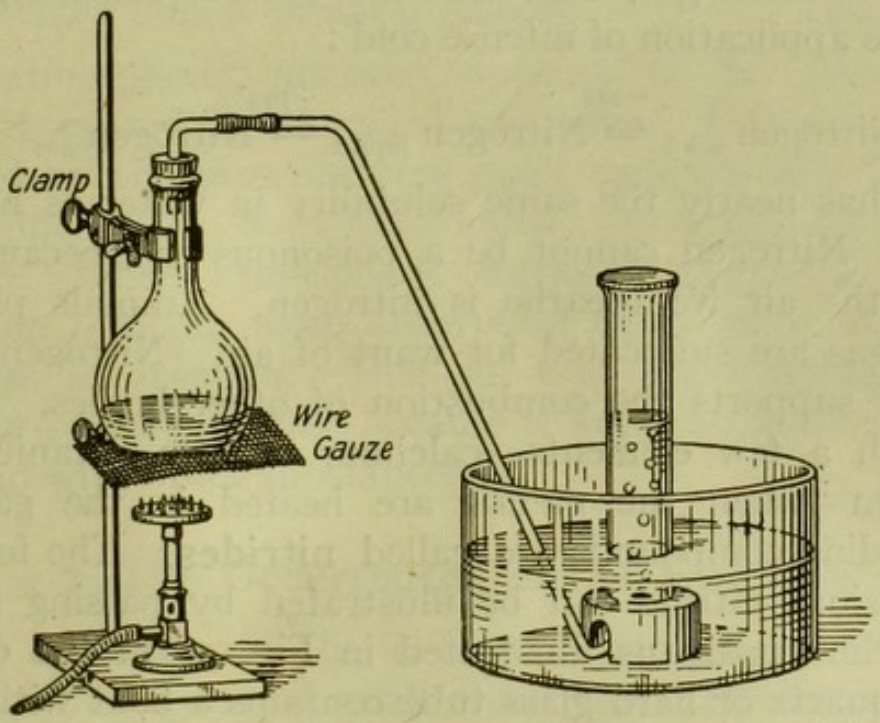


FIG. 57.—Preparation of Nitrogen from Ammonium Nitrite.

of the gasholder into the sink, and the gasholder, originally full of water, is filled with nitrogen. If the gasholder full of air had

been placed at the end *A*, and the lower opening of the gasholder closed, and water allowed to flow from the large funnel into the gasholder, air would be forced *from* the gasholder through the tube of copper, and the nitrogen gas could be collected in gas jars. The process of oxidation of course ceases when all the copper is oxidized ; but if the wash bottle *B* of concentrated sulphuric acid be replaced by an aqueous solution of ammonia, the process is continuous. Cold boiled water should be used in the gasholder so as to lessen the risk of contamination owing to the presence of oxygen dissolved in ordinary water.

Nitrogen can also be prepared by many other processes. For instance, by heating a solution of ammonium nitrite in a flask fitted, as in Fig. 57, with a delivery tube leading to a gas trough. Nitrogen gas collects in the gas jar.

§ 6. The Properties of Nitrogen

Nitrogen, at ordinary temperatures, is an odourless, tasteless, and colourless gas, although it has been liquefied and solidified by the application of intense cold :

$$\text{Nitrogen}_{\text{solid}} \overset{-214^\circ}{\leftrightharpoons} \text{Nitrogen}_{\text{liquid}} \overset{-195^\circ}{\leftrightharpoons} \text{Nitrogen}_{\text{gas}}$$

Nitrogen has nearly the same solubility in water as hydrogen in water. Nitrogen cannot be a poisonous gas, because four-fifths of the air we breathe is nitrogen. Animals placed in nitrogen gas are suffocated for want of air. Nitrogen neither burns nor supports the combustion of other bodies. It combines with a few elements—calcium, lithium, titanium, and magnesium—when the metals are heated in the gas. The corresponding compounds are called **nitrides.** The formation of magnesium nitride can be illustrated by passing nitrogen through the apparatus illustrated in Fig. 58 in the direction *AB*. A quartz or hard glass tube contains a boat with a little powdered magnesium. This tube is connected with a glass bulbed tube dipping in coloured water to serve as gauge. When all the air has been expelled by the nitrogen, close the stopcock *A*, heat the tube with a Bunsen's burner, and finally

with a large Méker's burner or a blast gas burner. When the temperature reaches 900° the bubbling of gas from the tube by thermal expansion will cease, and the rise of the coloured water in the gauge *B* indicates that the metal is absorbing the gas. The main characteristic of nitrogen gas is its chemical inactivity. If nitrogen be exposed to a brush electric discharge, it becomes more active chemically. What happens to the gas has not yet been determined.

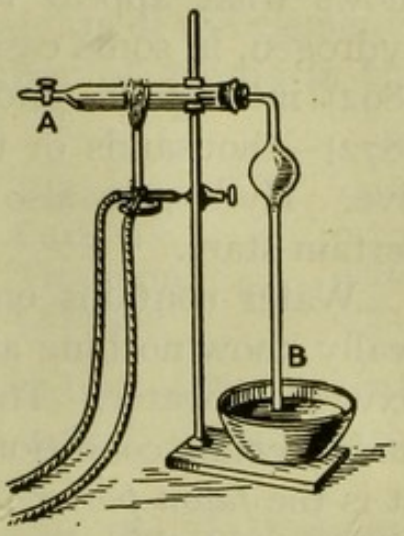


FIG. 58.—Formation of Nitrides.

Curiously enough, nitrogen prepared by a chemical process, Fig. 57, and nitrogen prepared from the atmosphere, Fig. 56, adopting every known precaution to ensure the purity of the products, have not the same weight per unit volume. For instance, the weights of these two products are related as :

Nitrogen from atmospheric air	14·070
Nitrogen from a chemical process	14·005

Hence, atmospheric nitrogen appears to be heavier than nitrogen prepared by chemical processes. This was found to be caused by the presence of a small quantity of a heavy gas in air, which had been overlooked by nearly all previous observers. When atmospheric nitrogen is passed over hot magnesium until no more absorption takes place, the residue is the gas in question. The gas was called **argon**—from a Greek word meaning idle—because it forms no known chemical compound with other substances.

§ 7. The Occurrences of the Elements.

Free hydrogen.—The element hydrogen occurs free in Nature in comparatively small quantities. The atmosphere is said to contain about one volume of hydrogen per 15,000 to 20,000 volumes of air. Hydrogen is also present in volcanic gases ; in the gases from the Stassfurt salt beds ; and in some meteorites. The presence of hydrogen in natural gas from the

oil fields has been denied, although many published analyses of these gases include "hydrogen." The sun's chromosphere shows what appear to be stupendous flames of incandescent hydrogen, in some cases towering over 300,000 miles (M. Fényi, 1892) into space, and 100,000 miles in width (C. A. Young, 1872)—thousands of times larger than the earth on which we live. Hydrogen also appears to be present in nebulæ and certain stars.

Water contains one-ninth of its weight of hydrogen. We really know nothing about the hydrogen as it is combined with oxygen in water. The fact is that when water is decomposed under certain conditions, this proportion of hydrogen is obtained. It is the *façon parler* to say that the compound "*contains*" the element, or that the element "*occurs*" in or is "*present*" in the compound, when the element can be obtained from the compound by suitable methods of decomposition. When we speak of the "occurrence of an element," reference is made not only to those places where the free elements may be found, but also to those natural compounds which contain the element united chemically with one or more different elements.

Combined hydrogen.—Combined hydrogen is common. Not only does hydrogen occur combined with oxygen as water, but hydrogen is one of the chief constituents of animal and vegetable tissue. Hydrogen also is present in nearly all organic compounds, and in many gases—methane, the hydrocarbons, hydrogen sulphide, etc.

Quantitative distribution of the elements.—By comparing a large number of analyses of rocks, etc., F. W. Clarke (1908) has tried to estimate the percentage composition—by weight—of the earth's crust (½ mile deep)—including the ocean and the atmosphere. His result is :

	Per cent.		Per cent.		Per cent.
Oxygen	49·78	Magnesium	2·24	Barium	0·09
Silicon	26·08	Hydrogen	0·95	Manganese	0·07
Aluminium	7·34	Titanium	0·37	Strontium	0·03
Iron	4·11	Chlorine	0·21	Nitrogen	0·02
Calcium	3·19	Carbon	0·19	Fluorine	0·02
Sodium	2·33	Phosphorus	0·11	Bromine	0·008
Potassium	2·28	Sulphur	0·11	All other elements	0·48

If we try to get an estimate of the *relative* number of atoms of the different *kinds* of elements distributed in the half-mile crust, the ocean and the atmosphere, Clarke's numbers must be divided by the corresponding atomic weights of the elements. We thus obtain for the **percentage number of atoms in the half-mile crust :**

Oxygen . .	53·81	Sodium . .	1·72	Potassium . .	1·02
Hydrogen .	16·30	Magnesium .	1·61	Carbon . . .	0·27
Silicon . .	15·87	Calcium . .	1·40	Titanium . .	0·16
Aluminium .	4·68	Iron . . .	1·29	Chlorine . .	0·11

This gives a better idea of the relative distribution of the elements from the chemical point of view than the actual weights in the preceding list.

Oxygen and water.—Thus about half the total weight of the rocks which make up the earth's crust is oxygen, and this element occurs more abundantly in the earth's crust than any other. About one-fourth of the atmospheric air, by weight, is oxygen, and water, which forms about three-fourths of the earth's crust, contains about 89 per cent. by weight of the same element. As just indicated on p. 100, hydrogen and oxygen, in the proportions to form water and united with other elements, make up the greater part of animal and vegetable tissue.

Nitrogen.—Nitrogen constitutes four-fifths of the total volume of atmospheric air. It is probable that certain nebulæ contain nitrogen. It is also found in certain minerals, where it is probably occluded or adsorbed. It occurs combined in ammonia, nitre, and a great many animal and vegetable products—*e.g.* white of egg, proteids, etc. It is a constant and essential constituent of all living organisms ; all life seems to depend upon the transformation of proteid compounds.

Summary.—In this chapter it will be observed that we have compiled a number of empirical facts without attempting to find their inter-relations. The more salient properties of the three gases just considered are indicated in Table III.

TABLE III.—COMPARISON OF THE PROPERTIES OF HYDROGEN, OXYGEN, AND NITROGEN.

Property.	Hydrogen.	Oxygen.	Nitrogen.
Colour, taste, and smell . .	nil	nil	nil
Combustible?	Yes	No	No
Supporter of combustion? .	No	Yes	No
100 vols. water dissolve at 12°	1·8 vols.	3 vols.	1·6 vols.
Unites with metals forming .	hydrides	oxides	nitrides
Liquefies at	−252°	−182·5°	−195°
Solidifies at	−259°	−227°	−214°
Weight of a litre under standard conditions (Air = 1·293 grm.)	0·090	1·429	1·251

None of these gases influence solutions of red or blue litmus, or of limewater.

Questions.

1. What is a pneumatic trough? What is it used for in the chemical laboratory?

2. How can you obtain pure and dry nitrogen from atmospheric air?—*London Univ. Matric.*

3. How, and by whom, was oxygen discovered? Who gave the gas this name, and why?—*London Univ. Matric.*

4. Describe exactly what you would see if a piece of sulphur were set on fire in air; of what do the products consist? How could they be collected, and what properties would they exhibit?—*London Univ. Matric.*

5. Why does hydrogen remain for a time in a jar held mouth downwards? Why does a lighted taper when passed up into a jar of hydrogen cease to burn? Why does the hydrogen itself burn only at the mouth of the jar? Why does the jar not explode?—*S. and A. Dept.*

6. How would you prepare nitrogen? What effect would an atmosphere of nitrogen produce on life and combustion?—*London Univ. Matric.*

7. Describe two processes for the preparation of nitrogen—one suitable for the production of small, and the other of large quantities of the gas.—*London Univ. Matric.*

8. State what happens when phosphorus and sulphur are burnt in air, and the products (separately) shaken with water.—*Sydney Univ.*

9. Describe and sketch the apparatus you would use to prepare hydrogen. Name all the parts of the apparatus, and the materials required. Describe three experiments you would perform with the gas, and say what they teach you.—*Oxford Junr. Locals.*

10. What becomes of the elements hydrogen, charcoal, and sulphur when each is burnt in a jar of oxygen ? What tests would you employ in each case to ascertain whether any new substance has been produced ?—*Science and Art Dept.*

CHAPTER VI

The Atomic Hypothesis

§ 1. The Law of the Conservation or Persistence of Weight.

It will be remembered that Lavoisier (1774) heated tin with air in a closed vessel, and found that the weight of the whole system, before and after the calcination of the tin, was the same, thus showing that the whole system had neither gained nor lost in weight. This experiment is mentioned because it emphasizes, very well, the fact that in spite of the most painstaking care, every time all the substances taking part in a chemical reaction are weighed before and after the change, there is no sign of any alteration in the quantity of matter.

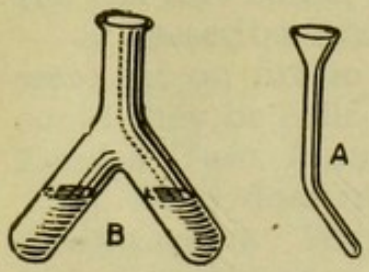


Fig. 59.—Landolt's Tube.

Every time a chemical reaction takes place in a closed vessel, which permits neither the egress nor the ingress of matter, the total weight remains unchanged within the limits of experimental error. The more carefully the experiments are made, the more nearly do the values approach identity. Several have tried to find if a loss in weight occurs during chemical action, taking the most extreme precautions known to man to secure the utmost accuracy. The experiments may be illustrated by introducing a solution of silver nitrate into one limb of the Λ-shaped tube *B*, Fig. 59, by means of the funnel *A*, and a solution of potassium chromate in the other limb. The opening is then corked—or, better, sealed—the tube is weighed, and then tilted so as to mix the solutions and start the reaction. There is no

difference in the weight of the tube before and after the reaction, within the limits of experimental error. After an examination of fifteen different reactions, all have failed to detect a variation in weight, and "since there seems no prospect of pushing the precision of the experiments further than the degree of exactness attained, the experimental proof of the law may be regarded as established." The law of the persistence of weight can thus be stated: **A variation in the total weight of the substances taking part in chemical reactions, greater than the limits of experimental error, has never been detected.**

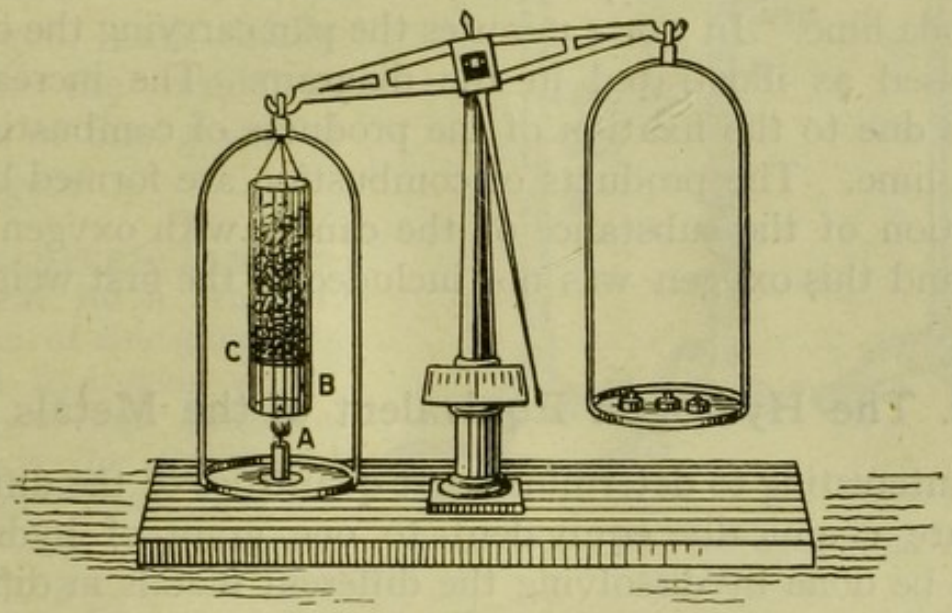


FIG. 60.—Apparent Increase in Weight during Combustion.

This fact is sometimes called the law of the indestructibility of matter, which really means what Democritus said twenty-four centuries ago: Nothing can ever become something, nor can something become nothing. Superficial observation might lead to the belief that a growing tree, the evaporation of water, and the burning of a candle prove the creation and the destruction of matter, but a careful study of these and innumerable other phenomena has shown that the apparent destruction of matter is an illusion. Matter may change its state, as when liquid water is vaporized, and when a candle is burnt. In the case of a growing tree, the nutrition the tree receives from the soil and from the air (carbon dioxide) is overlooked. Fig. 60 illustrates an instructive experiment which is commonly used

to show that the apparent destruction of matter in the burning of a candle is illusory. A candle, *A*, is fixed on one pan of a balance below a cylinder, *B*. A piece of coarse wire gauze, *C*, is fixed in the lower part of the cylinder *B*. The wire gauze supports a few lumps of quicklime (to prevent water subsequently dripping on the flame) ; a mixture of granulated soda lime and glass wool—the latter to prevent the soda lime clogging the tube—rests on the quicklime. Weights are added to the right scale pan until the beam of the balance is horizontal. The candle is lighted. The gases rising from the flame pass through the cylinder *B*—and the products of combustion are absorbed by the soda lime. In 3 or 4 minutes the pan carrying the candle is depressed as illustrated in the diagram. The increase in weight is due to the fixation of the products of combustion by the soda lime. The products of combustion are formed by the combination of the substance of the candle with oxygen from the air, and this oxygen was not included in the first weighing.

§ 2. The Hydrogen Equivalent of the Metals.

It is interesting to determine what quantities of the different metals are chemically equivalent to one gram of hydrogen. This can be done by dissolving the different metals in different acids. A pair of gas-measuring tubes—gas burette—*A* and *B*, Fig. 61, are arranged as shown in the diagram. *C* is a flask containing the necessary acid—cold—and a weighed amount of metal. The metal is contained in a test tube in the flask and left there until the necessary adjustments have been made. The levelling tube *B* is raised until the water in *A* is at zero, and on the same level as the water in the levelling tube *B*. The water in the levelling tube should be nearly at the bottom of the tube. The flask is closed with a rubber stopper. Raise or lower *B* until the level of liquid in the tubes is the same. This makes the pressure of the air confined in the flask, etc., the same as the external barometric pressure. Read the level of the liquid in *A*. The flask is then tilted so that the metal comes in contact with the acid, and the levelling tube is lowered at the same time. When all the metal has dissolved, and the

apparatus has had time to cool to the temperature of the room, bring the liquid in the tubes *A* and *B* to the same level by raising or lowering *B*, so as to equalize the internal pressure of the gas with that of the outside air. Read the volume of the gas, the thermometer and barometer. Calculate the weight of the hydrogen corresponding with the measured volume of hydrogen, and finally express the result in terms of one gram of hydrogen.

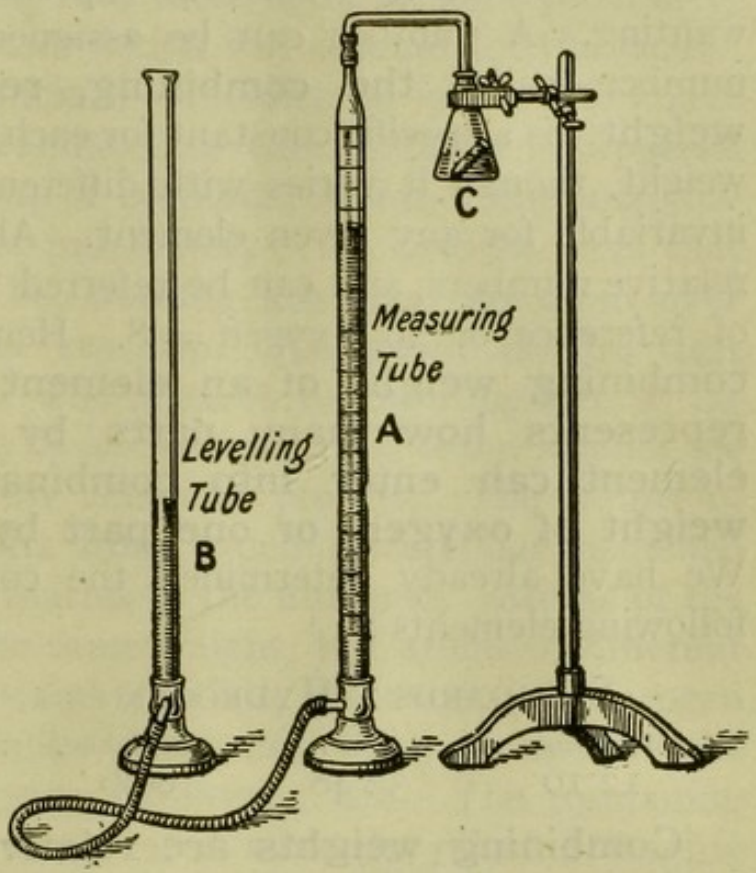


FIG. 61.—The Hydrogen Equivalent of the Metals.

EXAMPLE.—In an experiment by a student, 0·2 grm. of zinc gave 75·5 c.c. of hydrogen, at 15° and 758 mm. pressure. What is the equivalent of zinc? Here 75·5 c.c. at 15° and 758 mm. become 71·3 c.c. at 0° and 760 mm. Since one litre of hydrogen at 0° and 760 mm. weighs 0·090 grm., 71·3 c.c. of hydrogen will weigh 0·00642 grm. This weight of hydrogen comes from 0·2 grm. of zinc, hence 32 grms. of zinc are equivalent to one grm. of hydrogen.

One gram of a given metal will always displace the same amount of hydrogen, whatever be the reacting acid used—*e.g.* aluminium in sulphuric acid, or in hydrochloric acid; but the amounts furnished by different metals are different. **The weight of a metal required to displace one gram of hydrogen is called the hydrogen equivalent, or the chemical equivalent of the metal.** The following numbers for the chemical equivalents of three metals are taken from students' note-books:

Zinc.	Magnesium.	Aluminium.
32·48	12·14	8·96

These numbers agree closely with those obtained for the oxygen equivalents of the metals when referred to the standard oxygen = 8, p. 36, and they illustrate an important law which has been tested by numerous experimenters and never found wanting. A number can be assigned to each element, this number—called **the combining, reacting, or equivalent weight**—is a specific constant for each element. The combining weight, though it varies with different elements, is fixed and invariable for any given element. All combining weights are relative numbers, and can be referred to hydrogen = 1 as unit of reference or to oxygen = 8. Hence the definition: **The combining weight of an element is a number which represents how many parts by weight of the given element can enter into combination with 8 parts by weight of oxygen, or one part by weight of hydrogen.** We have already determined the combining weights of the following elements:

STANDARDS: HYDROGEN = 1, OR OXYGEN = 8.

Magnesium.	Zinc.	Aluminium.	Copper.	Tin.
12·16	32·48	8·96	31·76	29·76

Combining weights are relative.—We can express the combining weights of the elements in terms of any unit we please; it is quite immaterial whether a gram or a ton be imagined. **In dealing with combining weights, the conception of absolute quantity is quite irrelevant.** Given sufficient oxygen, 12·16 tons, kilograms, pounds, grams, or grains of magnesium will give 20·16 tons, kilograms, pounds, grams, or grains, respectively, of magnesium oxide.

§ 3. The Atomic Hypothesis.

> All bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, of atoms of matter bound together by a force of attraction which is more or less powerful according to circumstances, and which, as it endeavours to prevent their separation, is very properly called in that view, attraction of cohesion, or, more simply, affinity.—J. DALTON, 1808.

The facts.—The laws of chemical combination so far considered—(1) the law of the persistence of weight; (2) the

law of constant composition ; (3) the law of combining weights—summarize observed facts. They exist quite independently of any hypothesis we might devise about their inner meaning ; but we have an intuitive feeling that there must be some peculiarity in the constitution of matter which will account for the facts.

Guessing an explanation.—Chemists in imagination have invested matter with a granular structure. Matter is supposed to be discrete, and built up of corporeal atoms. The imagination can subdivide matter indefinitely ; the chemist says that however true this may be, nothing less than an atom ever takes part in a chemical reaction. **An atom is the unit of chemical exchange.** The atom is the limiting size so far as chemical combination is concerned. An atom cannot be subdivided by any known chemical process. The atoms of the elements are the units from which Nature has fashioned all the different kinds of matter in the universe. Atoms of the same element all have the same weight, but atoms of different elements have different weights ; thus, the atoms of nitrogen are supposed to be all alike, the same thing is said of the atoms of magnesium, of zinc, of oxygen, etc. The combining weights of the elements are related with the relative weights of the atoms of the different elements. For instance, the relative weights of an atom of oxygen and of magnesium are respectively 8 and 12·16.

With this conception of the atom, let us in imagination subdivide a mass of magnesium oxide which has been shown to be a compound of 8 grams of oxygen with 12·16 grams of magnesium. A stage will be reached when any further subdivision will separate the atoms of magnesium from those of oxygen which are still united in the ratio by weight 12·6 : 8. The smallest conceivable quantity of magnesium oxide consistent with the preceding conception of the atom thus contains an atom of magnesium and an atom of oxygen. For the time being it is convenient to use the word *molecule* for the smallest possible particle of a *compound*, and reserve the word *atom* for the smallest particle of an *element* which can take part in a chemical change. Hence, when the atoms of one element unite with the atoms of another element to form a compound, the atoms of the

respective elements behave as if they had been endowed with the power to attract or unite with one another to form small groups of atoms which we call molecules. Aggregates of atoms form molecules, aggregates of molecules form matter *en masse*. Magnesium oxide in bulk is thus a congerie of molecules, each of which contains an atom of magnesium united with an atom of oxygen.

Does the guess agree with the facts?—This ingenious hypothesis must now be subjected to the inexorable inquisition—comparison with facts. If the atoms can never be subdivided nor change in weight, it follows at once that the total number of atoms in a given system must always remain the same. Hence, the imaginary structure of matter fits in with the law of the persistence of weight. The law of constant composition simply means that the molecules of a given compound are all formed by the union of similar atoms, in other words, the molecules of a given compound are all alike. In a molecule of magnesium oxide, the weight ratio of magnesium to oxygen must be 12·16 to 8. The fact that 12·16 grams of magnesium cannot unite with 9 grams of oxygen means that during the formation of magnesium oxide, the atoms of magnesium and of oxygen continue pairing, so that 8 units of weight of oxygen pair with 12·16 units of weight of magnesium until all the magnesium atoms have been used. Hence one gram of oxygen atoms must remain unused. Fractions of an atom do not take part in chemical changes, and in forming magnesium oxide 8 grams of oxygen are required for every 12·16 grams of magnesium—no more, no less. Hence, if chemical combination be ultimately resolved into the formation of similar molecules by the union of a definite number and kind of atoms, the composition of the molecules, and also of the compound in bulk must also be fixed and invariable.

Conclusion.—In our attempt to reason from the seen to the unseen we have tested the unifying principle—the atomic hypothesis—by relentlessly applying it to the facts of nature and we find that the idea that chemical changes always involve the rearrangement of groups of atoms, is perfectly consistent with the laws of definite composition, definite combining

weights, and the persistence of weight. We may therefore accept the atomic hypothesis as a unifying principle until we discover one irreconcilable fact. In that case it will be necessary to either modify the conception or give it up altogether.

A prediction based on the atomic hypothesis.—Accepting the atomic hypothesis, it follows that the proportions in which one element can combine with another element can alter only by steps one atom at a time. It is conceivable that 1, 2, 3, . . . atoms of one element can combine with 1, 2, 3, . . . atoms of another element. One atom of mercury unites with one atom of oxygen to form red oxide of mercury. If two atoms of mercury were to unite with one atom of oxygen, the result would not be red oxide of mercury—if otherwise, the law of constant composition would be false. Hence the atomic hypothesis leads us to predict (1) the existence of more than one compound of two elements ; and further, (2) that *when one element unites with another element in more than one proportion, these different proportions must bear a simple relation to one another by weight.* We must therefore be on the look out for facts condemning or confirming these deductions from the atomic hypothesis.

Dalton's atomic hypothesis.—The ancient philosophers of India and Greece made many quaint guesses about the constitution of matter, and among these guesses we find an atomic hypothesis similar to that which lives more or less modified in modern chemistry. So far as the experimental evidence available to the Grecian philosophers in support of this particular hypothesis is concerned, its long life in the form of the chemists' atomic theory can only be attributed to chance. The modern theory, unlike the old speculation, is based upon the observed laws of chemical change, and it cannot exist apart from them. At the beginning of the nineteenth century, John Dalton employed the atomic hypothesis to explain the structure of matter and the facts of chemical combination, and it has accordingly been named " Dalton's atomic hypothesis." This can be summarized in the following assertions :

1. Atoms are real discrete particles of matter which cannot be subdivided by any known chemical process.

2. Atoms of the same element are similar to one another, and equal in weight.
3. Atoms of different elements have different properties, weight, etc.
4. The combining weights of the elements represent the combining weights of the atoms.
5. Compounds are formed by the union of atoms of different elements in simple numerical proportions, say, 1 : 1, 1 : 2, 2 : 1, 2 : 3, etc.

§ 4. The Language of Chemistry.

> However certain the facts of any science, however just the ideas derived from these facts, we can only communicate false or imperfect impressions to others, if we want words by which these may be properly expressed.—A. L. LAVOISIER.

The nomenclature of chemistry, that is, the group of technical terms peculiar to that science, is of vital importance. It is virtually impossible to separate the nomenclature from chemistry itself. Lavoisier emphasized the importance of this in his classical *Traité Élementaire de Chimie* (1789). Every science consists of three things : (1) the facts which form the subject-matter ; (2) the ideas represented by those facts ; and (3) the words in which those ideas are expressed. " Like three impressions of the same seal, the word ought to produce the idea ; and the idea ought to be a picture of the fact."

Special technical words are employed to fix and describe the ideas and principles of chemistry—as of all other sciences. Technical terms should be precise and clear, and not tainted with ambiguity and vagueness. Such technical terms form part of the current language of chemistry. However strange the terms may appear at first, they soon grow familiar to the ear, and they can then be used without effort. W. Whewell has pointed out, very aptly, that " technical terms carry the results of deep and laborious research. They convey the mental treasures of one period to the generations that follow ; and laden with this, their precious freight, they sail safely across the gulfs of time in which empires have suffered shipwreck, and the language of common life has sunk into oblivion "—witness

many of the terms used in the chemistry of to-day were coined by the early Arabian chemists—*e.g.* alembic, alkali, elixir, borax, etc.

Naming the elements.—A great number of the elements have been christened with names derived from Greek roots. *E.g. iodine*—from its violet vapour ; *chlorine*—from its green colour ; *chromium*—from the colour of its compounds ; *helium*—from its occurrence in the sun, etc. Other elements have been named more or less capriciously ; thus some elements are named after particular localities—*strontium*, from Strontian (in Scotland) ; *uranium*, is a name given in honour of the discovery of the planet Uranus ; *beryllium* is derived from the name of the mineral beryl ; *platinum*, from the Spanish " plata," silver ; *thorium*, from " Thor," the son of Odin, a god in Scandinavian mythology ; *tantalum*, from Tantalus in Grecian mythology, etc.

Symbols.—The old alchemists used to represent different substances by quaint and sometimes fantastic symbols. For example, gold was represented by the symbol ☉ or ☼, for the sun, by a king on his throne, etc. Silver, by ☾, the crescent moon, and also by a swan ; etc. Lavoisier used the symbol ▽ for water ; ⊕ for oxygen ; etc. Dalton made a step in advance by representing the atoms of the elements by symbols, and combining these symbols so as to show the elements present in a compound. Thus, ⊙ represented hydrogen ; ○ oxygen ; ● carbon ; etc. Water was represented by ⊙○ ; carbon monoxide by ○● ; carbon dioxide by ○●○ ; etc. These symbols have all been abandoned. They are too cumbrous. To-day we follow J. J. Berzelius' method, suggested in 1811, and use one or two letters from the recognized name of the element to represent any particular element. If two letters are needed the first letter is always a capital and the second a small letter. Thus, O represents oxygen ; H, hydrogen ; C, carbon ; N, nitrogen ; Cl, chlorine ; etc. The names of ten elements start with C, and to prevent the possibility of confusion, a second leading letter is selected either from the name, or from the alternative Latin name of the element. Thus, C (carbon), Cb (columbium), Ca (calcium), Cd (cadmium), Ce (cerium), Cl (chlorine), Co (cobalt), Cr

(chromium), Cs (cæsium), and Cu (cuprum, copper). The elements with alternative Latin names are symbolized: Sb for antimony (Lat. *stibium*); Cu for copper (Lat. *cuprum*); Au for gold (Lat. *aurum*); Fe for iron (Lat. *ferrum*); Pb for lead (Lat. *plumbum*); Hg for mercury (Lat. *hydrargyrum*); Ag for silver (Lat. *argentum*); K for potassium (Lat. *kalium*); Na for sodium (Lat. *natrium*); and Sn for tin (Lat. *stannum*).

Naming the compounds.—Each element forms with other elements a group of compounds which are said *to contain* the respective elements, because the elements in question can be obtained unchanged from the compounds. Consequently, **every compound has an elementary or ultimate composition.** Compounds are symbolized by joining together the letters corresponding with the different elements in the compounds. Thus, HgO represents mercury oxide, a compound of mercury and oxygen. When only two elements are united to form a compound, the name of the second element is modified so that it ends in **ide.**

The symbol for the element also represents one of its atoms. If more than one atom is present in a compound, a small figure is appended to the bottom right-hand corner of the symbol for an atom of the element, to indicate the number of atoms present. Thus "H_2O" represents a molecule of water, *i.e.* a compound containing two atoms of hydrogen and one of oxygen; "CO" represents a molecule of carbon monoxide—a compound containing one atom of carbon and one atom of oxygen; "Na_2CO_3" represents a molecule of sodium carbonate—a compound containing two atoms of sodium, one atom of carbon, and three atoms of oxygen. A letter affixed in front of a group of symbols represents the number of times that group occurs in the given compound. Thus crystallized sodium carbonate is symbolized: $Na_2CO_3 \cdot 10H_2O$. This means that this compound contains the equivalent of one Na_2CO_3, and ten equivalents of the group H_2O.

Compounds of one element with oxygen are called **oxides.** When an element forms more than one oxide, a Greek numerical suffix is often prefixed to the word "oxide." Thus, SO_2 is sulphur dioxide; SO_3, sulphur trioxide; CO, carbon monoxide;

CO_2, carbon dioxide; PbO, lead monoxide; PbO_2, lead dioxide or lead peroxide.

Some of the commoner prefixes are:

	1	2	3	4	5	6
Latin . .	Uni-	Bi-	Ter-	Quadri-	Quinque-	Sexa-
Greek . .	Mono-	Di-	Tri-	Tetra-	Penta-	Hexa-

	7	8	9	10	11	12
Latin . .	Septa-	Octo-	Novem-	Decem-	Undecem-	Duodecem-
Greek . .	Hepta-	Octo-	Ennea-	Deka	Endeka-	Dodeka-

	Half	Whole	Equal	Many
Latin . .	Semi-	Omni-	Equi-	Multi-
Greek . .	Hemi-	Holo-	Homo-	Poly-

It is considered bad style to mix Latin and Greek root words and prefixes. Consequently, we usually try to keep Greek with Greek, and Latin with Latin. Thus, we say "diatomic," not "biatomic"; "bimolecular," not "dimolecular," and "bivalent," not "divalent," because "atomic" is derived from a Greek word, while "molecular" and "variant" are derived from Latin words. There are, however, many hybrids universally recognized. *E.g.* millimetre, centimetre, etc. Monovalent, divalent, etc., are also used at times in spite of their hybrid character. We cannot, therefore, always be "purists" without defying custom, which, as Horace has said, decides the language we must use.

Sometimes the termination **-ic** is affixed to the name of the metal for that oxide which contains the greater proportion of oxygen, and **-ous** for the oxide containing the lesser proportion of oxygen.[1] For instance, SnO is either stannous oxide, or tin monoxide; and SnO_2 is either stannic oxide, or tin dioxide; FeO is ferrous oxide; and Fe_2O_3 ferric oxide. The method of naming the compounds now under discussion is not always satisfactory when the elements form more than two compounds. To get over the difficulty, a prefix **hypo-** (meaning "under," or "lesser") is sometimes added to the

[1] For historical reasons, the names of some compounds do not conform to this system because the affix "ic" was assigned to the compound first discovered, and the compounds subsequently discovered were named accordingly.

compound containing the least, and **per-** ("beyond," "above") is added to the one with the most oxygen. Thus:

Persulphuric acid	$H_2S_2O_8$	Perchloric acid	$HClO_4$
Sulphuric acid	H_2SO_4	Chloric acid	$HClO_3$
Sulphurous acid	H_2SO_3	Chlorous acid	$HClO_2$
Hyposulphurous acid	$H_2S_2O_4$	Hypochlorous acid	$HClO$

The six nitrogen oxides—nitrogen monoxide, dioxide, trioxide, tetroxide, pentoxide and hexoxide—would be awkwardly named by this system, because more prefixes are required. Oxides, like alumina—Al_2O_3; ferric oxide—Fe_2O_3, etc., are sometimes called **sesquioxides** (Latin, *sesqui*, one-half more).

The nomenclature of inorganic chemistry is thus based upon the principle that the different compounds of an element with other elements can be named by a simple change in the beginning or termination of the word—witness ferric and ferrous oxides; and also by the addition of a numerical suffix showing the relative number of atoms of the corresponding element in its compounds. These little artifices, apparently trivial, are really important advances in the language of chemistry. The method has some defects, but when the necessity for a modification becomes acute, it will probably not be difficult to change. Language generally lags in the wake of progress.

Questions.

1. Describe an experiment by which you can show that when a piece of charcoal or sulphur is burnt in the air, the substance of the charcoal or sulphur is not destroyed, but only changes its form.—*Science and Art Dept.*

2. What do you understand by the term "chemical action"? Explain how the recognition of the fact that chemical action always takes place between definite proportions of matter led to the establishment of Dalton's atomic theory.—*Science and Art Dept.*

3. The ancients regarded air as an element. Prove by experiments that it consists mainly of oxygen and nitrogen.—*London Univ. Matric.*

4. State the laws of chemical combination by weight, and show that they are the natural consequences of an atomic structure of matter.—*N.Z. Univ.*

5. In measuring the volumes of gases what do you understand

by " standard conditions " ? Should such conditions be specified when measuring the volumes of liquids and solids ? Why ?

6. What evidence can you bring forward in support of the view that matter can neither be created nor destroyed ? How do you explain the statement that the products of combustion of a candle weigh more than the original candle ?

7. From an experiment it was found that 20 grms. of zinc, when treated with hydrochloric acid, yielded 7·28 litres of hydrogen measured at 12° and 7·48 mm. pressure. The equivalent weight of hydrogen being 1, find the equivalent weight of zinc. (The result may be expressed as a fraction which need not be simplified.) —*Cape Univ.*

8. Describe with full details the method you would adopt in order to determine the volume of hydrogen liberated when one gram of zinc is dissolved in dilute acid. Supposing in such an experiment 100 c.c. of hydrogen at 26° and 740 mm. were obtained, what weight of zinc must have been used ? (Atomic weight of zinc, 65.)—*London Univ. Matric.*

9. Give examples, with the formulæ, of bodies the names of which terminate in *-ide*, *-ate*, and *-ite*.—*Science and Art Dept.*

CHAPTER VII

The Composition of Water

§ 1. Burning Hydrogen in Air.

Kipp's apparatus is very convenient when a steady current of hydrogen is needed for some time ; or when variable quantities of gas are required intermittently. *A*, Fig. 62, is one of the numerous modifications of the original " Kipp." Connect the exit tube from the Kipp's apparatus with a calcium chloride tower, *B*, packed with granulated calcium chloride, and a plug of glass wool at each end. The object of this tube is to remove moisture from the gas. Place a bell-jar, *K*, in a dish of distilled water, *H*, and arrange the delivery tube *J* so that it can be quickly fixed as illustrated in the diagram. Collect a test tube of the gas by downward displacement as it leaves the exit tube in order to make sure that all air has been displaced from the tubes. When the test is satisfactory, light the jet of hydrogen, and adjust the flame until it is about the size of a candle-flame ; lower the burning jet into the cylinder of air as shown in Fig. 62. Note that the water rises in the jar, and that the flame of hydrogen gradually expires. Immediately this occurs, stop the current of hydrogen by means of the stop-cock, otherwise hydrogen gas will pass from the gas-holder and mix with the residual air.

The gas remaining in the jar has quite similar properties to the gas remaining after mercury is calcined in air, p. 31. Consequently, it is inferred that **when hydrogen burns in air, it unites with the oxygen and leaves nitrogen behind.** If the experiment be carefully done, four-fifths of the original volume of air remain. The burning hydrogen removes one-fifth of the original volume of air. Hydrogen does not burn in the

residual nitrogen. A certain amount of " dew " collects on the inner walls of the bell-jar, but that, of course, may come from the water in the dish below. In fine, we have reasons for supposing that hydrogen, in burning, combines with oxygen to form an oxide of hydrogen in the same sense that mercury, when calcined in air, combines with oxygen to form mercuric oxide. It remains to try and isolate the hydrogen oxide whose existence we have just inferred, but not proved.

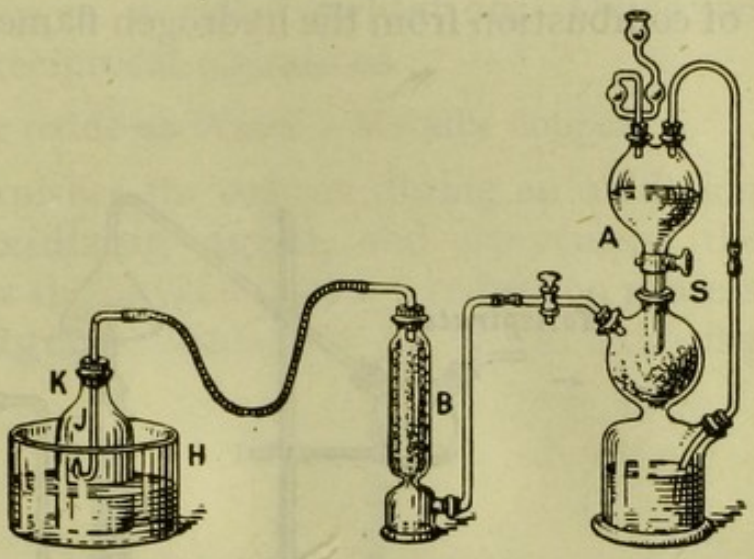


FIG. 62.—The Synthesis of Water.

To prepare Kipp's apparatus for work.—Zinc is placed in the middle bulb, and dilute sulphuric acid (1 vol. acid ; 4 vols. water) or hydrochloric acid in the lower and upper bulb, as shown in the diagram. Open the stopcocks so that the acid trickles from the upper bulb on to the zinc until the resulting gas has displaced the air. The velocity of the current of gas is regulated by the stopcocks. When the smaller stopcock is closed, the acid is forced away from the gas, and the apparatus is ready for a further supply of gas. The side tube helps to prevent an accumulation of spent acid near the zinc. There are over a hundred modifications of the principle for supplying a continuous stream of gas.

Connect the Kipp's apparatus, *A*, Fig. 63, with the drying tower packed with calcium chloride, *B*, and fitted with a jet, *C*, for burning the hydrogen. A piece of narrow quartz-glass tubing makes an excellent jet. If this is not available, use a jet of hard " combustion " glass tubing. Test the gas, to ensure the absence of air, by bringing a *dry* test tube over the jet of gas issuing from the drying tower. Bring a lighted taper to the mouth of the tube. The hydrogen should burn quietly, in that case ; it will be noticed that a kind of " dew " collects on the inside of the test tube. Bring the jet of burning gas under the inverted funnel fitted, as shown in the diagram, with a bulb, *D*,

connected with an aspirator for sucking a gentle current of air through the bulb. The current of air carries along the products of combustion from the hydrogen flame. A clear colourless liquid

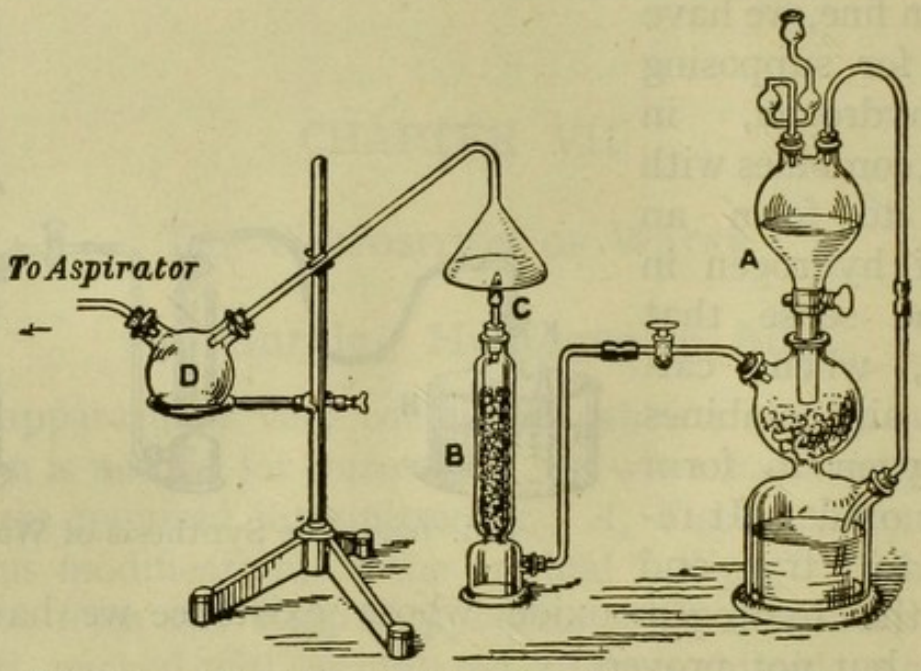


FIG. 63.—The Effect of burning Hydrogen in Air.

collects in the bulb. This liquid has all the properties of water —clear, colourless, tasteless, no smell, freezes at 0°, boils at 100°, etc. It is therefore provisionally inferred that **water is a hydrogen oxide formed when hydrogen burns in air.**

§ 2. The Composition of Water by Weight.

If hydrogen gas be passed over copper oxide heated in a hard glass tube, *C*, Fig. 64, metallic copper is obtained. All the air must have been expelled from the apparatus as shown by testing the gas collected at the exit tube of *D* before the tube *C* is heated. If the hydrogen from the gas generator *A* be dried by passage through a tower *B*, containing fused calcium chloride, water will collect in the little test tube *e* resting on some glass wool inside the U-tube *D* which is otherwise charged with fused calcium chloride. It has already been established that copper oxide is formed by the union of copper with oxygen in the proportions: Copper 31·76 grams, oxygen 8 grams. Hydrogen can remove the oxygen from copper oxide so that the metal is restored. The hydrogen unites with the oxygen

of the copper oxide and forms water. The removal of oxygen from a compound is called **reduction,** just as the combination of a substance with oxygen is called **oxidation.** Oxidation and reduction are thus reciprocal operations :

$$\text{Hydrogen} + \text{Copper oxide} \rightleftharpoons \text{Water} + \text{Metallic copper}$$

The substance which furnishes the oxygen during an oxidation process is called an **oxidizing agent,** and conversely, the substance which removes the oxygen during a reduction process is calling a **reducing agent.** Thus, hot air is the oxidizing

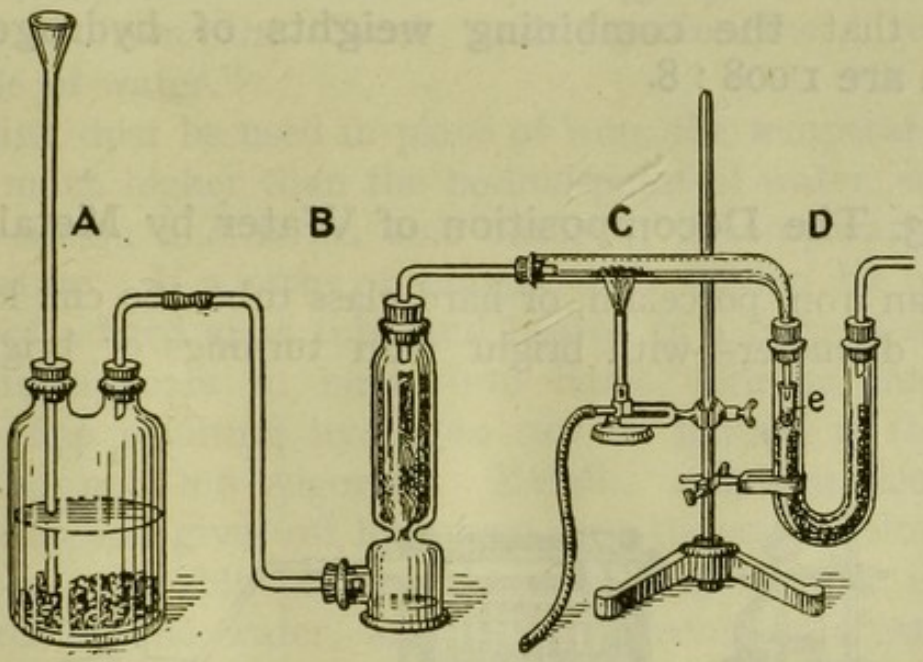


FIG. 64.—The Composition of Water by Weight.

agent when copper oxide is formed by roasting metallic copper in air, and hydrogen is the reducing agent in the reduction of the copper oxide in the above experiment.

The preceding experiment can be conducted quantitatively by weighing the U-tube *D*, and the copper oxide tube *C* before and after the experiment. The gain in weight of the U-tube represents the water formed during the operation, and the loss in weight of the copper oxide tube represents the amount of oxygen required to produce the water. Thus, in an experiment by Dumas, more than half a century ago,

Copper oxide lost in weight	44·23 grams
Water produced	49·76 „
Hydrogen (by difference)	5·53 „

Hence, 44·23 grms. of oxygen united with 5·53 grms. of hydrogen to produce 49·76 grms. of water. Reducing these weighings to the oxygen standard 8, and they show that the combining weight of hydrogen is 1·001 if oxygen is 8. In the above experiment, Fig. 64, we have made no very refined precautions to purify the hydrogen, nor has a temoin tube been used to prove that the hydrogen which passed over the copper oxide was really free from water, but chemists have made experiments with scrupulous care, using every known precaution to secure the extremest accuracy. From these results it is usually considered that **the combining weights of hydrogen and oxygen are 1·008 : 8.**

§ 3. The Decomposition of Water by Metals.

Fill an iron, porcelain, or hard glass tube—60 cm. long and 1·5 cm. diameter—with bright **iron** turnings or bright iron

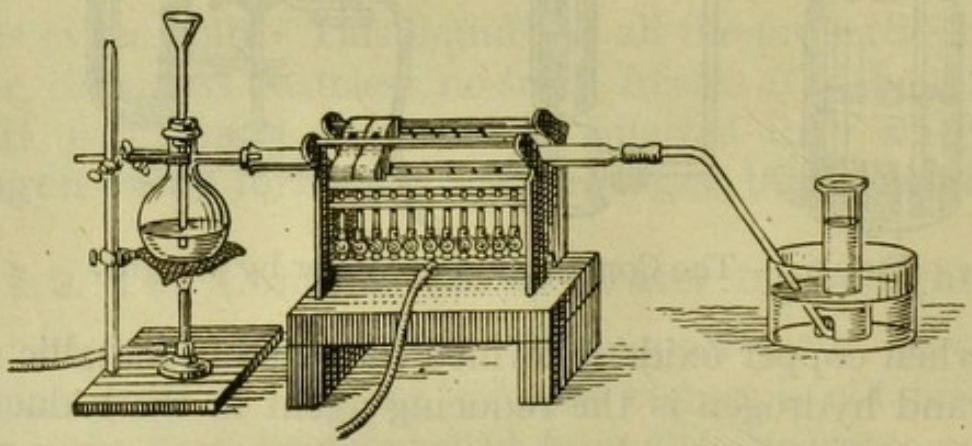


FIG. 65.—Decomposition of Steam by Hot Iron.

nails. In Fig. 65 a hard glass tube is used. This is drawn out at one end as shown in the diagram. This end is fitted with a delivery tube dipping in a gas trough. A roll of previously ignited asbestos paper, 6 cm. long, is inserted in the opposite end. This end is closed with a red rubber stopper, and the exit tube of the flask so arranged that it passes a short distance into the core of the asbestos paper. The asbestos roll, later on, prevents the liquid water coming into contact with the hot glass and breaking the tube. Water is boiled in the flask, and

the steam, passing through the iron turnings, is decomposed. When all the air has been driven out of the apparatus, hydrogen may be collected in the gas-jar. The usual tests for hydrogen, indicated on p. 86, may be applied. Lavoisier made a similar experiment to this in 1783, and stated that the metallic iron "is converted into a black oxide precisely similar to that produced by the combustion of iron in oxygen gas." The iron is oxidized by the water, and the water is reduced, forming "a peculiar inflammable gas," which Lavoisier named "hydrogen," because "no other term seemed more appropriate." The word is derived from the Greek, and signifies the "generative principle of water."

If **zinc** dust be used in place of iron, the temperature need not be much higher than the boiling-point of water, since zinc reduces steam and forms zinc oxide at a comparatively low temperature. If a strip of **magnesium** ribbon be placed in a bulb of a hard glass tube and heated in a current of steam, the metal appears to burst into flame, forming magnesium oxide. The resulting hydrogen can be ignited if the jet of steam be not too vigorous. Metallic **calcium** decomposes cold water and gives off hydrogen, but the action slows down very soon, probably because the calcium hydroxide is not all dissolved by the water, and in consequence a crust of this substance forms over the surface of the metal. The calcium can be advantageously warmed with water in a flask, Fig. 57, connected directly with a delivery tube leading to the gas trough. If the water is not free from carbonates, a crust of calcium carbonate also forms over the surface of the metal. Calcium hydroxide is formed as well as hydrogen. **Sodium** decomposes cold water, giving off hydrogen, and forming sodium hydroxide. The experiment is liable to unpleasant explosions when the sodium is confined so as to enable the resulting hydrogen to be collected. The following is Benedict's way of showing the action. A glass tube—4 or 5 cm. long and 1·5 cm. diameter, and open at both ends—is thoroughly dried inside. This is lowered and clamped vertically in a dish of water so as not to wet the sides of the tube above the level of the water, Fig. 66. A small piece of dry sodium, about 2 mm.

in diameter, is dropped into the tube. The hydrogen evolved can be lighted at the upper end of the tube. Sodium amalgam —that is, a solution of metallic sodium in mercury—decomposes water much less turbulently than sodium alone. The result is similar when a small piece of **potassium**—3 or 4 mm. diameter—is placed on water, but it reacts so violently that the temperature rises high enough to set fire to the hydrogen. This burns with a flame tinged violet, owing to the presence of the vapour of potassium; the hydrogen produced by the action of sodium on water burns with a yellow flame, owing to the contamination of the hydrogen by the vapour of sodium.

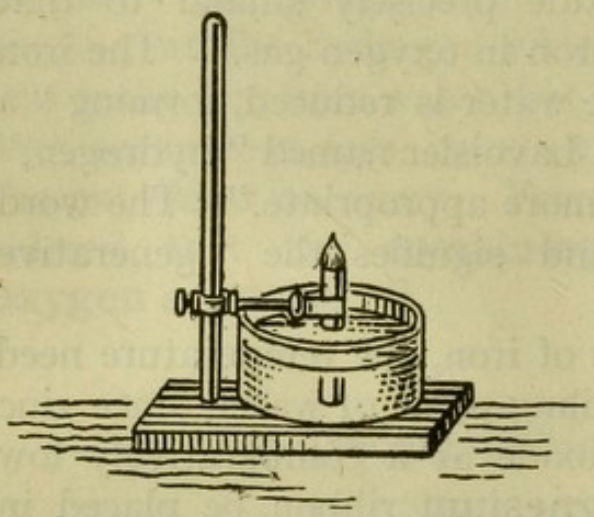


FIG. 66.—The Action of Sodium on Water.

This set of experiments gives a series of metals which appear to react with water with increasing violence, the metals seem to have an increasing "avidity" or "affinity" for oxygen:

Iron, zinc, magnesium, calcium, sodium, potassium.

§ 4. The Decomposition of Water by Electricity.

W. Nicholson and A. Carlisle, May 2, 1800, happened to put a drop of water in contact with two wires from an electric battery and noticed the formation of small bubbles of gas about the tips of the wires when the tips of the wires were not in contact. They then immersed the two wires in a glass of water, and found that gases were formed about both wires. They found the gas collected at one wire to be hydrogen, and at the other wire, oxygen. Two volumes of hydrogen were collected for every volume of oxygen. The gases were mixed and exploded. The result was water. This is very interesting. We have seen that chemical combination can produce an electric current; here an electric current is used to produce chemical decomposition.

The electrolysis of water.—It will be convenient to modify Nicholson and Carlisle's experiment. A trough, Fig. 67, is half filled with water slightly acidulated with sulphuric acid. Test tubes full of acidulated water are placed in the position shown in the diagram over two plates of gold or platinum. The plates are put in communication with an accumulator or galvanic battery. During the passing of the electric current, bubbles of gas from about the metal plates rise into the test tubes. More gas is given off at one plate than at the other. The gas in each tube can be examined by means of a lighted taper or otherwise. In the one tube, the taper burns with the

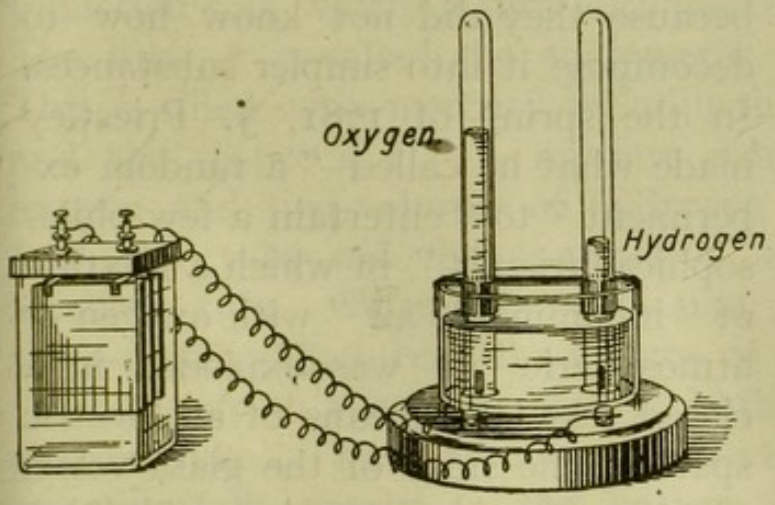


FIG. 67.—Electrolysis of Water—Gases separated.

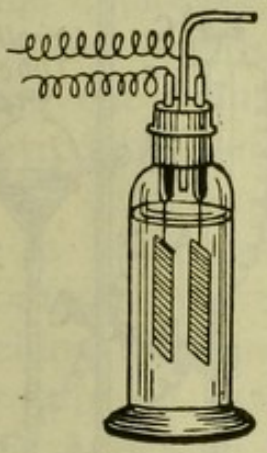


FIG. 68.—Electrolytic Gas.

"blinding brilliance" characteristic of oxygen; and the gas in the other tube burns with the blue flame characteristic of hydrogen. Some of the water has disappeared, but no change can be detected in the amount of sulphuric acid mixed with the water. Hence it is inferred that the water, not the acid, has been decomposed. The experiment succeeds equally well if a very dilute solution of sodium or potassium hydroxide be used with nickel or iron electrodes. Here again the water, not the alkali, is decomposed. These reagents are used because water alone does not conduct an electric current very well. In fact, pure water is said to be a non-conductor of electricity. Dilute solutions of acids or alkalies are good conductors. If iron electrodes are used in the acidulated solution, much of the

oxygen formed during the decomposition of the water is used in oxidizing the metal.

A mixture of one volume of oxygen and two volumes of hydrogen, called **electrolytic gas** or **detonating gas,** can be obtained by placing both electrodes under one receiver. The apparatus illustrated in Fig. 68 can be used for this work.

§ 5. Cavendish's Experiment on the Synthesis of Water by Volume.

The older chemists considered water to be an element. They were quite right so far as their knowledge went, p. 37. because they did not know how to decompose it into simpler substances. In the spring of 1781, J. Priestley made what he called "a random experiment" to "entertain a few philosophical friends," in which a mixture of "inflammable air" with oxygen or atmospheric air was exploded in a closed vessel by means of an electric spark. The sides of the glass vessel were found "bedewed" with moisture after the explosion, but Priestley paid no particular attention to the phenomenon. H. C. Cavendish looked upon the deposition of the dew as a fact "well worth examining more closely" and immediately followed up the subject, in 1781, by exploding a mixture of "one measure of oxygen with two measures of inflammable air (hydrogen)" in a closed vessel. No gas remained in the globe after the explosion, but the hydrogen and oxygen lost their gaseous form, and produced a certain weight of water. The vessel and its contents underwent no change

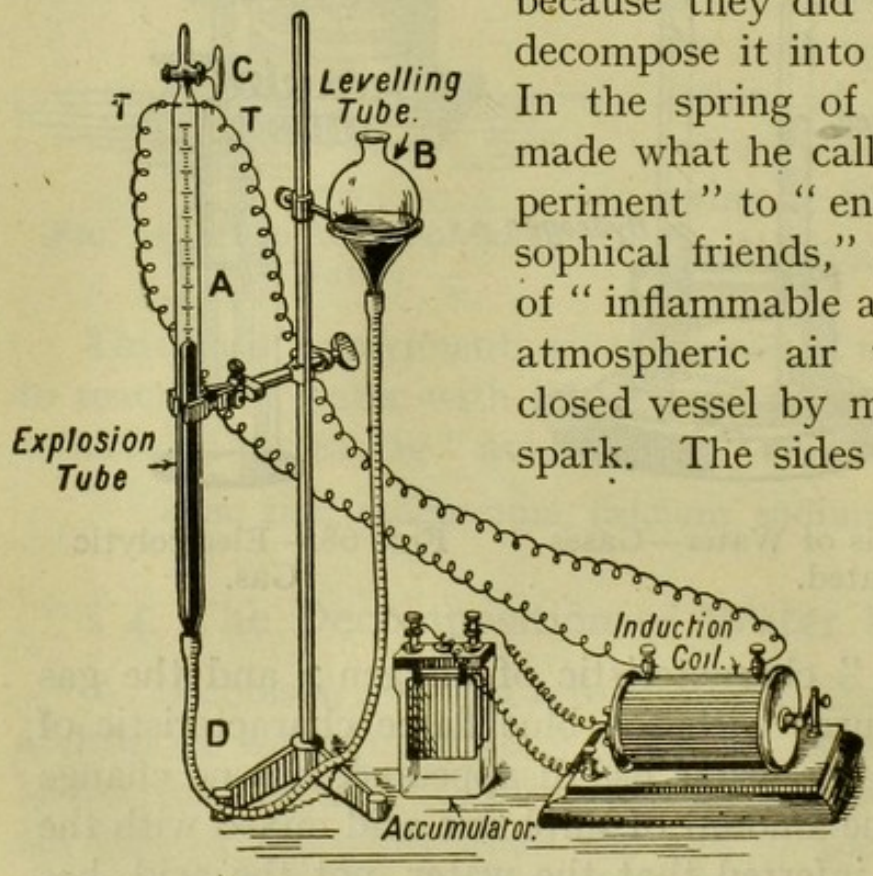


FIG. 69.—Synthesis of Liquid Water by Volume.

in weight, or parted with anything ponderable during the explosion, whilst a certain volume of gas was replaced by a certain weight of water. Hence Cavendish deduced that **liquid water consists, weight for weight, of the hydrogen and oxygen gases lost in its production.**

The experiment can be illustrated in the following manner: A stout glass vessel, *A*, is fitted with a stopcock, *C*, at one end, and with a piece of strong pressure tubing, *D*, connected with a reservoir at the other end, Fig. 69. A pair of platinum wires, *T*, are sealed into the stout glass measuring vessel just below the stopcock. These wires are put in communication with an induction coil, which in turn is connected with an accumulator. The tube *A* is called the eudiometer, or the explosion tube. This is filled with mercury by adjusting the levelling tube *B* and the stopcock *C*. A mixture containing one volume of oxygen and two volumes of hydrogen is introduced into the explosion tube *viâ* the stopcock *C* and by depressing the levelling tube. When the explosion tube is about half or three-fourths filled, read the volume of its contents by bringing the mercury to the same level in both levelling tube and explosion tube. Then depress the levelling tube so that the mercury falls nearly to the bottom of the explosion tube. Pass a spark from the induction coil through the wire terminals of the explosion tube. The gases explode, and the level of the mercury is again adjusted after the apparatus has stood for a few minutes in order to regain the temperature of the room. The mercury rises nearly to the level of the stopcock.

Suppose the experiment be repeated a number of times with, say, one volume of oxygen and three volumes of hydrogen —one volume of hydrogen remains after the explosion; again try the experiment with two volumes of oxygen and two volumes of hydrogen—one volume of oxygen will remain uncombined after the explosion. It is inferred, from this experiment, that **two volumes of hydrogen and one volume of oxygen combine to form water, and if an excess of either oxygen or hydrogen be present, the excess will remain uncombined after the reaction.**

§ 6. The Volumetric Synthesis of Steam.

Let us modify the preceding experiment. Place a hot vapour jacket about the explosion tube so that the water remains in the gaseous condition, and does not condense to a liquid after the explosion. The experiment is illustrated in Fig. 70. The upper end of the glass jacket surrounding the explosion tube of Fig. 70 is connected with a flask, *M*, containing toluene, boiling at about 110°, or amyl alcohol, boiling at about 130°. The lower end of the jacket is connected with a flask and condenser *N*, so that the amyl alcohol can be recovered. When the amyl alcohol is steadily boiling, and the explosion tube has been filled as described in the preceding experiment, the gases are sparked. In a few minutes, when the temperature has had time to adjust itself, bring the levelling tube in position for a reading. It will be found that the steam occupies just two-thirds the original volume of the mixed gases. Otherwise expressed,

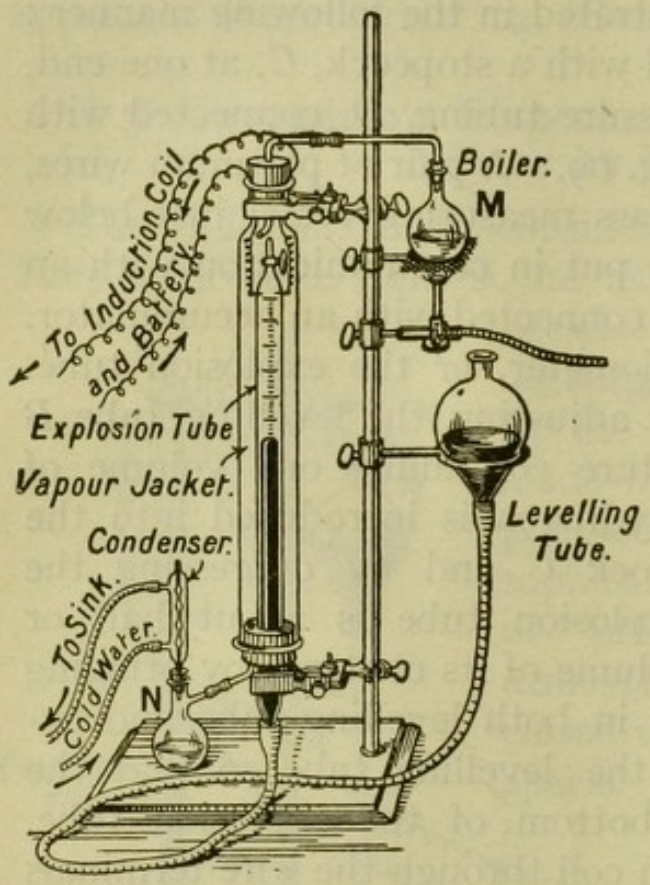
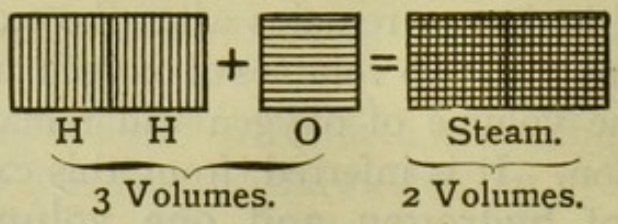


FIG. 70.—Synthesis of Steam by Volume.



Hence, it is inferred that **when water is synthesized at a temperature above the point of condensation, two volumes of hydrogen react with one volume of oxygen to form two volumes of steam.**

The formula for water used to be written HO when the atomic weight of hydrogen was taken as unity, and oxygen 8. This agrees quite well with the determinations of Dumas. But we naturally ask for an explanation of the result of the electrolysis and synthesis of water. Does an atom of hydrogen occupy twice the volume of an atom of oxygen ?

Questions.

1. Describe the methods and give sketches of the apparatus you would use to determine the composition of water (*a*) by volume, (*b*) by weight.—*London Univ. Matric.*

2. Why do we call hydrogen and oxygen chemical elements, and why do we consider water to be a compound of these two elements ?—*London Univ. Matric.*

3. Explain how the volumetric composition of water may be ascertained. If the weight of one litre of hydrogen at the standard temperature and pressure be 0·0896 grm., and the weight of one litre of oxygen under the same conditions be 1·4303 grms., calculate the percentage composition by weight of water.—*London Univ. Matric.*

4. What volume of water vapour results from the explosion of a mixture of two volumes of hydrogen and one volume of oxygen ? Explain how the fact that one volume of oxygen unites with two volumes of hydrogen to form water may be made use of in order to determine the amount of oxygen in the air.—*London Univ. Matric.* (Hint : Mix a measured volume of air with its own weight of hydrogen in an " explosion tube." Pass an electric spark through the mixture, and note the contraction owing to the union of two volumes of hydrogen with one volume of oxygen to form water vapour, and the subsequent condensation of the water to a liquid whose volume is negligibly small in comparison with the volume of the gases from which it was derived.)

5. Describe some of the most characteristic physical and chemical properties of water, and state exactly how you would demonstrate them without the use of very special or elaborate apparatus.—*London Univ. Matric.*

6. What do you understand by the equivalent of an element ? One gram of magnesium displaces from combination 0·083 grm. of hydrogen, 9 grms. of silver, and 5·25 grms. of copper. What are the equivalents of these elements ?—*Science and Art Dept.*

7. Sketch an apparatus for showing that water results from burning a jet of hydrogen in air. Why is the flame extinguished when it is passed into an inverted jar filled with hydrogen ?—*Science and Art Dept.*

8. Suppose it be objected that the water formed in the experiment, p. 120, Fig. 63, comes from moisture in the hydrogen in spite of the drying column, how would you proceed to demonstrate whether or not the objection stultifies the experiment? (Hint. What is a temoin tube?)

9. An experiment to ascertain the composition of water by weight gave the following results :—

Weight of tube and copper oxide			before experiment		32·325 grms.
,,	,,	,,	after	,,	24·333 ,,
Weight of calcium chloride tube			before	,,	40·462 ,,
,,	,,	,,	after	,,	49·494 ,,

Find the simplest proportion in which these elements are combined. —*Science and Art Dept.*

10. A mixture of five volumes of hydrogen and three volumes of oxygen are exploded by an electric spark ; will any gas remain ? If so, how much, and how will you ascertain what it is ? What modification would be required in your answer, supposing three volumes of hydrogen and five volumes of oxygen were substituted for five volumes of hydrogen and three volumes of oxygen ?

CHAPTER VIII

Chlorine and some of its Compounds

§ 1. Sodium and Potassium Chlorides.

Sodium chloride, commonly called "salt," is considered to be an essential constituent of animal food. One writer estimates that about 30 lbs. of salt per head of population per annum is used directly or indirectly with the food of man. The 0·1 per cent. of hydrochloric acid present in the gastric and mucous fluids of the alimentary canal is derived from the decomposition of the salt taken in with the food. Plant-eating animals get the salt they require from grass and leaves; herbivorous animals have been known to travel hundreds of miles to a "salt-lick" ("salt spring") in order to satisfy their craving for salt. Carnivorous animals get their salt from the blood of the animals on which they feed.

The occurrence of salt.—Rock salt occurs in transparent or translucent cubic crystals, either colourless or varying in tint from white to dirty grey, to yellow, to reddish yellow; and sometimes blue or purple. It is sometimes called *halite*. Some crystals are illustrated in Fig. 71 with an ideally perfect crystal in outline. Rock salt is found in Nantwich (Cheshire); Droitwich [1] (Worcestershire); California, Utah, Kansas, New York, Virginia, Ohio, Michigan (United States); and numerous other places. The mines at Wielicza (Galicia, Austria) have been worked continuously for 600 years. That salt deposit is said to be 500 miles long, 20 miles broad, and 1200 feet thick.

[1] The names of these localities indicate the antiquity of the salt industry, since, in Saxon times, a place where salt was dug was called a "wich."

The galleries and chambers in this mine extend over 30 miles in length and yield 55,000 tons per annum. A comparatively large amount of salt is dissolved in sea-water, and in the water of many salt springs and salt wells (*see* page 59). The remarkable deposit of potassium, magnesium, and sodium salts in the country around Stassfurt, in Prussian Saxony, is the centre of a very important industry for potassium salts. The deposit is supposed to be the residue left after the natural evaporation of an inland sea during pre-historic times.

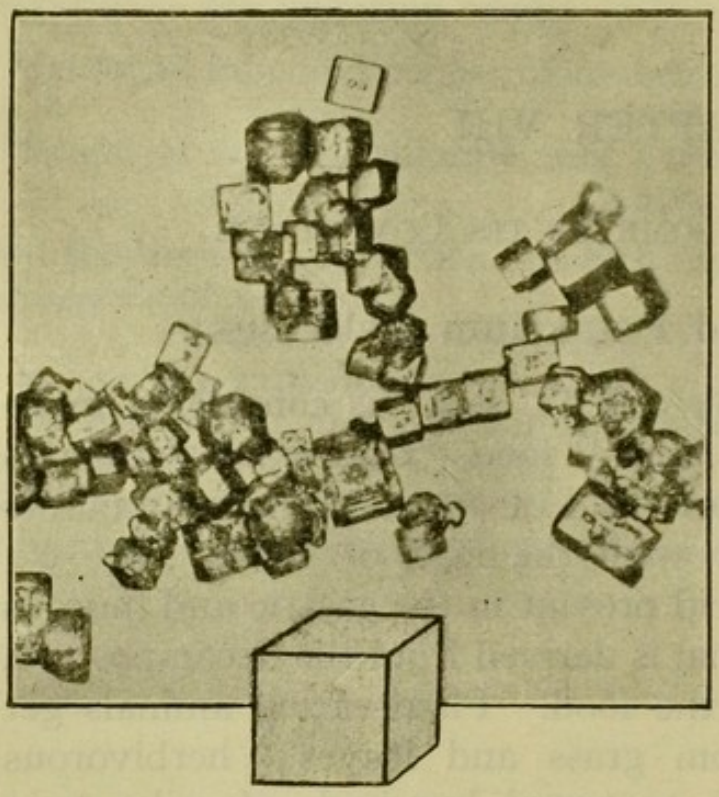


FIG. 71.—Crystals of Sodium Chloride.

The separation of salt from sea-water.—Countries not supplied with rock salt must either import salt from more favoured countries, or resort to the concentration of sea-water, or the water of salt springs. Evaporation is not an expensive process in warm countries, or where coal is cheap; *e.g.* on the shores of the Mediterranean Sea the sea-water is concentrated by evaporation in large shallow tanks—"salterns"—exposed to wind and sun. As the solution—"brine"—becomes concentrated, the crystals of salt which separate are lifted out by means of perforated shovels, and allowed to drain beside the evaporation tanks. In cold countries, *e.g.* on the shores of the White Sea (Russia), the sea-water is concentrated by freezing. Ice first separates; and the residual brine is further concentrated by evaporation over a fire.

The purification of rock salt.—Rock salt is often mined by bringing the solid salt to the surface in lumps. In some salt beds, the salt is mined by forcing water into the beds *viâ* a

well made for the purpose. The brine is afterwards pumped to the surface, and the liquid concentrated in salterns ; or by allowing the solution to trickle from elevated tanks over ricks of brushwood—" graduators "—so arranged that the solution is fully exposed to the prevailing winds. The liquid may be afterwards concentrated by evaporation in shallow pans heated artificially, particularly if fuel is cheap. As the salt crystallizes out, it is removed by means of perforated shovels. If much calcium sulphate be present, it will separate first. It must therefore be removed before the salt. The potassium and magnesium salts separate last. If fine-grained " table salt " is needed, the brine is evaporated rapidly near its boiling-point ; but for the manufacture of coarse-grained " fish-salt " the evaporation is conducted slowly at a comparatively low temperature (45°), so as to get the salt in comparatively large crystals. The salt obtained by the evaporation of sea-water will be contaminated with small quantities of other salts as impurities. Cheshire salt contains about 98·3 per cent. of sodium chloride ; the remaining impurities are mainly insoluble matter, calcium sulphate, and magnesium and calcium chlorides.

Potassium chloride is extracted from carnallite found in the Stassfurt deposits by repeated crystallization.

Properties.—Both chlorides crystallize in cubes, and the two salts are accordingly said to be isomorphous—from a Greek word meaning " the same shape." The crystals are anhydrous, that is, they are free from water. A little water may be mechanically entangled with the crystals, which causes the salts to decrepitate when heated. Sodium chloride melts at 801°, and potassium chloride is said to melt at about 790° ; on cooling a hard white cake of the respective chloride is obtained. Both salts sublime at higher temperatures with very little decomposition. The solubilities of the two salts in water were discussed on pp. 55 and 56.

Uses of sodium chloride.—Salt is used for seasoning food —table salt. Salt for table use should be free from magnesium and calcium chlorides, for these substances make salt very deliquescent—particularly in moist weather. Salt is also used for preserving meat, fish, etc. ; in the manufacture of sodium

salts, soaps, etc.; in glazing common pottery—drain pipes, some sanitary goods, etc.—"salt glaze"; and also in the manufacture of chlorine compounds, directly or indirectly.

2. Hydrogen Chloride—Preparation and Properties.

When sodium or potassium chloride is heated with sulphuric acid in a large test tube fitted with a delivery tube as indicated in Fig. 72, the salt effervesces and a colourless gas is given off. The gas fumes strongly in air, and it has an irritating effect on the mucous membranes when inhaled. If a piece of red litmus paper is held at the exit of the delivery tube it remains unaffected, but a piece of blue litmus paper is at once coloured red. Collect a test tube of the gas as indicated in Fig. 72, replenishing the mixture in the large test tube if necessary—the gas is so much heavier than air that this can easily be done. Cover the mouth of the test tube with the thumb and invert the tube so that its mouth is under water when the thumb is withdrawn. The water immediately rises in the tube; this shows that the gas is very soluble in water. Indeed, the gas is so extremely soluble that 1 c.c. of water will dissolve 525 c.c. of the gas at 0°, and at 20°, 440 c.c.; the liquid also becomes hot while the gas is dissolving. The great avidity of the gas for water can be illustrated by filling the flask, Fig. 4, with the gas; inserting the stopper; and dipping the tube in water (stopcock open) as shown in the diagram. If the water be coloured with blue litmus, it will be changed red as it sprays into the flask. The gas was once called "spirit of salt," but it is now called "hydrogen chloride." The aqueous solution is strongly acid, and it is called "spirits of salt," **hydrochloric acid**, or "muriatic acid" from the Latin *muria*, brine.

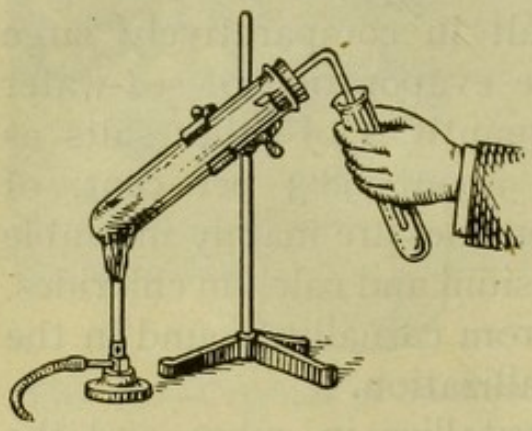


FIG. 72.—Collecting Hydrogen Chloride by the Upward Displacement of Air.

Specific gravity tables.—The specific gravity of the

solution varies with the amount of gas dissolved in the water, so that the strength of the acid can be roughly estimated from the specific gravity. Thus—

TABLE IV.—SPECIFIC GRAVITY OF SOLUTIONS OF HYDROCHLORIC ACID.

	Specific gravity.	One litre of the solution contains HCl grams.
Highest concentration . . .	1·20	469
Concentrated	1·18	418
Medium concentration . .	1·10	220
Dilute	1·05	107
Very dilute	1·01	0·22

What is here stated with respect to hydrochloric acid applies, *mutatis mutandis*, to the other acids and to ammonia. Hence the so-called tables of specific gravities or densities of the acids, etc., are useful laboratory adjuncts.

Hydrogen chloride can be made on a larger scale by heating the sulphuric acid and salt mixture in a flask as indicated in Fig. 73, but the gas is far too soluble to be collected over water. The gas is much heavier than air, consequently, if a slight contamination of the gas with air does not matter, it is most conveniently collected by the **upward displacement of air** in a fume closet. Contrast this with the method used for collecting the light gas hydrogen, Fig. 47. When a jar of the gas is desired quite free from air, it must be collected over mercury, *DF*, Fig. 18. The gas can be dried by passing it through wash bottles of concentrated sulphuric acid, Fig. 73. A litre of the dry gas weighs 1·64 grms. under normal conditions—the

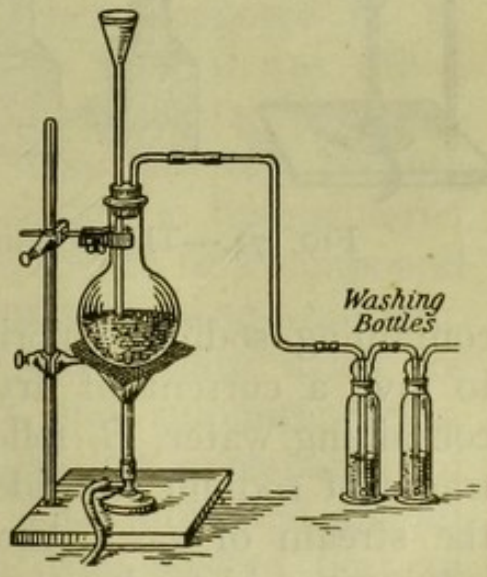


FIG. 73.—The Preparation of Hydrogen Chloride.

weight of a litre of air, it will be remembered, is 1·294 grms. The gas does not support combustion, nor is it combustible.

The purification of sodium and potassium chlorides.—Sodium as well as potassium chlorides can be purified by adding concentrated hydrochloric acid to a cold concentrated aqueous solution of the respective salts ; better results are obtained by passing gaseous hydrogen chloride through the salt solutions. The impurities usually remain in solution while the chlorides are precipitated in a very fair state of purity, because they are much less soluble in solutions of hydrogen chloride than in water.

The action of hydrogen chloride on metals.—Fit up the apparatus shown in Fig. 74. *A* represents a flask

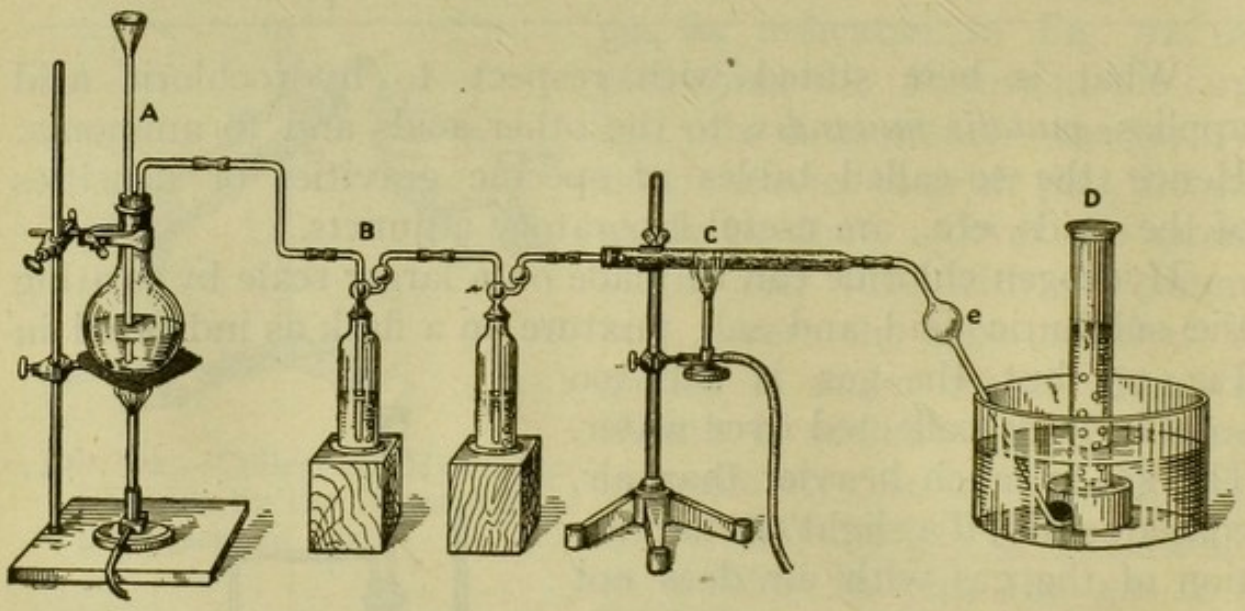


FIG. 74.—The Action of Hydrogen Chloride on Metals.

containing sodium chloride and concentrated sulphuric acid to give a current of dry hydrogen chloride ; a wash bottle containing water, *B*, follows with the object of removing any traces of sodium chloride which might be carried along with the stream of gas. Another wash bottle follows containing sulphuric acid to dry the gas. The latter is connected with a hard glass tube containing iron turnings or granulated zinc. Then follows a delivery tube dipping in the pneumatic trough. The delivery tube may have a bulb *e* to prevent liquid suddenly spurting into the hot glass tube in case of a sudden back pressure.

The tube containing the metal is heated and a gas then begins to collect in the gas cylinder *D*. On examination the gas proves to be hydrogen. From this it is inferred that **hydrogen chloride contains hydrogen combined with some other substance.** If zinc be used in the tube *C*, and the contents be digested in water and crystallized, we obtain a substance—zinc chloride—identical with that previously obtained by the action of zinc on hydrochloric acid ; and with iron we get iron chloride—page 85.

§ 3. The Action of Oxidizing Agents on Hydrogen Chloride.

The action of oxidizing agents on hydrogen chloride or hydrochloric acid is very interesting. K. W. Scheele (1774) found that when hydrochloric acid is heated with manganese dioxide, a yellowish-green gas, soluble in water, is given off. The experiment may be conducted in the apparatus indicated in Fig. 73. The red lead or manganese dioxide may be mixed with the common salt and sulphuric acid, or these oxides can be mixed with a concentrated solution of hydrochloric acid and heated. Scheele considered the yellowish-green gas to be muriatic acid freed from hydrogen (then supposed to be phlogiston), hence, in the language of his time, it was called "dephlogisticated muriatic acid." A. L. Lavoisier (1789) named the gas **oxymuriatic acid,** or oxygenated muriatic acid, because he considered it to be an oxide of muriatic (*i.e.* hydrochloric) acid ; and Lavoisier considered muriatic acid to be a compound of oxygen with an hypothetical **muriatic base**—murium. Hence, added Lavoisier, muriatic and oxymuriatic acids are related to each other like sulphurous and sulphuric acids. This certainly seemed to be a most plausible explanation of the reactions. Lavoisier's hypothesis was supported by an observation of C. L. Berthollet (1785), who noticed that an aqueous solution of the so-called oxymuriatic acid, when exposed to sunlight, gives off bubbles of oxygen gas, and forms muriatic acid.

J. L. Gay-Lussac and J. Thénard (1809) tried to deoxidize oxymuriatic acid, so as to isolate the hypothetical "muriatic

base " of Lavoisier, by passing the dry gas over red hot carbon, but when the carbon was freed from hydrogen, the attempt to separate from oxymuriatic acid anything but itself was a failure. While favouring Lavoisier's hypothesis, Gay-Lussac and Thénard added : " The facts can also be explained on the hypothesis that oxymuriatic acid is an elementary body." Here, then, are two rival hypotheses as to the nature of oxymuriatic acid —the yellowish-green gas discovered by Scheele !

In 1810, H. Davy tried, without success, to decompose oxymuriatic acid. He found that when hydrogen chloride is heated with metallic sodium or potassium, the metallic chloride and hydrogen are formed, but neither water nor oxygen is obtained. Davy claimed that Scheele's view is an expression of the facts, while Lavoisier's theory, though " beautiful and satisfactory," is based upon a dubious hypothesis. In spite of repeated efforts, nothing simpler than itself has ever been obtained from the gas. " Hence," added Davy, " we have no more right to say that oxymuriatic gas contains oxygen than to say that tin contains hydrogen. Until a body is decomposed it should be considered simple." In order to avoid the hypothesis implied in the term " oxymuriatic acid," H. Davy proposed the alternative term **chlorine** and symbol " Cl "— from a Greek word meaning green. The term " chlorine " is thus " founded upon one of the obvious and characteristic properties of the gas—its colour." Lavoisier's hypothesis died a lingering death, and Davy's view is now generally adopted. Hence **hydrogen chloride is a compound of the two elements, hydrogen and chlorine.**

Whence comes the chlorine in hydrochloric acid ?— Pour a little hydrochloric acid into a test tube, add a little water and a drop of silver nitrate. A white curdy precipitate separates which dissolves in ammonia. Repeat the experiment with sulphuric acid and with sodium chloride. The absence of the white precipitate with the sulphuric acid, and its formation with sodium chloride, makes it probable that **the chlorine in the hydrochloric acid is derived from the sodium chloride,** not the sulphuric acid. If the solution in the retort after heating sulphuric acid with sodium chloride be evaporated until it

crystallizes when cold, and the crystals are dried on a piece of unglazed porous earthenware; dissolved in water; and again crystallized, a compound identical with **sodium sulphate,** or Glauber's salt, is obtained.

Recognition of hydrochloric acid and of chlorides.—Hydrochloric acid—and indeed any soluble chloride, *e.g.* sodium or potassium chloride—gives a white precipitate when added to a solution of silver nitrate. The white precipitate, unlike corresponding precipitates with lead and mercurous nitrates, is soluble in ammonia. The precipitate is called **silver chloride.**

§ 4. Experiments with Hydrogen Chloride.

The action of hydrogen chloride on some oxides.—Let the vessels *A* and *B*, Fig. 74, be attached to the hard glass tube *C*, Fig. 75, containing a porcelain boat with some zinc oxide, and the hard glass tube in turn attached to a dry U-tube cooled by placing it in a jar of cold water, *D*. Pass dry hydrogen chloride over the heated zinc oxide. A liquid collects in the U-tube. Test separate portions of the liquid with blue litmus paper (paper reddens); add a drop of silver nitrate (white precipitate, soluble in ammonia, is formed); add a little zinc, and test the gas which comes off (it is hydrogen). Whatever test be applied, the liquid behaves like hydrochloric acid, *i.e.* a solution of hydrogen chloride in water. It is easy to see the source of the hydrogen chloride; but whence the water? The following is the most reasonable hypothesis: When zinc oxide is heated in a current of hydrogen chloride, water is produced, and any excess of hydrogen chloride passing along, dissolves in the condensed water. The residue in the boat is tested by solution in water, and the addition of silver nitrate (it is zinc chloride). Hence the reaction can be represented:

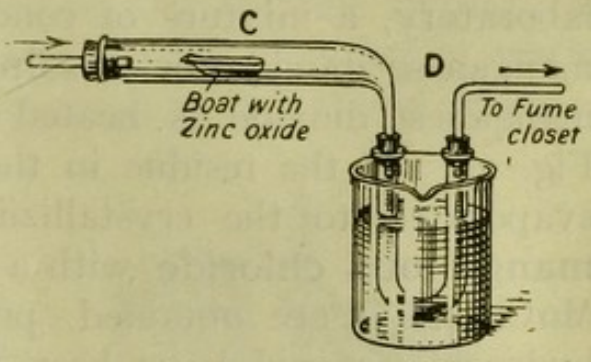


FIG. 75.—The Action of Hydrogen Chloride on Zinc Oxide.

Zinc oxide + Hydrogen chloride → Water + Zinc chloride.

The metal and hydrogen appear to have changed places. Similar results are obtained with calcium oxide, magnesium oxide, etc.

The action of hydrogen on silver chloride.—If dry hydrogen be passed over silver chloride in a boat placed in a tube, *C*, Fig. 75, and some water in the U-tube, metallic silver will remain as a residue in the boat, and most of the hydrogen chloride will be absorbed by the water in the U-tube. By weighing the boat before and after the reduction, the relative combining weights of silver and chlorine can be computed from the data.

§ 5. The Preparation and Properties of Chlorine.

Chlorine, as just indicated, can be prepared by the action of an oxidizing agent upon hydrochloric acid, and in the laboratory, a mixture of concentrated hydrochloric acid and manganese dioxide, or of sulphuric acid, sodium chloride and manganese dioxide, is heated in a flask like that shown at Fig. 73. If the residue in the retort be boiled, filtered, and evaporated to the crystallizing point, rose-pink crystals of **manganous chloride** with a composition corresponding with $MnCl_2.4H_2O$ are obtained, provided manganese dioxide and hydrochloric acid have been used in the preparation of the chlorine. With the sulphuric acid mixture, **sodium sulphate** with **manganese sulphate** crystals are obtained.

Chlorine is a heavy gas, nearly $2\frac{1}{2}$ times as heavy as air, and it is conveniently collected by the upward displacement of air. It cannot be collected over mercury, because it forms a white solid with that element. 100 volumes of water dissolve $22\frac{1}{2}$ vols. of chlorine gas at 20°. A solution of the gas in water is called **chlorine water**. If the water be saturated at 0°, crystals of **chlorine hydrate** separate. Chlorine is sometimes collected over warm water or a warm solution of brine, because less gas is then dissolved than with cold water, and still less with a hot solution of brine. The gas, as we have just seen, is a greenish-yellow colour. When breathed, it attacks the membrane of the nasal passages and the lungs, inducing

symptoms like those of a bad cold. Inhaling alcohol or ammonia produces a little relief. The gas is poisonous, and experiments must be conducted in the fume chamber.

The liquefaction of chlorine.—On March 5, 1823, M. Faraday was operating with chlorine hydrate in a sealed tube. Dr. J. A. Paris called at the laboratory and noticed some oily matter in the tube Faraday was using; he rallied Faraday upon "the carelessness of employing soiled vessels." Faraday started to open the tube by filing the sealed end; the contents of the tube suddenly exploded, and the "oil" vanished. Faraday repeated the experiment, and Dr. Paris, next morning, received the laconic note :—

"Dear Sir,—The *oil* you noticed yesterday turned out to be liquid chlorine.—Yours faithfully, MICHAEL FARADAY."

Chlorine can be condensed to a golden-yellow liquid at 0° and 6 atmospheres pressure. By sealing chlorine hydrate in one limb of a Λ-shaped tube, and placing that leg in warm water while the other leg is immersed in a freezing mixture (Fig. 76) of, say, ice and salt, yellow oily drops of liquid chlorine condense in the cold limb. The liquid boils at −33·6° under atmospheric pressure, and freezes to a pale yellow crystalline mass which melts at −102°. Liquid chlorine is sold commercially in steel cylinders.

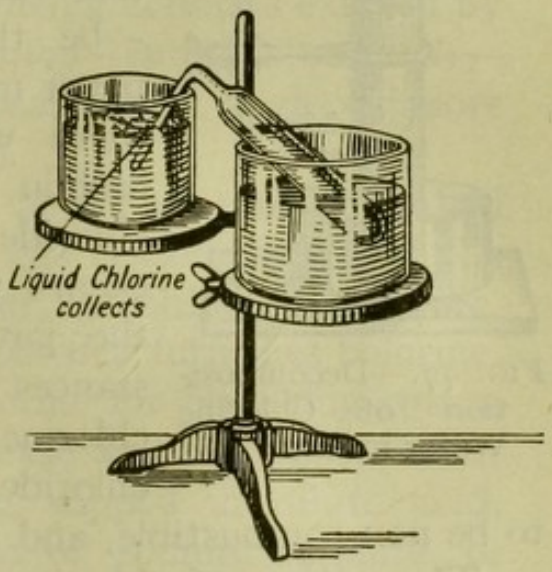


FIG. 76.—Liquefaction of Chlorine.

The action of chlorine on the metals and non-metals.—Chlorine combines with many elements, producing **chlorides.** Powdered antimony gives brilliant sparks when sprinkled in the gas, and antimony chloride is formed; similar remarks apply to arsenic. Phosphorus burns brilliantly in chlorine. A piece of warm copper foil fires spontaneously, forming copper chloride. Zinc and iron form chlorides. Molten sodium in a

deflagrating spoon when plunged into a jar of chlorine burns with a dazzling flame, producing sodium chloride; thus common salt is really a compound of the metal sodium and of the poisonous gas chlorine.

The action of chlorine on hydrogen.—A jet of hydrogen burning in air, continues burning when plunged in a jar of chlorine, and colourless fumes of hydrogen chloride are formed. If jars of chlorine and of hydrogen be placed mouth to mouth, shaken so as to mix the gases, and then separated, a light applied to one will produce a loud explosion, and powdered charcoal sprinkled in the other jar will probably ignite the mixture. In both cases hydrogen chloride is formed. A mixture of equal volumes of chlorine and hydrogen does not form hydrogen chloride in darkness, but in daylight the gases unite slowly, and in sunlight an explosion may occur. Chlorine has so great an affinity for hydrogen that it can remove that element from many combinations. For instance, if a piece of blotting-paper soaked with warm turpentine—a compound of carbon and hydrogen—be thrown into a jar of the gas, the paper may or may not ignite, in any case there will be a copious separation of carbon, and the formation of hydrogen chloride is evidenced by the fuming which occurs when the breath is directed into the jar. Candles and many other substances containing hydrogen burn in chlorine with the formation of hydrogen chloride, so that chlorine is usually said to be non-combustible, and a supporter of combustion.

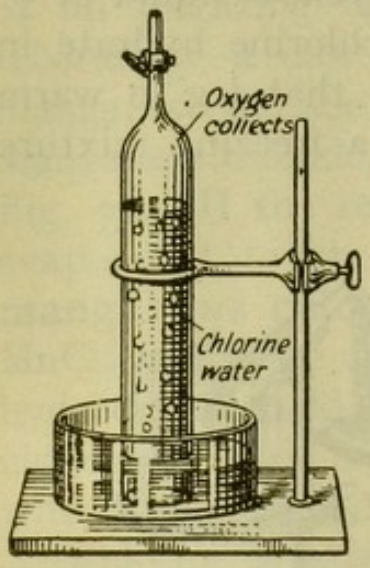


FIG. 77.—Decomposition of Chlorine Water in Light.

The action of chlorine on water.—Even water is decomposed by chlorine, for if a saturated solution of chlorine in water be exposed to sunlight in a tube like that shown in Fig. 77, bubbles of oxygen are developed, as can easily be verified by testing the gas which collects in the upper part of the cylinder. If the stopcock of Fig. 77 be opened, air will of course rush in as the water inside falls to the level of that in the

outer vessel. Hence to displace the oxygen it will be necessary to put the small cylinder into a deeper vessel and depress the cylinder until the level of the liquid is higher outside than inside the cylinder *before* opening the stopcock. Hydrochloric acid is formed at the same time, so that the reaction can be represented :

Water + Chlorine → Hydrochloric acid + Oxygen.

This explains Berthollet's observation, page 137, and the explanation is quite consistent with the elementary nature of chlorine. Moist chlorine is usually regarded as an oxidizing agent, and this reaction explains how the chlorine does its work. Dry chlorine does not oxidize. Moist chlorine bleaches vegetable colouring matters ; for instance, a piece of blue litmus paper when placed in a jar of the gas first turns red, and then bleaches. The **bleaching action** can be illustrated by placing a piece of cloth dyed blue with indigo, or red with, say, alizarine in a jar of dry chlorine, and another piece in moist chlorine. The colour of the latter will be bleached when the colours in the other seem unaffected. Ordinary oxygen does not bleach in this way, and it appears as if the oxidizing action is exerted by the gas *at the moment of its formation—in statu nascendi*— in the **nascent state.** It thus appears as if a gas is more active when it is nascent (being born).

If chlorine be passed over powdered freshly-slaked lime, a considerable amount of the gas is absorbed, and the product is called **bleaching powder, or chloride of lime.** When treated with acids, bleaching powder furnishes chlorine. Bleaching powder is preferred to chlorine for bleaching cotton and linen. The fabric (free from grease and oil) is soaked in an aqueous solution of the powder, dipped in dilute acid, and then washed first in a solution of sodium sulphite to remove the chlorine, and finally in water.

§ 6. The Composition of Hydrogen Chloride.

1. The combining weight of chlorine.—The experiment, Fig. 74, can be conducted quantitatively : (1) The hard glass tube is weighed before and after the experiment ; (2) the volume

of the escaping hydrogen is carefully measured; and (3) precautions are taken to drive out all the air before the metal is heated. There will then be data enough to determine the relative combining weights of chlorine and hydrogen in hydrogen chloride. Careful experiments under different circumstances give: chlorine 35·46; hydrogen 1·008 (oxygen 16).

If hydrogen be passed over many chlorides, *e.g.* silver chloride, page 140, the compound is reduced to metal, and volatile hydrogen chloride is formed. The loss in weight of the vessel containing the metal gives the amount of chlorine which was combined with a given weight of the metal, and if the combining weight of the metal with respect to oxygen is known, the combining weight of chlorine can be computed by simple rule of three.

2. The electrolysis of hydrochloric acid.—When concentrated hydrochloric acid is electrolyzed, a mixture of equal volumes of hydrogen and chlorine is obtained. Carbon electrodes are used because the chlorine slowly attacks platinum. Chlorine gas is also soluble in concentrated hydrochloric acid, so that the acid should be saturated with chlorine before the attempt is made to measure the gaseous products of electrolysis. If the vessel containing the acid is arranged so that the acid about one electrode is connected with the acid about the other electrode by a glass tube junction, Fig. 78, it is only necessary to saturate the solution about one electrode with chlorine. The apparatus illustrated, Fig. 78, devised by L. Meyer, has two limbs filled with concentrated hydrochloric acid, and an electric current is passed until the liquid about one electrode

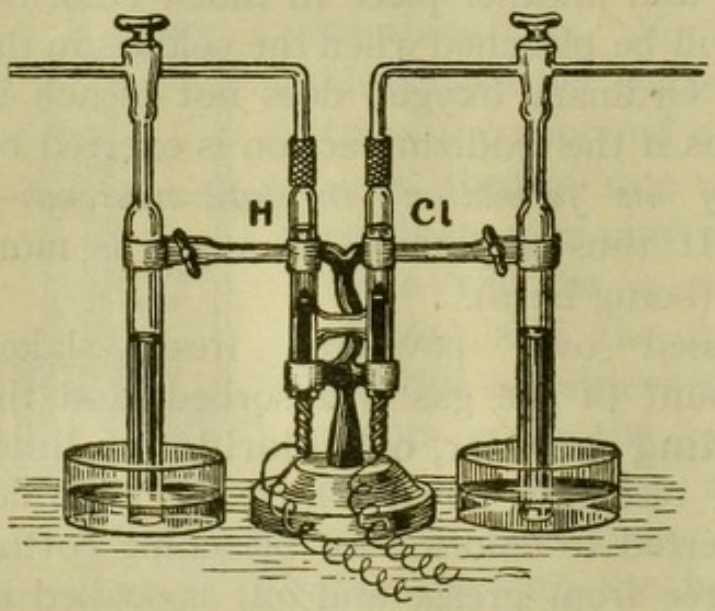


FIG. 78.—Meyer's Apparatus for the Electrolysis of Hydrochloric Acid.

is saturated with chlorine. The two gas receivers are put into communication with the electrolytic vessel by suitably turning the three-way stopcocks. The gas receivers have, of course, been previously filled with liquid—a saturated solution of sodium chloride—by placing a dish of the liquid below each receiver and applying suction at the proper exit tube when the three-way cocks are suitably turned. The gases collect in the tubes at equal rates. The experiment shows that **during the electrolysis of concentrated hydrochloric acid, the volume of hydrogen liberated at the one electrode is equal to the volume of chlorine liberated at the other electrode.** Assuming that the hydrogen chloride dissolved in the water is alone decomposed by the electric current, it follows that **hydrogen chloride contains equal volumes of hydrogen and of chlorine.**

When concentrated acid is diluted with eight volumes of water and electrolyzed, some oxygen is evolved along with the chlorine ; with nine volumes of water, still more oxygen is evolved. The more dilute the acid the greater the amount of oxygen, until, with water acidified with a few drops of acid, no chlorine, but oxygen alone is obtained at the anode, p. 125.

3. The synthesis of hydrogen chloride.—The mixed gases obtained by the electrolysis of concentrated hydrochloric acid in an apparatus resembling Fig. 79 are passed through a stout glass " explosion " tube with a stopcock at each end, *A*, Fig. 79. The tower is packed with lime and glass wool to absorb the chlorine. Instead of using this tower the exit tube may lead to the fume closet. When all the air is displaced, the stopcocks are closed. One of the stopcocks may be opened while the corresponding end of the tube is dipping under concentrated sulphuric acid ; no gas enters or leaves the apparatus. The tube and contents are exposed to sunlight or to the light from burning magnesium. The face

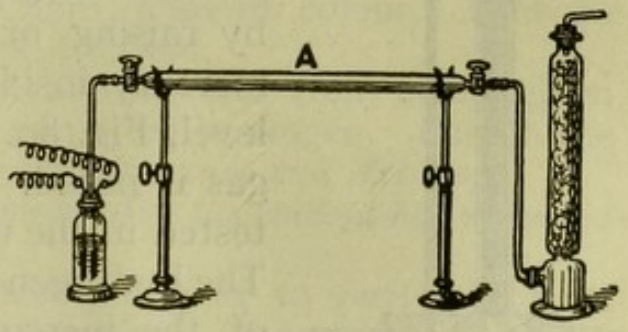


FIG. 79.—Collecting Electrolytic Hydrogen and Chlorine.

must be protected in case the tube should burst during the explosion. When the tube is cold, open one of the stopcocks while the corresponding end is dipping under concentrated sulphuric acid; no gas enters or leaves the tube. This shows that no change in volume has taken place as a result of the explosion. It can be proved that the tube contains nothing but hydrogen chloride by opening the stopcock while the tip of the tube is submerged under water. The hydrogen chloride will be absorbed and water will rise and fill the tube except for a little air (or perhaps a slight excess of hydrogen) which might have been present. This experiment shows that **one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride.**

4. Analysis of hydrogen chloride by sodium amalgam.—A stoppered glass tube—about 70 cm. long and 1·5 cm. in diameter—is filled with dry hydrogen chloride over mercury. Sodium amalgam—*i.e.* a solution of metallic sodium in mercury—is then dropped into the tube, and the tube *immediately* closed with its stopper. The tube is inverted several times in succession, and then opened while its mouth is dipping under mercury. Mercury rushes into the tube, and the residual gas is brought under atmospheric pressure by raising or lowering the tube until the mercury inside and outside is at the same level, Fig. 80. The volume of the residual gas is noted. The residual gas can then be tested in the usual manner. It is hydrogen. The hydrogen chloride reacts with the sodium of the mercury amalgam, forming sodium chloride and liberating hydrogen. The object of using sodium amalgam in place of metallic sodium is one of convenience. This experiment demonstrates that **hydrogen chloride contains half its own volume of hydrogen.**

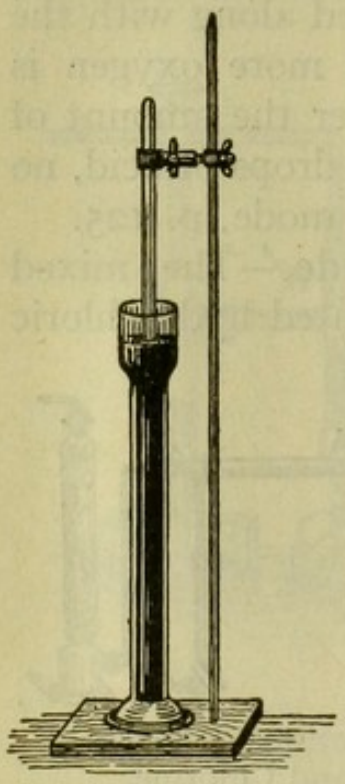


FIG. 80. — Volume Composition of Hydrogen Chloride.

In the case of water, we found two volumes of steam were formed by the union of two volumes of hydrogen with one of

oxygen ; and here we find two volumes of hydrogen chloride are formed by the union of one volume of hydrogen with one volume of chlorine. It is now necessary to investigate these phenomena more closely.

Questions.

1. Plot the solubility of sodium chloride in solutions of hydrochloric acid of different concentrations, given litres of saturated solutions containing in grams :—

Hydrogen chloride	0	9·8	20·8	94·8	102·1	120·6
Sodium chloride	35·8	33·8	31·8	20·0	19·0	16·0

2. How would you prove that hydrochloric acid contains chlorine and hydrogen ?—*London Univ. Matric.*

3. How would you prepare pure and dry hydrogen chloride, and prove by experiment that it contains half its volume of hydrogen and half its volume of chlorine ?—*Science and Art Dept.*

4. Of a certain substance, 0·732 grm. gives 0·861 grm. of silver chloride, AgCl. What is the percentage of chlorine in the substance ? (Ag = 108, Cl = 35·5.)—*Staffs. Intermediate Schol.*

5. Give details of the preparation of chlorine from common salt, and describe what happens when the following are introduced separately into jars of chlorine : (1) a red rose, (2) powdered antimony ; (3) a jet of burning hydrogen.—*Cape Univ.*

6. What meaning have you been taught to attach to the word " salt " ? Discuss the title of hydrogen chloride to be called a salt.—*Science and Art Dept.*

7. Chlorine water exposed to light loses its colour. How do you account for this ?—*Science and Art Dept.*

8. Water, sodium, hydrogen chloride, and iron being given to you, describe four methods for preparing hydrogen. Sketch the apparatus you would use in each case.—*Science and Art Dept.*

The next three problems can be solved after the student has mastered the ideas in the next chapter.

9. Describe the methods you would employ to verify the facts implied by the formula HCl.—*London Univ. Matric.*

10. What volume of hydrogen chloride measured at 15° and 740 mm. is obtained by heating 100 grms. of common salt with an excess of sulphuric acid ? (Na = 23, Cl = 35·5, H = 1.)—*Bombay Univ.*

11. Write an equation representing the action that takes place when a solution of silver nitrate is added to a solution of sodium chloride, and explain the meaning of the equation. If an excess of silver nitrate be added to a solution of 1 lb. of sodium chloride, what will be the weight of each new compound formed ? (N = 14, O = 16, Cl = 35, Na = 23, Ag = 108.)—*Madras Univ.*

CHAPTER IX

Revision of the Atomic Hypothesis

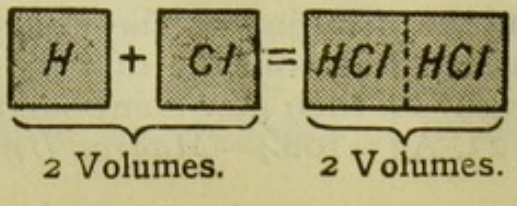
§ 1. Gay-Lussac's Law of Combining Volumes.

A. von Humboldt, the naturalist and explorer, collected samples of air from different parts of the world, and, with the aid of J. F. Gay-Lussac, analyzed them with the idea of finding if the composition of air was variable or constant. As a preliminary, Humboldt and Gay-Lussac investigated the proportion by volume in which hydrogen and oxygen combine, and found the ratio of hydrogen to oxygen, by volume, to be nearly as 2 : 1. If either hydrogen or oxygen was in excess of these proportions, the excess remained, after the explosion, as a residual gas. Humboldt and Gay-Lussac (1805) found :

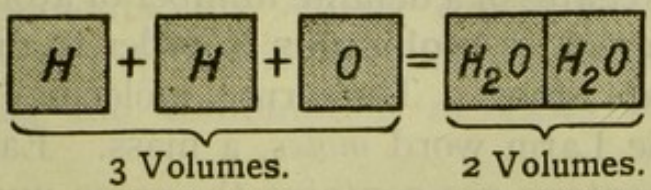
Vols. oxygen.	Vols. hydrogen	Vols. residue.
100	300	101·3 hydrogen
200	200	101·7 oxygen

After making corrections for impurities, etc., in the gases, Gay-Lussac and Humboldt stated that " 100 volumes of oxygen requires for complete saturation 199·89 volumes of hydrogen, for which 200 may be put without error."

Struck by the simplicity of the relation thus found, J. F. Gay-Lussac (1808) followed up the subject by numerous experiments with different gases. As a result, he concluded that " gases always combine in the simplest proportions by volume." For instance, one volume of hydrogen combines with one volume of chlorine, forming two volumes of hydrogen chloride ; this fact can be represented diagrammatically :



Two volumes of hydrogen combine with one volume of oxygen, forming two volumes of water vapour (which condenses to liquid water if the temperature be below 100°).



The experimental results are such as to leave no doubt that Gay-Lussac's generalization is valid, and accordingly, we define **Gay-Lussac's law: When gases react together, they do so in volumes which bear a simple ratio to one another, and to the volume of the gaseous product of the action.** It is assumed, of course, that the initial and final products of the reaction are under the same conditions of temperature and pressure. We traced the remarkable way in which elements combine by weight to a peculiarity in the constitution of matter; so here, we are tempted to make a similar quest.

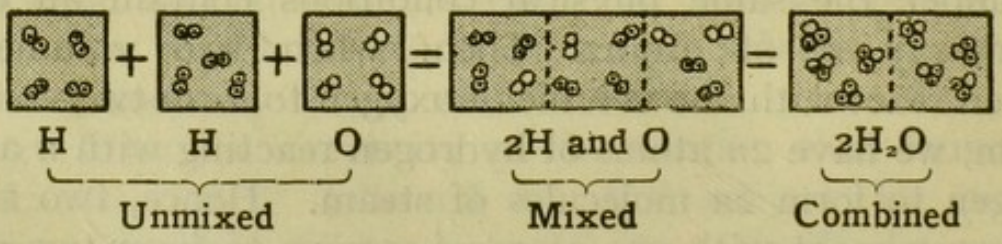
§ 2. Attempts to explain the Law of Combining Volumes.

Gay-Lussac's abortive attempt.—With Gay-Lussac let us make a guess. Assume that equal volumes of the different gases under the same physical conditions contain an equal number—say n—of atoms. Then, when two volumes of hydrogen react with one volume of oxygen to form two volumes of steam, we have $2n$ atoms of hydrogen reacting with n atoms of oxygen to form $2n$ molecules of steam. Hence, two atoms of hydrogen react with one atom of oxygen to form two molecules of steam. In that case, every atom of oxygen must be split into half an atom to make two molecules of steam. This contradicts the fundamental postulate of the atomic theory—atoms are indivisible in chemical reactions. Similar contradictions are encountered in nearly every case of combination between gases: hence Gay-Lussac's guess is untenable; we must try another.

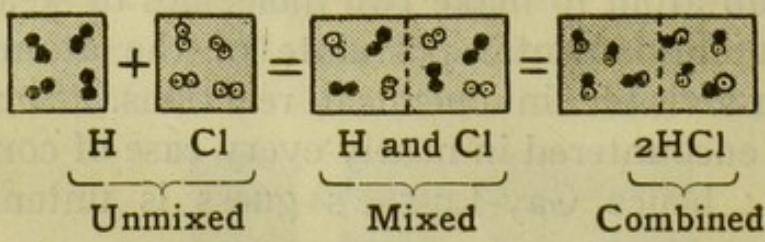
Avogadro's successful attempt.—A. Avogadro (1811)

pointed out that the fallacy in Gay-Lussac's reasoning can be avoided if we distinguish clearly between elementary atoms and the small particles of a gas. Assume that the small particles of a gas are aggregates of a definite number of atoms. Avogadro called these aggregates **molecules** in order to distinguish them from the ultimate atoms. The term " molecule " is the diminutive form of the Latin word *moles*, a mass. Each molecule of any given elementary gas contains the same number and kind of atoms. For the sake of simplicity, assume that each molecule of hydrogen gas is composed of two atoms of hydrogen, and make a similar assumption for oxygen gas. Hence, try Avogadro's hypothesis that **equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules.** Suppose that two volumes of hydrogen contain $2n$ molecules of hydrogen, then one volume of oxygen will contain n molecules. These react to form $2n$ molecules of steam—each molecule of steam contains two atoms of hydrogen and one atom of oxygen.

The idea can be more clearly illustrated by means of the subjoined diagrams. Each square represents one volume of a gas. Each volume contains n molecules. We do not know the numerical value of n, but, for the sake of simplicity, take $n = 4$. It makes no difference to the final conclusion what numerical value we assign to n. Then we have :



Again, with hydrogen and chlorine,



It must not be supposed for one moment that these diagrams

are intended as pictures of the actual molecules. They are to be regarded as aids to the understanding of how Avogadro's hypothesis has led chemists to conclude that the molecules of gaseous elements are really compounded atoms, and how Avogadro's hypothesis reconciles the observed volume relations during the combination of gases with the atomic theory.

We have assumed for the sake of simplicity, that the molecule of water contains three atoms, and that each molecule of hydrogen and oxygen contains two atoms. As a matter of fact, all we can infer from the observed facts is that the molecule of oxygen is split into halves, and in the absence of evidence to the contrary, we must assume for every substance the simplest molecular structure consistent with the observed facts.

Avogadro thus modified the atomic hypothesis, and adapted it particularly to gases. According to Avogadro, **a molecule is the smallest particle of an element or compound which exists free in a gas.** This definition of a molecule is usually extended into: **A molecule is the smallest particle of an element or compound which exists in a free state,** which is an extension of the definition developed on p. 109. Diatomic molecules for gaseous chlorine, hydrogen, and oxygen at ordinary temperatures, satisfactorily explain what we know to-day.

Increasing knowledge has made the hypothesis more and more probable ; it has been tested in hundreds of experiments, and never found wanting. The hypothesis has done such good service in giving a rational explanation of many different phenomena that it has been accepted as a fundamental truth. Avogadro's hypothesis is the basis of the current theory of chemistry.

§ 3. The Relative Weights of the Molecules.

By definition, **the relative density of a gas is a number which represents how much heavier any volume of the gas is than an equal volume of the standard gas**—generally hydrogen, oxygen, or air—measured at the same

temperature and pressure—generally at 0° and 760 mm. pressure. Thus, the relative density of steam is 8·95 (H = 1). This means that any volume, say a litre of steam, is nearly nine times as heavy as the same volume of hydrogen.

By Avogadro's hypothesis, equal volumes of gases contain the same number of molecules, consequently, **the relative density of a gas is proportional to its molecular weight.** If we accept this deduction, it enables us to determine the molecular weights of gases, once we have fixed an arbitrary standard for the density. Cannizzaro's unit: hydrogen = 2, is frequently taken as the standard, or else, as Cannizzaro expressed it, " the quantity of hydrogen contained in a molecule of hydrogen chloride " is taken as unity. **The determination of the molecular weight of a gas is thus deduced to a laboratory measurement—the determination of the relative density of the gas.** The numerical values for the molecular weight and the relative density of a gas referred to hydrogen (= 2) are the same. That is,

$$\text{Molecular weight} = \text{Relative density } (H_2=2) \quad . \quad . \quad (1)$$

If the density be determined, as is frequently the case, with reference to air = unity, then, since the density of air with reference to $H_2=2$ is 28·75; or with reference to $O_2=32$, 28·98, it follows:

$$\text{Molecular weight} = 28{\cdot}98 \times \text{Relative density (air} = 1) \quad . \quad (2)$$

and

$$\text{Molecular weight} = \text{Relative density } (O_2=32) \quad . \quad . \quad . \quad (3)$$

Cannizzaro gave the following numbers, among others, for the densities of the different gases referred to hydrogen taken as 2, or to a semi-molecule of hydrogen taken as unity:

	Relative densities.
Hydrogen	2·0
Ordinary oxygen	32·0
Chlorine	71·0
Nitrogen	28·0
Water vapour	18·0
Hydrogen chloride	36·5

If, therefore, the molecules of hydrogen, oxygen, nitrogen, and

chlorine contain two atoms, the atomic weights of these gases will be half the respective molecular weights. Hence :

TABLE V.—CANNIZZARO'S TABLE OF ATOMIC WEIGHTS.

Element.	Relative density of gas.	Atomic weight. Density ÷ 2.
Hydrogen . . .	2	1·0
Oxygen	32	16·0
Chlorine	71	35·5
Nitrogen	28	14·0

In the case of compounds, if the molecule of hydrogen chloride contains an atom of chlorine and an atom of hydrogen, the molecular weight will be 35·5+1=36·5 ; and the molecule of water vapour containing two atoms of hydrogen and one atom of oxygen, will have a molecular weight of 16+2=18. This can only mean that **the molecule of water vapour must be symbolized H_2O, and the molecule of hydrogen chloride HCl.** Hence, given the molecular weight of a compound gas, and the weights of the atoms of all but one of the elements, it is possible to compute the weight of the atom or atoms of that element in the molecule in question. The *modus operandi* will be discussed in the next two sections.

§ 4. The Formulæ of Compounds.

Since Cannizzaro's time, an enormous number of molecular weights have been determined by the vapour density method. If the molecule cannot be decomposed, we must assume that it is composed of one kind of matter only. If the substance is compound, it must be analyzed so as to find the ratio, by weight, of its component elements referred to the oxygen standard (16). For instance, suppose that the analysis of a gaseous compound furnished :

Nitrogen 82·35 per cent. ; Hydrogen 17·65 per cent.

Using Cannizzaro's atomic weights, Table V., oxygen=16,

hydrogen = 1, and nitrogen 14, the compound has its nitrogen and hydrogen atoms in the following proportion by weight :

$$\frac{82{\cdot}35}{14} \text{ Nitrogen atoms} : \frac{17{\cdot}65}{1} \text{ Hydrogen atoms.}$$

That is,

5·9 Nitrogen atoms : 17·65 Hydrogen atoms.

By hypothesis we cannot have fractions of atoms. The nearest whole numbers are 3 hydrogen atoms for one nitrogen atom. Since the sum of the atoms in the compound must represent the molecular weight, it follows that the molecular weight must be $3n+14n=17n$. Or the molecular weight is 17×1 ; 17×2 ; 17×3 ; . . . or $17n$. The formula is N_nH_{3n}. We can get no further until we know the molecular weight. If the vapour density of the compound (hydrogen=2) be 17, the molecular weight is 17. Hence, $17=17n$, or $n=1$. The compound analyzed can therefore be represented by the formula NH_3.

Example.—Two different compounds have the same ultimate composition, namely : carbon 92·31 per cent., hydrogen 7·69 per cent., but the one has a relative density 26, and the other a relative density 78 (H=2). What is the formula of each compound ? There are $92{\cdot}31\div12=7{\cdot}7$ carbon atoms per $7{\cdot}7\div1=7{\cdot}7$ hydrogen atoms. But we cannot have fractions of atoms, hence dividing by 7·7 we get the ratio 1 : 1. That is, the formula of the compound is C_nH_n. The molecular weights of this series of compounds is $(12+1)n$ or $13n$. If $n=2$, the molecular weight will be 26. Hence, one of the compounds is C_2H_2, and the other is C_6H_6.

In calculating formulæ for substances which cannot be vaporized, and one of the methods to be described later cannot be applied, it is usual to assume that the molecule has the simplest possible formula. In that case the formula is said to be *empirical*. Some prefer to use the term " formula weight " in place of " molecular weight " when the actual molecular weight has not been determined. The **formula weight** of a compound is the sum of the atomic weights of the elements represented in the known or assumed formula of the compound.

Examples.—(1) 10 grams of pure tin when oxidized in air

gave 12·7 grams of oxide. What is the formula of tin oxide? The atomic weight of tin is 119, and of oxygen 16. Hence the ratio: Tin : oxygen = 10 ÷ 119 : 2·7 ÷ 16 = 0·084 : 0·17 = 1 : 2. The formula is therefore written SnO_2, although there is nothing to show why it is not Sn_2O_4; Sn_3O_6; or Sn_nO_{2n}.

(2) A sample of crystallized sodium carbonate furnished on analysis 37·2 per cent. of Na_2CO_3, and 62·8 per cent. of H_2O. What is the formula of the compound? The ratio $Na_2CO_3 : H_2O$ = 37·2 ÷ 106 : 62·8 ÷ 18 = 0·35 : 3·49 = 1 : 10. Hence, the formula is taken as $Na_2CO_3.10H_2O$, although there is nothing to show why it is not some multiple of this, say, $n Na_2CO_3.10n H_2O$.

§ 5. The Relative Weights of the Atoms.

It has already been stated that the conceptions "molecular weight" and "atomic weight" are quite independent of our theories about the nature of atoms and molecules; nor are the conceptions much affected by the actual weights of the atoms and molecules, because the terms under consideration are definite expressions of Avogadro's hypothesis coupled with observed facts. Let us try to fix a value for the atomic weight of chlorine. Suppose that we do not know the atomic weight of chlorine, but that we do know the composition of a number of volatile chlorine compounds as well as their relative densities or molecular weights.

TABLE VI.—MOLECULAR WEIGHTS OF VOLATILE CHLORINE COMPOUNDS.

Volatile chloride.	Molecular weight and vapour density.	Formula of compound: molecular weight = vapour density.	Amount of chlorine in the molecule.
Hydrogen chloride . .	36·5	HCl	35·46
Chlorine	70·9	Cl_2	70·92
Mercuric chloride . .	273·6	$HgCl_2$	70·92
Arsenic trichloride . .	182·1	$AsCl_3$	106·38
Tin tetrachloride . . .	260·2	$SnCl_4$	141·84
Phosphorus pentachloride	208·3	PCl_5	177·30

The smallest combining weight of chlorine in any one of these compounds corresponds with the combining weight

35·46 (oxygen=16), and accordingly this number is taken to represent the atomic weight of chlorine. The atomic and equivalent weights of chlorine have the same numerical value. The atomic weights of a great number of the elements have been determined in a similar manner.

The actual method used in finding the atomic weight of an element thus involves :

(1) An exact analysis of a compound containing the given element ; and consequently the compound investigated must be one which lends itself to exact analysis.

(2) The compound must be one which can be prepared in a highly purified condition.

(3) The compound must be volatile without decomposition, so that its vapour density can be determined.

(4) The compound must contain the smallest proportion of the element under investigation.

These remarks emphasize the importance of examining as large a number of volatile compounds as possible when fixing the atomic weight of an element. If only a small number of compounds be examined, there is always a possibility, and perhaps a probability, that the actual minimum weight does not occur amongst the set of compounds taken. It follows, therefore, that the **atomic weight of an element is the least amount of that element present in any molecule of all its known volatile compounds.** The value so obtained is the maximum possible value ; the real value may afterwards prove to be a submultiple of this. Owing to the fact that the molecular weights of so many volatile compounds of chlorine are known, it is not very probable that the atomic weight of chlorine is less than 35·46.

§ 6. The Elements.

What are the best representative values for the atomic weights of the elements ?—The best available determinations of the value of the oxygen-hydrogen ratio give numbers ranging between 1·005 and 1·008 when the standard of reference is oxygen 16. **All measurements made by man**

are affected by unavoidable errors of experiment; and measurements of the numerical value of all constants differ within certain limits amongst themselves. It is convenient to select one representative value from the set of different observations ranging between the limits 1·005 and 1·008. The majority of chemists have agreed to let the International Committee of Atomic Weights decide what are the best representative values for the atomic weights of all the elements year by year. A careful consideration of all the available evidence considerably reduces the risk of error, and this method, adopted by the Committee, appears to be a fairly satisfactory solution of the problem.

The atomic weights of a few of the more important elements are indicated in the following table. The numbers are those recommended by the International Committee on Atomic Weights. The full table appears inside the front cover of this book.

TABLE VII.—INTERNATIONAL ATOMIC WEIGHTS. O=16.

Elements	Symbol.	Approximate value.	International value.	Element.	Symbol.	Approximate value.	International value.
Aluminium	Al	27	27·1	Iron . .	Fe	56	55·85
Antimony	Sb	120	120·2	Lead . .	Pb	207	207·10
Arsenic .	As	75	74·96	Magnesium	Mg	24	24·32
Barium .	Ba	137	137·37	Manganese	Mn	55	54·93
Bismuth .	Bi	208	208·0	Mercury .	Hg	200	200·6
Boron . .	B	11	11·0	Nickel . .	Ni	59	58·68
Bromine .	Br	80	79·92	Nitrogen .	N	14	14·01
Calcium .	Ca	40	40·07	**Oxygen . .**	**O**	**16**	**16**
Carbon .	C	12	12·00	Phosphorus	P	31	31·04
Chlorine .	Cl	35·5	35·46	Platinum .	Pt	195	195·2
Chromium	Cr	52	52·0	Potassium	K	39	39·10
Cobalt .	Co	59	58·97	Silicon .	Si	28	28·3
Copper .	Cu	63·5	63·57	Silver . .	Ag	108	107·88
Fluorine .	F	19	19·0	Sodium .	Na	23	23·00
Gold . .	Au	197	197·2	Sulphur .	S	32	32·07
Hydrogen	H	1	1·008	Tin . .	Sn	119	119·0
Iodine .	I	127	126·92	Zinc . .	Zn	65	65·37

For ordinary calculations involving the use of atomic weights, most of the atomic weights are rounded off to the nearest whole numbers.

Why is oxygen = 16 taken as the standard?—During the latter part of the nineteenth century, J. Dalton's (1803) standard, hydrogen=1, was used for the atomic weights instead of oxygen=16. Hydrogen was selected because it is the lightest element known. J. S. Stas (1860–65) pointed out that the determination of the atomic weight of an element should be connected with the standard as directly as possible. Very few compounds of the metals with hydrogen are suitable for an atomic weight determination, while nearly all the elements form stable compounds with oxygen. Hence, if hydrogen be the standard, it is necessary to find the exact relation between the given element and oxygen, and then calculate what that relation would be on the assumption that the relation between hydrogen and oxygen is known. Every improved determination of the relation between hydrogen and oxygen would then be followed by an alteration in the atomic weight of every other element whose value, with respect to hydrogen as a standard, has been determined by the indirect process just indicated. The determination of the exact relation between hydrogen and oxygen appears to be more difficult than many other determinations, and hence the majority of chemists think it better to refer the atomic weights of the elements to oxygen=16 as the standard instead of making the atomic weights depend on the more or less uncertain relation H : O.

§ 7. Division of the Elements into Metals and Non-metals.

It is often convenient to divide the elements into two groups —metals and non-metals—and the attempt has been made to mark the metals by a term ending in **um**, and the non-metals by a term ending in **en, in, ine,** or **on.** For example :

METALS.—Aluminium, sodium, magnesium, calcium, etc.
NON-METALS.—Carbon, boron, oxygen, argon, silicon, chlorine, etc.

The idea persists in many, not *all*, of the modern names of the elements. The metals: iron, silver, copper, gold, etc., have alternative Latin terms: *ferrum*, *argentum*, *cuprum*, *aurum*, etc., from which the modern symbols are derived. Originally the term metal meant a "mine," and it was afterwards applied to anything found in a mine—*e.g.* the metals. Like most systems of classification, an exact subdivision is not possible, because some elements exhibit properties characteristic of both classes, and the method is therefore more or less vague, ambiguous, and contradictory. Very roughly, the properties of the metals can be contrasted against the properties of the non-metals as indicated in the subjoined scheme:

TABLE VIII.—THE PROPERTIES OF THE METALS AND NON-METALS CONTRASTED.

Metals.	Non-metals.
1. Form basic oxides.	1. Form acidic oxides.
2. Generally dissolve in mineral acids, giving off hydrogen.	2. Do not usually dissolve easily in mineral acids.
3. Either form no compounds with hydrogen, or form unstable compounds—usually non-volatile.	3. Form stable compounds with hydrogen — these are usually volatile.
4. Solid at ordinary temperature (excepting mercury).	4. Gases, liquids or solids at ordinary temperatures.
5. Usually volatilize only at high temperatures.	5. Excepting carbon, boron, and silicon, the non-metals are either gaseous or volatilize at low temperatures.
6. When in bulk the metals reflect light from polished or freshly cut surfaces.	6. Do not usually reflect light very well.
7. Specific gravity is generally high.	7. Specific gravity generally low.
8. Good conductors of heat and electricity.	8. Bad conductors of heat and electricity.
9. More or less malleable and ductile.	9. Malleability and ductility are not well-defined.

To show how difficult it is to draw a hard-and-fast line

of demarcation between metals and non-metals, the non-metals arsenic and antimony would be classed with the metals if we depended exclusively upon 6, 7, and 8; hence, some introduce a third division—the **metalloids**—to include the hybrids, or elements which have properties characteristic of both the metals and the non-metals. The metals sodium, potassium, magnesium, and aluminium have a low specific gravity, and when potassium was first discovered in 1807, some argued that it could not be a metal because it is light enough to float on water. The non-metals carbon, boron, and silicon are less volatile than most metals. The non-metal hydrogen is a good conductor of heat; and the non-metal graphitic carbon is a good conductor of heat and electricity. Some elements give both basic and acidic oxides. Hence, the division of the elements into metals and non-metals is but a rough system of classification, arbitrarily adopted because it is convenient.

§ 8. The Relation between the Molecular Weights and the Volumes of Gases.

The molecular weight of any gas is numerically equal to the weight of any volume of the gas when the weight of an equal volume of hydrogen under the same physical conditions of temperature and pressure is 2. Two grams of hydrogen, taken as the standard, occupy **22·3** litres at normal temperature —0°—and normal pressure—760 mm. of mercury. Hence, it follows directly from Avogadro's hypothesis that **the molecular weight of any gas, expressed in grams, occupies, approximately, 22·3 litres at 0° and 760 mm. pressure.** Consequently, to find the molecular weight of a gaseous substance, weigh 22·3 litres of the gas at a convenient temperature and pressure; calculate the corresponding volume at 0° and 760 mm. pressure, and calculate by proportion the weight of 22·3 litres.

EXAMPLE.—A litre of gas at 20° and 730 mm. weighs 1·764 grams, what is the molecular weight of the gas? By the method of calculation indicated in the first chapter, one litre of a gas at 20° and 730 mm. pressure contracts to 894·5 c.c. at 760 mm. and 0°.

Hence, if 894·5 c.c. weigh 1·764 grams, 22·3 litres will weigh 43·97 grams. Hence, the molecular weight of the gas is 44.

It must here be mentioned that the number 22·3 is not quite right for all gases. Thus, experiment shows :

Hydrogen.	Oxygen.	Nitrogen.	Chlorine.	Hydrogen chloride.	Carbon dioxide.	Steam (0°, 760 mm.).	Mercury.
22·40	22·39	22·45	22·01	22·22	22·26	22·39	22·55

The deviation from 22·3 can be neglected in ordinary chemical calculations.

The molecular weight of a compound not only tells us a weight, but it also tells us that if the molecular weight be expressed in grams, the gas will occupy 22·3 litres at 0° and 760 mm. Further, **the molecular weight of a gas, expressed in kilograms, occupies, approximately, 22·3 cubic metres at 0° and 760 mm. pressure.** By mere chance, the number of avoirdupois ounces in a kilogram is 35·26, which is very nearly the same as the number of cubic feet in a cubic metre (35·31)—J. W. Richards. The difference is only one-seventh of one per cent. Hence, **the molecular weight of any gas, expressed in avoirdupois ounces, occupies, approximately 22·3 cubic feet at 0° and 760 mm. pressure.** These factors are useful in calculations involving cubic feet, cubic metres, and litres.

§ 9. Chemical Equations, and Chemical Arithmetic.

When the initial and final products of a chemical reaction as well as the composition and proportions of the molecules concerned in the reaction are known, the facts can usually be symbolized in the form of a chemical equation. There are some limitations which will be described later.

1. **The equation indicates the nature of the atoms and the supposed composition of the molecules concerned in the reaction; as well as the proportions of the different molecules in the initial and final products of the reaction.**—For instance, when mercury is heated in air, and mercuric oxide, HgO, is formed, the reaction can be represented in symbols : $2Hg + O_2 = 2HgO$. We here ignore the nitrogen of the air because, so far as we can tell, it plays

no direct part in the chemical reaction. Similarly, when mercuric oxide is heated to a high temperature, it decomposes, forming metallic mercury and oxygen. In symbols, $2HgO = 2Hg + O_2$. The symbol " = " or " → " is used instead of the words " produces " or " forms," and the symbol " + " is used for " together with " on the right side of the " = " or " → " sign, and for " reacts with " on the left side. The latter equation reads : " Two molecules of mercuric oxide, on decomposing, produce a molecule of oxygen and two molecules of monatomic mercury." The number and kind of the atoms of the two sides of the equation must always be the same (persistence of weight).

2. The equation indicates the proportions by weight of the substances concerned in the reaction.—The atomic weight of mercury is 200, and the atomic weight of oxygen is 16, hence the molecular weight of mercuric oxide is 216, and of oxygen 32. The latter equation can therefore be read : " 432 grams (ozs. or tons) of mercuric oxide, in decomposing, form 32 grams (ozs. or tons) of oxygen gas and 400 grams (ozs. or tons) of metallic mercury." Hence, the chemical equation can be employed in all kinds of arithmetical problems dealing with weights of substances formed or produced.

EXAMPLES.—(1) How much mercuric oxide is required to furnish 20 grams of oxygen gas ? Write down the proper equation ; write 432 below the mercuric oxide, and 32 below the oxygen. We are not concerned with the mercury in this problem. Since we read, from the equation : 32 grams of oxygen are furnished by 432 grams of mercuric oxide, one gram of oxygen will be furnished by $432 \div 32 = 13{\cdot}5$ grams of mercuric oxide ; and 20 grams of oxygen will come from $20 \times 13{\cdot}5 = 270$ grams of mercuric oxide.

(2) How much oxygen can be obtained from 30 grams of mercuric oxide ? Answer : $2\frac{2}{9}$ grams.

3. The equation indicates the proportions by volume of the gases concerned in the reaction.—We have seen in the preceding section that if we express

Molecular weight in	Volume at 0° and 760 mm. per molecular weight.
Grams	**22·3 litres.**
Kilograms	**22·3 cubic metres.**
Ozs. (avoir.)	**22·3 cubic feet.**

Consequently, we can express the idea conveyed by the equation, $2HgO = O_2 + 2Hg$, in these words : " 432 grams (kilograms or ozs.) of mercuric oxide will furnish 32 grams (kilograms or ozs.) of oxygen, or 22·3 litres (cub. metres or cub. ft.) of oxygen gas at 0° and 760 mm., and 400 grams of mercury."

EXAMPLES.—(1) What volume of oxygen will be obtained by heating 30 grams of mercuric oxide ? 432 grams of mercuric oxide will furnish 22·3 litres of oxygen gas, hence 30 grams will furnish $30 \times 22{\cdot}3 \div 432 = 1{\cdot}55$ litres of oxygen gas at 0° and 760 mm. pressure.

(2) How much mercuric oxide will be needed for 10 cub. ft. of oxygen gas at 0° and 760 mm. pressure ? Here 22·3 cub. ft. of the gas come from 432 ozs. of mercuric oxide, hence $432 \times 10 \div 22{\cdot}3 = 193$ ozs., or 12 lbs. 1 oz. of mercuric oxide are required.

§ 10. The Relation between Atomic and Combining Weights—Valency.

Observation shows that the relative combining weights of oxygen and hydrogen are very nearly as O : H = 8 : 1 ; and that the atomic weights of oxygen and hydrogen, deduced from the atomic theory and Avogadro's hypothesis, are very nearly as O : H = 16 : 1. In fine, the atomic weight of oxygen is twice its combining weight. For carbon in carbon dioxide, we have the combining weight 3, while the atomic weight of carbon is 12, that is, the atomic weight of carbon is four times the combining weight. In the case of hydrogen and chlorine, the atomic and combining weights are the same. The number of times the combining weight or equivalent is contained in the atomic weight is called the valency of the element. Hence,

$$\frac{\text{Atomic weight}}{\text{Combining weight}} = \text{Valency.}$$

This means that when the combining or equivalent weight of an element is multiplied by an integer representing the valency of the element, the product is the atomic weight. The valencies of hydrogen and chlorine is one ; oxygen two ; and of carbon four.

The meaning of " valency " can be represented another way, for valency also represents a " habit " of an element for

combination ; it has nothing to do with the force called affinity holding the atoms together. The valency of an element is obtained by finding—directly or indirectly—how many atoms of hydrogen can combine with or be replaced by an atom of the given element. The valency of hydrogen is always taken as unity. Hence the definition : **The valency of an element is a number which expresses how many atoms of hydrogen, or of other atoms equivalent to hydrogen, can unite with one atom of the element in question.**

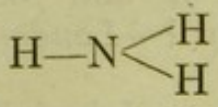
Nomenclature.—With hydrogen and chlorine the atomic and combining weights are the same, and the valency is unity. These elements are accordingly said to be univalent, or monads ; for similar reasons oxygen is bivalent, or a dyad ; nitrogen is tervalent, or a triad ; and carbon is quadrivalent, or a tetrad. The valency of an element is frequently represented by attaching the necessary number, in dashes or Roman numerals, to the top right-hand corner of the symbol for the element, as suggested by W. Odling in 1855. Thus, the symbols H^{I} and Cl^{I} respectively mean that hydrogen and chlorine are univalent ; O^{II} means that oxygen is bivalent ; N^{III} means that nitrogen is tervalent ; and C^{IV} that carbon is quadrivalent. Let us consult a dictionary of chemistry and compile a list of a few compounds with their symbols :—

Univalent.	Bivalent.	Tervalent.	Quadrivalent.	Quinquevalent.	Sexivalent.
$H^{I}Cl^{I}$	$H_2{}^{I}O^{II}$	$H_3{}^{I}N^{III}$	$H_4{}^{I}C^{IV}$	$P^{V}F_5{}^{I}$	$S^{VI}F_6{}^{I}$
$Na^{I}Cl^{I}$	$Hg^{II}O^{II}$	$Fe^{III}Cl_3{}^{I}$	$C^{IV}O_2{}^{II}$	$W^{V}Br_5{}^{I}$	$U^{VI}F_6{}^{I}$
$K^{I}I^{I}$	$Zn^{II}Cl_2{}^{I}$	$P^{III}H_3{}^{I}$	$S^{IV}O_2{}^{II}$	$Mo^{V}Cl_5{}^{I}$	$Mo^{VI}F_6{}^{I}$

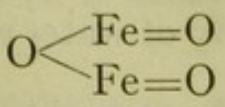
The elements generally combine in such a way that an equal number of valencies are opposed to one another. Some heptads and octads are known.

Structural, graphic, or constitutional formulæ.—The valency of an element is sometimes represented by attaching the necessary number of hyphens to the symbol for the element. This enables the molecules of a substance to be represented by a kind of graphic formula. The symbol for hydrogen will have one hyphen ; oxygen, two ; nitrogen, three ; carbon, four, etc. The symbol for hydrogen chloride then becomes H—Cl ; potassium iodide, K—I ; water, H—O—H ; mercuric

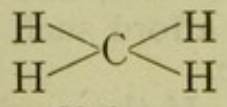
oxide, Hg=O ; a molecule of hydrogen, H—H ; a molecule of oxygen, O=O ; carbon dioxide, O=C=O ; and



Ammonia.



Ferric oxide.



Methane.

Accordingly, the terms " bonds " or " links " are sometimes employed instead of " valencies." Graphic formulæ are to be regarded as conventional artifices for representing the composition of compounds in terms of the atomic theory and Avogadro's hypothesis. The student would err rather seriously if he supposes that the symbol given above for ammonia represents the way the atoms are actually grouped in the molecule of ammonia.

Questions.

1. What law describes the combination of gases by volume ? Give examples. What hypothesis explains the law ? and show how the hypothesis gives rise to a method for expressing the relative weights of molecules.

2. What is meant by the statement that the vapour density of hydrogen chloride ($H_2=2$) is 36·5 ?

3. How can you find the probable molecular weight of a gaseous substance when its composition is not known ?

4. State the general characters of the metals as a class, and show in what respects they differ from the non-metals.—*Science and Art Dept.*

5. What volume of gas under standard conditions is produced when 9 grms. of water are (*a*) decomposed by sodium, (*b*) passed as steam over red-hot iron, (*c*) decomposed by an electric current ?—*Owens Coll.*

6. What weight of oxygen could be obtained by the complete decomposition of 100 grms. of pure potassium chlorate ? If the chlorate used contained 10 per cent. of its weight of potassium chloride, what would be the difference in the amount of oxygen obtained ?—*Science and Art Dept.*

7. Describe two methods of obtaining hydrogen from water. What weight of hydrogen is contained in 250 grms. of water ?—*Science and Art Dept.*

8. A salt has the following composition, calculate its formula : Fe_2O_3, 47·34 per cent. ; SO_3, 47·33 per cent. ; H_2O, 5·33 (Fe=56, S=32, O=16, H=1).

9. A cubic metre of steam, measured at 110° and under standard pressure, is condensed to water at 4°. What would be the bulk of the water, and what volume of hydrogen at (0° and 760 mm.) would afford such a quantity of water when burnt ?—*London Univ. Matric.*

10. If the equivalent of magnesium be 12·1, explain fully how you would proceed in order to find whether or not the equivalent and atomic weights are identical.—*Science and Art Dept.*

11. You are supplied with a small quantity of a colourless liquid. By what six tests, physical and chemical, would you ascertain whether it is only water ?—*Science and Art Dept.*

12. Formerly the atomic weight of oxygen was reckoned as 100. With this standard calculate the atomic weight of hydrogen.—*College Preceptors.*

CHAPTER X

Acids, Bases, and Salts

§ 1. The Origin of the Terms: Acid, Base, and Salt.

The early chemists appear to have gradually learned to arrange certain substances into two groups according as these substances possessed certain qualities in common with vinegar or with wood ashes. The former were called **acids** (from the Latin, *acidus*, sour) on account of their sour taste; and the latter, **alkalies** (from the Arabian, *alkali*, ashes of a plant), because the alkalies were generally obtained by calcining various materials and reducing them to ashes. Towards the end of the seventeenth century, Robert Boyle (1661) summarized the properties of acids as substances which (1) have a sour taste; (2) dissolve many substances (corrosive); (3) precipitate sulphur from alkaline solutions of sulphur; (4) change many vegetable blue colours (*e.g.* blue litmus) red; and (5) lose their acid characteristics when brought into contact with the alkalies. The alkalies were considered to be substances which (1) possessed detergent and soapy properties; (2) dissolved oils and sulphur; (3) restored vegetable colours reddened by acids; and (4) had the power of reacting with acids to produce indifferent substances. These facts can be verified with a few common acids and alkalies; but the student had better not try the tasting test, unless these substances are diluted with a large proportion of water

Acids.	Molecular formulæ.	Alkalies.	Molecular formulæ.
Sulphuric acid . .	H_2SO_4	Sodium hydroxide .	NaOH
Hydrochloric acid .	HCl	Potassium hydroxide	KOH
Nitric acid . . .	HNO_3	Calcium hydroxide .	$Ca(OH)_2$
Acetic acid (vinegar)	CH_3COOH	Aqueous ammonia .	NH_4OH
Carbonic acid . .	H_2CO_3	Barium hydroxide .	$Ba(OH)_2$

The properties of acids and alkalies were thus opposed to one another. Acids and alkalies have "a strong disposition to unite" chemically, for when mixed together, although each constituent of the mixture is itself pungent or corrosive, yet the final result is mild and inoperative. Each component of the mixture neutralizes the activity of the other. The products obtained by the interaction of acids and alkalies are called **salts.** It was soon found that some substances with alkaline qualities did not melt nor change when heated, and were almost insoluble in water—these substances were called **earths.** In 1744, F. G. Rouelle employed the word **base** to include the earths, alkalies, metallic oxides ("calces"), and all substances which produce salts by reacting with the acids.

§ 2. Lavoisier's Oxygen Theory of Acids.

In his study of the properties of oxygen, Lavoisier noticed that when certain elements were burnt in oxygen, the resulting oxide forms an acid with water—*e.g.* carbon, sulphur, and phosphorus. Hence Lavoisier jumped to the conclusion (1777) that "oxygen is an element common to all acids, and the presence of oxygen constitutes or produces their acidity." Lavoisier considered oxygen to be the essential constituent of all acids. The very name *oxygen*, given to this element, was derived from Greek words signifying "the generative principle of acids"—because, said Lavoisier, "one of the most general properties of this element is to form acids by combining with many different substances."

Comparison of the theory with facts.—We have found (1) That hydrogen chloride, the active principle of hydrochloric acid, contains no oxygen; and (2) the products obtained by the combustion of different elements in oxygen gas may be divided into three classes:

(*a*) The elements which have not a metallic appearance—sulphur, charcoal, phosphorus—furnish **acidic oxides,** so named because they give solutions which turn blue litmus red.

(*b*) The elements which have a metallic appearance—

sodium, calcium, magnesium—furnish **basic oxides,** so named because they give solutions which turn red litmus blue.

(*c*) Iron gives an oxide which does not dissolve in water, and it is neutral towards litmus—red or blue.

Collapse of the theory.—With increasing knowledge, Lavoisier's oxygen theory of acids was found to lead to confusion and error, and it was abandoned by chemists when it was recognized that :

1. *Some oxides form alkalies, not acids, with water.—E.g.* sodium, potassium, and calcium oxides. As Humphrey Davy expressed it, " the principle of acidity of the French nomenclature might now likewise be called the principle of alkalescence."

2. *Some acids do not contain oxygen.*—In 1810–11, Humphrey Davy proved that hydrochloric acid is a compound of hydrogen and chlorine, and that no oxygen could be detected in the compound. Hence, added Davy, " acidity is not connected with the presence of any one element." As a result of Davy's work, the acids came to be classed as **hydracids**—acids containing no oxygen, *e.g.* HCl ; and **oxyacids**—acids formed from acidic oxides, *e.g.* H_2SO_4.

§ 3. Neutralization.

A solution of sulphuric acid, like other acids, colours blue litmus red ; and a solution of sodium hydroxide, like other alkalies, colours red litmus blue. It is possible to mix the acid with the alkali so as to furnish a solution which neither tastes like sulphuric acid nor like sodium hydroxide. The mixture on evaporation furnishes a crystalline solid which neither colours blue litmus red nor red litmus blue. The product of the reaction is said to be **neutral,** and the process of neutralization consists in adding an acid to an alkali, or of an alkali to an acid, until a neutral substance is obtained. The result of the reaction is called a **salt.** The salt contains the metal of the base, and the radicle of the acid. The litmus used to determine the point of neutralization is called an **indicator.** It will be observed that the determination of the neutral point

is here referred *arbitrarily* to the behaviour of litmus, because several other indicators besides litmus are available. A few are shown in Table IX.

TABLE IX.—COLOUR CHANGES WITH FOUR INDICATORS.

Indicator.	Acids.	Alkalies.	Neutral.
Litmus	red	blue	purple
Phenolphthalein . .	colourless	pink	colourless
Methyl orange . .	pink	yellow	orange
Red cabbage juice .	red	green	grey

Richter's work.—The above experiment, coupled with numerous others with different acids and bases, have proved that **acids and alkalies unite to form salts in constant proportions.** Otherwise expressed, a definite weight of a base neutralizes a definite amount of a given acid, and conversely. J. B. Richter, in an important study of this subject between 1791 and 1802, demonstrated conclusively that the weights of the various acids which neutralize a certain fixed weight of one of the bases are the same for certain fixed weights of all the bases ; and the same numbers hold good for the neutralizations of the acids by the bases. Consequently, it is possible to assign equivalent numbers to the acids and bases. For instance, using modern data and terms, we can compile a **table of equivalent weights.**

Acids.	Equivalent weight.	Bases.	Equivalent weight.
Hydrofluoric acid . .	20	Ammonium hydroxide .	35
Hydrochloric acid . .	36·5	Calcium hydroxide . .	37
Sulphuric acid . . .	49	Sodium hydroxide . .	40
Nitric acid	63	Potassium hydroxide .	56

The weights of the acids in one column represent the amounts required to neutralize a quantity of any of the bases indicated by the numbers in the other column ; and conversely, the weights of the bases in the second column represent the amounts required to neutralize the quantity of any one

of the acids indicated in the first column. Thus 56 grams of potassium hydroxide will neutralize 20 grams of hydrofluoric acid, 36·5 grams of hydrochloric acid, 49 grams of sulphuric acid, 63 grams of nitric acid, etc.; and 63 grams of nitric acid will neutralize 35 grams of ammonium hydroxide, 37 grams of calcium hydroxide, etc. Richter mixed up much valuable work with several fantastic hypotheses, and he also "cooked" some of his results so that they represent what he thinks he ought to have obtained rather than what he actually observed. Such a procedure is quite antagonistic to the "spirit of science," and made chemists reasonably sceptical about the accuracy of the whole of Richter's work. It was thought, wrongly as it happens: false in one thing, false in all. Consequently, Richter's generalization did not attract the attention it deserved.

§ 4. Acidimetry and Alkalimetry.

A **standard solution** containing a known amount of acid or base per litre is prepared, and just sufficient of this solution is added to neutralize a solution of a given base or acid. The standard solution is poured into a 50 c.c. burette clamped vertically on a stand, and the solution to be neutralized or titrated is mixed with the desired indicator, and placed in a beaker or flask below the nozzle of the burette as illustrated in Fig. 81. The volume of the standard solution required to just change the colour of the indicator is noted. It is possible to calculate the amount of "chemically pure" substances present in the given solution from the volume of the standard solution required for the neutralization. A standard solution containing one equivalent weight of the acid or base in grams per litre is called a **normal solution,** written "N-solution," and a solution containing one-tenth the concentration of a normal solution is called a

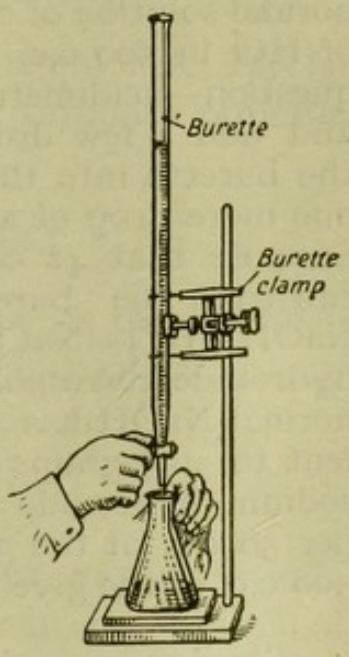


FIG. 81.—Burette in use.

decinormal solution, written "$\frac{1}{10}$ N-solution." **The equivalent weight of a base is that quantity which just completely neutralizes one molecular weight of a monobasic acid; and the equivalent weight of an acid is that quantity which contains unit weight of replaceable hydrogen.** Thus 36·5 grams of HCl per litre gives a normal solution of hydrochloric acid; and 49 grams of H_2SO_4 per litre gives a normal solution of sulphuric acid. Here the molecular weight of the acid is 98·08, and the acid is dibasic, for it contains two replaceable hydrogen atoms; and, by definition:

$$\text{Equivalent of acid} = \frac{\text{Molecular weight of acid}}{\text{Basicity of acid}}$$

that is, the equivalent of sulphuric acid is $98 \div 2 = 49$. A normal solution of sodium hydroxide contains 40 grams of NaOH per litre, and a litre of a normal solution of any acid so far considered will just neutralize a litre of a normal solution of any base.

EXAMPLE.—Suppose that a 50 c.c. burette be charged with a normal solution of sodium hydroxide, and suppose that the amount of HCl in 500 c.c. of a dilute solution of hydrochloric acid be in question—acidimetry—pipette 50 c.c. of the acid into a beaker and add a few drops of litmus. The alkali solution is run from the burette into the acid in the beaker until the addition of but one more drop of acid is needed to change the red litmus to blue. Suppose that 42 c.c. of the normal sodium hydroxide has been run from the burette. The argument runs: The neutralization $NaOH + HCl = NaCl + H_2O$ shows that 40 grams of sodium hydroxide corresponds with 36·5 grams of HCl; and 1000 c.c. of normal NaOH has 40 grams of sodium hydroxide, which is equivalent to 36·5 grams of HCl. Consequently 42 c.c. of the standard sodium hydroxide solution is equivalent to 1·53 grams of HCl per 50 c.c. of the given acid or 15·3 grams of HCl are present in 500 c.c. of the given acid.

Similar remarks apply to the determination of alkalies—alkalimetry—by standard solutions of the acids. This process of analysis is called *volumetric analysis* in contradistinction to *gravimetric analysis*, which involves several weighings during each determination.

§ 5. The Formation of Salts.

Salts can be prepared in many different ways. For instance, by dissolving zinc oxide, ZnO, in sulphuric acid and evaporating the solution until zinc sulphate, $ZnSO_4$, crystallizes out. The reaction is symbolized by the equation :

(1) $$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

This type of reaction represents a **mutual exchange** of elements sometimes called a **double decomposition.** The same remarks apply to the next three reactions. Zinc carbonate, $ZnCO_3$, reacts with the sulphuric acid, producing water, a gas—symbolized CO_2—which escapes from the solution, and zinc sulphate remains behind :

(2) $$H_2SO_4 + ZnCO_3 = ZnSO_4 + H_2O + CO_2$$

If zinc nitrate, $Zn(NO_3)_2$, be treated with sulphuric acid, zinc sulphate, and nitric acid, HNO_3, are formed :

(3) $$Zn(NO_3)_2 + H_2SO_4 = ZnSO_4 + 2HNO_3$$

If silver sulphate, Ag_2SO_4, be treated with zinc chloride, $ZnCl_2$, silver chloride, AgCl, is precipitated and zinc sulphate remains in solution :

(4) $$ZnCl_2 + Ag_2SO_4 = ZnSO_4 + 2AgCl$$

When a solution of copper sulphate, $CuSO_4$, is treated with metallic zinc, metallic copper is precipitated and zinc sulphate remains in solution :

(5) $$CuSO_4 + Zn = ZnSO_4 + Cu$$

This reaction represents a simple **displacement, replacement, or substitution.** The same remarks apply to the action of zinc on sulphuric acid, where zinc sulphate is formed and hydrogen is set free :

(6) $$H_2SO_4 + Zn = ZnSO_4 + H_2$$

Lastly, but not finally, the same salt, zinc sulphate is

produced when sulphur trioxide gas, SO_3, reacts with zinc oxide :

$$(7) \qquad ZnO + SO_3 = ZnSO_4$$

This reaction—**direct combination**—is called a **synthetical reaction,** as contrasted with a **decomposition** or **analytical reaction** typified by the action of heat on mercuric oxide :

$$(8) \qquad 2HgO = 2Hg + O_2$$

The student may wonder why $HgO = Hg + O$ has not been written. It is usual to write the molecular formulæ of the gases when they are known, although we are not always consistent. Substances whose molecular formulæ are unknown are usually represented by the simplest possible empirical formulæ.

It will be observed that in all these reactions, certain groups of elements persist unseparated through a series of chemical changes. For instance, the groups SO_4 and NO_3 during these particular reactions behave *as if* they were elements. A great many similar aggregates are known. In order to fix the idea, the word **radical or radicle** has been devised as a general term for aggregates of atoms which do not separate during certain reactions and fall apart in other reactions. Hence, the definition : **A radicle is a group of atoms which can enter into and be expelled from combination without itself undergoing decomposition.**

§ 6. Acids.

There is no one property which can be used as a decisive test for acidity, since substances not acids may respond to some of the tests as if they were really acids. A review of the list of acids on p. 167 shows that they all contain hydrogen, and accordingly it is sometimes said that **acids are salts of hydrogen.** Hence, we can revise the preceding definition of acids and say that **Acids usually have a sour taste ; are usually corrosive ; redden the blue colour of litmus ; and they all contain hydrogen, part or all of which can be replaced when the acid is treated with a metal, metallic**

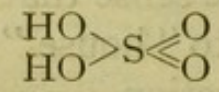
oxide, hydroxide, or carbonate. In deciding whether a given compound is or is not an acid, it is necessary to *balance the evidence* as was done in deciding whether a given substance is or is not a chemical compound.

Salts of the **binary acids** (*i.e.* acids compounded of two elements like hydrochloric acid and hydrofluoric acid) are usually named by dropping the prefix " hydro- " and changing the termination " -ic " into " -ide." Thus the acids just named furnish **chlorides** and **fluorides.** To show what chlorides, etc., are in question, the name of the corresponding element (or elements) is introduced as an adjective. Thus we have sodium chloride, potassium chloride, calcium chloride, etc. The names of the elements are thus used adjectivally in the same sense that the words " stone," " brick," and " wood " prefixed to " house " are adjectival, and indicate the kind of house in question.

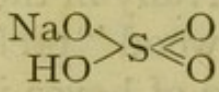
The salts of the **ternary acids** (*i.e.* acids with three elements) are named by changing the " -ic " termination of the acid into " -ate," or the " -ous " termination of the acid into " -ite," and adding the word so obtained to the name of the base or bases forming the salt. Thus sulphuric acid forms **sulphates** —*e.g.* copper sulphate ; sulphurous acid forms **sulphites**—*e.g.* zinc sulphite ; nitric acid, **nitrates**—*e.g.* calcium nitrate ; acetic acid forms **acetates**—*e.g.* sodium acetate ; carbonic acid, **carbonates**—*e.g.* calcium carbonate ; etc.

Normal and acid salts.—It always requires just 56 parts of potassium hydroxide and 40 parts of sodium hydroxide to neutralize 49 parts of sulphuric acid or 36·5 parts of hydrochloric acid (Richter's law). The resulting solutions on evaporation furnish crystals of the corresponding salts : sodium or potassium sulphate or chloride, as the case might be. Suppose just twice as much acid be added to neutral sodium sulphate as was required for its neutralization, and the solution be crystallized. The salt which is obtained has a composition corresponding with the formula $NaHSO_4$, whereas the salt first formed has the composition Na_2SO_4. Hence in the former salt only part of the hydrogen is displaced by sodium. If this salt be neutralized with potassium hydroxide, a crystalline mixed salt with a composition corresponding with $KNaSO_4$ is

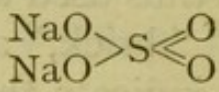
obtained. In the so-called **normal salts** all the displaceable hydrogen of the acid is replaced by the base. For instance, sodium sulphate—Na_2SO_4—is a normal salt because all the replaceable hydrogen of sulphuric acid is displaced by sodium. In **acid salts** only part of the replaceable hydrogen has been displaced by a base, and the salt still contains replaceable hydrogen. For instance, acid sodium sulphate—$NaHSO_4$—contains half the replaceable hydrogen of sulphuric acid, and half as many equivalents of sodium as normal sodium sulphate. If an acid contains two or more replaceable hydrogen atoms, it does not follow that all need be displaced by the same element. These ideas can be illustrated graphically—sulphur sexivalent :



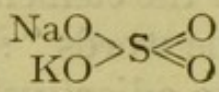
Sulphuric acid.



Acid sodium sulphate.



Normal sodium sulphate.



Sodium potassium sulphate.

Sometimes the term " hydrogen " is used in place of " acid " for the acid salts, and sometimes the prefix " bi- " or " di- " is appended to the term for the acid in the salt. Thus " acid sodium sulphate " is also called " sodium hydrogen sulphate," " sodium bisulphate," as well as " mono-sodium sulphate," etc. The normal salts are sometimes called **neutral salts** in the sense that all the replaceable hydrogen has been " neutralized " or displaced from the acid. These salts, however, are not necessarily neutral to litmus—thus normal zinc and copper sulphates react towards litmus as if they were acids ; borax and normal sodium carbonate react as if they were alkalies. Many acid salts are acid to litmus, *e.g.* sodium hydrogen sulphate ; others are alkaline, *e.g.* sodium hydrogen carbonate ; others again are neutral, *e.g.* disodium hydrogen phosphate.

The number of atoms of hydrogen in one molecule of an acid which are replaceable by a metal, or a radicle, is termed the basicity of the acid. Thus hydrochloric acid—HCl—is monobasic because each molecule of hydrochloric acid contains one replaceable hydrogen atom ; sulphuric acid—H_2SO_4—is dibasic.

Anhydrides.—When sulphur dioxide and phosphorus pentoxide, formed respectively by the combustion of sulphur

and phosphorus in oxygen, are mixed with water, sulphurous and phosphoric acids are formed. The water in these compounds has completely lost its identity. The oxides from which the acids are produced do not contain the elements of water. They are called **anhydrides,** or "acid anhydrides"—from Greek words meaning without water. Thus SO_2 is not only called sulphur dioxide, but it is also sulphurous anhydride; and P_2O_5 is not only phosphorus pentoxide, but phosphoric anhydride. An anhydride can be regarded as the residue left when the elements of water are removed from the oxyacids. Thus sulphuric acid, less water, gives sulphuric anhydride—SO_3—also called sulphur trioxide; sulphurous acid, less water, gives sulphurous anhydride—SO_2. **Thus an anhydride with water forms an acid, and with a base it forms a salt:** $ZnO + SO_3 = ZnSO_4$ (zinc sulphate)

§ 7. Bases.

A base is a substance which usually reacts with an acid to produce a salt and water. For instance, zinc oxide reacts with sulphuric acid to produce zinc sulphate and water: $ZnO + H_2SO_4 = H_2O + ZnSO_4$. Sodium hydroxide reacts with sulphuric acid to produce sodium sulphate and water: $2NaOH + H_2SO_4 = 2H_2O + Na_2SO_4$. The bases include the oxides and the hydroxides of the metals, and certain radicles groups of elements equivalent to a metal. For convenience, certain groups of elements like ammonia NH_3, are called bases, although they form salts by direct addition or combination without the separation of water. Thus ammonia and hydrogen chloride form ammonium chloride: $NH_3 + HCl = NH_4Cl$.

The definition of a base indicated above is highly unsatisfactory because it involves the definition of an acid, and we have just acknowledged that a satisfactory definition of an acid is not yet possible. Hence our definition of a base defines the unknown in terms of the unknown, or the obscure in terms of the obscure.

"Alkali" and "base" are not synonymous terms. **Every alkali is a base, but every base is not an alkali.** The alkaline oxides—*e.g.* potassium oxide—form very soluble hydroxides with marked basic properties; while the oxides of

the alkaline earths—*e.g.* calcium oxide—form sparingly soluble hydroxides with less marked basic properties. The other oxides, as a rule, do not react directly with water, and the hydroxides are made indirectly.

Hydroxides.—The basic oxides are sometimes called "basic anhydrides," and they form hydroxides with water, *e.g.* calcium oxide, CaO—calcium bivalent—with water forms calcium hydroxide, $Ca(OH)_2$:

$$Ca{=}O + H{-}OH \rightarrow Ca\begin{matrix}OH\\OH\end{matrix}$$

The radicle OH is called **hydroxyl,** and its compounds are usually called **hydroxides.** It will be noticed that the hydroxyl OH group is common to all the bases in the same way that replaceable hydrogen atoms are common to all the acids. From this point of view water can be regarded as hydrogen hydroxide, H—OH, analogous with K—OH, potassium hydroxide, and Na—OH, sodium hydroxide. The hydroxides of the non-metallic elements are usually acids, and the hydroxides of the metals are usually bases.

Basic salts.—On comparing the graphic formulæ of the hydroxides of sodium (univalent), lead (bivalent), and bismuth (tervalent) :

Na—OH	$Pb\begin{matrix}OH\\OH\end{matrix}$	$Bi\begin{matrix}OH\\OH\\OH\end{matrix}$
Uniacidic base.	Biacidic base.	Teracidic base.

with the graphic formulæ for mono- and di-basic acids, we naturally inquire if the OH or hydroxyl group can be replaced by acid radicles one by one so as to furnish uni-, bi-, and ter-acidic bases. In the particular examples just selected, the salts :

$Pb\begin{matrix}OH\\NO_3\end{matrix}$	$Pb\begin{matrix}NO_3\\NO_3\end{matrix}$
Basic lead nitrate.	Normal lead nitrate.

are known. The former is called **basic lead nitrate,** the latter **normal lead nitrate,** or simply lead nitrate. Similarly, $Bi(OH)_2NO_3$, **basic bismuth nitrate,** is known. The basic

salts are usually, not always, less soluble in water than the corresponding normal salts.

The preparation of some hydroxides.—The hydroxides of many elements can be made by adding an aqueous solution of sodium or potassium hydroxide to an aqueous solution of the salt, the precipitated hydroxide must then be filtered and washed to get rid of the alkali. The reaction in the case of ferric chloride may be symbolized :

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$$

The precipitates are often gelatinous and slimy, difficult to filter and wash clean. Aqueous ammonia can be advantageously used in place of sodium and potassium hydroxides with the iron, chromium, aluminium salts. Some of the hydroxides are soluble in an excess of the alkali hydroxide—*e.g.* the white coloured hydroxides of aluminium, zinc, lead, and tin. Some of the hydroxides have characteristic colours which enable them to be identified if only one is present.

TABLE X.—SOME CHARACTERISTIC HYDROXIDES PRECIPITATED BY SODIUM HYDROXIDE (INSOLUBLE IN AN EXCESS OF SODA).

Hydroxide.	Colour.	Remarks.
Ferrous, $Fe(OH)_2$ . .	dirty green (white when pure)	Rapidly deepens in tint owing to the absorption of oxygen. The colour becomes black and finally brown—ferric hydroxide.
Ferric, $Fe(OH)_3$ . .	reddish-brown	
Manganous, $Mn(OH)_2$	white	Rapidly darkens in colour owing to the absorption of oxygen, forming the hydrated oxide $MnO(OH)_2$.
Nickel, $Ni(OH)_2$ . .	grass-green	
Cobalt, $Co(OH)_2$ . .	dirty pink	A blue precipitate is first formed. This is a basic nitrate NO_3—Co—OH.
Chromic, $Cr(OH)_3$.	green	Soluble in excess.
Cuprous, CuOH . .	orange	
Cupric, $Cu(OH)_2$ . .	light blue	
Bismuth, $Bi(OH)_3$. .	white	
Magnesium, $Mg(OH)_2$	white	

With mercurous and silver salts, black oxides—Hg_2O and Ag_2O—not hydroxides are produced ; and with mercuric salts, a yellow oxide HgO.

The hydroxides usually decompose when heated, forming the corresponding oxide, *e.g.* $Cu(OH)_2 \rightarrow CuO + H_2O$. The hydroxides of sodium and potassium only decompose at exceedingly high temperatures. The hydroxides, as indicated above, react with acids to form salts.

§ 8. Opposing Reactions.—Guldberg and Waage's Law.

Some of the earlier chemists—*e.g.* Tobern Bergmann (1783)—argued that the result of a chemical change must be in favour of that substance with the stronger affinity. Accordingly, " Affinity Tables " were compiled to show the order in which the different substances would displace one another from a given compound : *If A displaces B from one compound, and B displaces C from another compound, the order of the affinity of these three substances is A, B, C.* It was clearly recognized that this method of work does not give a numerical measure of affinity, but it was thought that relative results were obtained. The suggestion is certainly a good trial hypothesis. Let us compare it with the facts.

We have seen that iron can displace hydrogen from its combination with oxygen ; hence iron has a stronger affinity than hydrogen for oxygen. Similarly, we have seen that hydrogen can displace iron from its combination with oxygen ; consequently, hydrogen has a stronger affinity than iron for oxygen. These two conclusions are contradictory ; both cannot be true. Therefore *the affinity hypothesis must be either false, or some powerful perturbing influence must be at work.*

C. L. Berthollet clearly recognized an important disturbing factor in 1799. Berthollet noticed large quantities of " trona " —sodium carbonate—on the shores of the natron lakes of Egypt. He suggested that the sodium chloride brought down by the rivers was decomposed by the calcium carbonate present on the banks of these lakes :

$$CaCO_3 + 2NaCl = CaCl_2 + Na_2CO_3$$

Berthollet knew, quite well, that this reaction is the reverse of that which usually obtains in the laboratory, for sodium carbonate, when added to calcium chloride, precipitates calcium carbonate :

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl$$

But, added Berthollet, the large masses of calcium carbonate on the banks of these lakes is able to " strengthen " the weak affinity of carbon dioxide for sodium, or of chlorine for calcium. Here Berthollet brings the disturbing factor into bold relief : **Chemical action is conditioned not only by affinity but by the relative concentrations of the reacting bodies.** Excessive concentration can compensate for a weakness of affinity. A chemical reaction can be reversed by changing the concentrations of the reacting bodies. We must apply Berthollet's hypothesis to the reaction under consideration—the action of iron on steam.

At the outset, it will be obvious that we have to deal with two opposing reactions : steam reacts with iron to produce iron oxide and hydrogen :

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

and iron oxide and hydrogen react to produce steam and metallic iron,

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$$

Two independent and antagonistic changes take place simultaneously in the system. The result of the change will be determined by the fleeter reaction. When steam is passed over red-hot iron, the hydrogen does not get much chance, it is carried away into the gas jar before it has had time to set up the reverse change. Similarly, when hydrogen is passed over red-hot iron oxide, the steam does not get a chance, for it is carried away from the reduced iron by the stream of hydrogen.

In order to study the affinity relations between these different substances, they should be heated in closed vessels so that the products of the reaction are not whisked away from the seat of the reaction as soon as they are formed. The result is then very curious. It seems as if the reaction stops after a time.

At any rate, if the temperature remains constant, no further change can be detected, however long the system be heated. In other words, the system assumes a state of equilibrium. Experiment shows that at 200°, the system is in equilibrium when the volume of the steam is to the volume of hydrogen nearly as 20 : 1. Otherwise expressed, for equilibrium at 200° :

$$\frac{\text{Volume of hydrogen}}{\text{Volume of steam}} = \frac{1}{20}$$

If a mixture of one volume of steam and twenty volumes of hydrogen be passed over iron filings or over iron oxide at 200°, no apparent change will occur, for the mixture, after passing through the tube at 200°, will have the same composition as when it entered if no secondary actions occur. If more than this proportion of hydrogen be present at 200°, some iron oxide will be reduced until the equilibrium ratio 1 : 0·05 obtains ; and conversely, if less than this amount of hydrogen be present, iron oxide will be reduced until the equilibrium ratio is obtained. If the temperature be raised, the velocity of the two reactions is altered in such a way that at 440° the volume of steam will be to that of hydrogen nearly as 6 : 1, or as 1 : 0·17 ; and at 1500°, as 1 : 1. This means that if equal volumes of steam and hydrogen be passed over iron filings or iron oxide at 1500°, no change will take place.

Chemical equilibrium is dynamic, not static.—Let us now try to picture what is taking place. Start with metallic iron and steam. At the outset when the reaction is just starting, the velocity of decomposition of the steam will be greatest because the system then contains the greatest amount of reacting substance ; and it has been proved that " the velocity of chemical action is proportional to the concentration of the substances taking part in the reaction." From this moment the velocity of the reaction gradually slows down as the concentration of the reacting steam becomes less and less. On the other hand, the velocity of the reverse action will be zero at the commencement, because none of the reacting hydrogen is then present. The speed of the reverse change will become faster and faster as the product of the first-named reaction—

hydrogen—accumulates in the system. Ultimately, a point will be reached where the velocities of the two opposing reactions will be equal. The one will be balanced by the other. The reaction will appear to have stopped in spite of the fact that more or less of the original substance still remains untransformed. The system is then in a state of equilibrium. No further change will occur, however long the substances be heated under the same physical conditions of temperature, etc. Chemical changes of this kind are conveniently styled **opposing or balanced reactions.** The idea of a dynamic and not a static equilibrium in such reactions was emphasized by A. W. Williamson about 1850, while studying the action of acids on alcohol. He said: "An exchange is constantly going on between the elements of the molecules of a compound, so that each atom of hydrogen in the molecules of HCl present in a drop of hydrochloric acid does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with the other atoms of hydrogen, or, what is the same thing, changing chlorine"; and he further adds that when a system appears to be in equilibrium, that condition "is only kept up by the number of exchanges in one direction being *absolutely* the same in each moment of time as those in the opposite direction."

Reversed pointers "$\rightleftharpoons$" are conventionally used in place of the symbol "$=$" for opposing reactions, so as to indicate that two reactions are proceeding simultaneously "from right to left" and "from left to right." Accordingly, the reaction under consideration is symbolized:

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

Opposing reactions are also called **incomplete or reversible reactions** in contradistinction to **irreversible or complete reactions** typified by the action of zinc on sulphuric acid, where the reaction is completed in one direction and is not opposed by a counter reaction.

It is not difficult to see that the *absolute quantities* of steam, hydrogen, iron, and iron oxide, in the reaction under consideration, do not matter. The velocities of the two opposing

reactions, and therefore **the distribution of the reacting substances, when in equilibrium, is determined by the relative concentrations of the changing substances.** This is conveniently expressed by the number of gram-molecules of each present in unit volume. Thus 18 grams of water—H_2O—per litre represents one gram-molecule; 36 grams of water per litre, two gram-molecules; etc. The concentration of a reacting substance is sometimes (inappropriately) called its **active mass.**

If the surface of the iron were doubled, it is true that twice as many molecules of the black oxide, Fe_3O_4, might be formed in a given time by the decomposition of the steam, but then twice as many molecules of Fe_3O_4 would be decomposed by the hydrogen in the same time. Hence, **the amount or the concentration of the solid can have no appreciable influence on the equilibrium; although it may affect the speed at which the state of equilibrium is attained.** In studying equilibria in gases and liquids, anything which separates in the solid condition is often supposed to be thrown out of the reacting system because the state of equilibrium is independent of the concentration of the solid; and a liquid which separates when studying gaseous equilibria is also supposed to be thrown out of the reacting system. We shall find an analogy in studying the vapour pressure of water in presence of its own liquid. The vapour pressure is independent of the *amount* of liquid water present.

The decomposition and formation of mercuric oxide at different temperatures (p. 29) in a closed vessel is another example of opposing reactions, because the two reactions proceed simultaneously: $2HgO \rightleftharpoons 2Hg + O_2$. Again, when sulphuric acid reacts with sodium chloride, hydrogen chloride is evolved not necessarily because hydrochloric acid is weaker than sulphuric acid, but because hydrogen chloride, being more volatile than sulphuric acid, escapes from the solution as a gas, and thus no longer competes with the sulphuric acid for sodium.

Steam alone is decomposed when heated to a high temperature. The higher the temperature the greater the amount

decomposed, or dissociated into its elements : $2H_2O \rightleftharpoons 2H_2+O_2$. For instance :

Temperature	1000°	1500°	2000°	2500°
Amount dissociated . .	0·00003	0·0221	0·5880	3·98 per cent.

This means that if 100 grms. of steam be heated to 2500°, at atmospheric pressure, the mixture will be in equilibrium when it contains approximately 96 grms. of steam, 3·55 grms. of free oxygen, and 0·45 grm. of free hydrogen. If the temperature be lowered, some of the hydrogen and oxygen will recombine ; if the temperature be raised, more steam will be decomposed. When a substance decomposes with a change in the physical conditions—temperature, pressure, etc.—and the products of decomposition recombine when the original conditions are restored, the process of decomposition is said to be dissociation.

Chemical affinity.—To summarize the preceding discussion : chemical affinity is a convenient term for the driving force which causes certain substances to combine together and to remain united with one another.

1. The force seems to act only when the reacting substances are in contact with one another ; or, as it is sometimes expressed : " when the substances are brought within ' insensible ' distances of each other."
2. It is a selective force, and it seems to act more intensely the more unlike the substances are ; or, as it is sometimes expressed : " like reacts with the unlike."
3. The affinity of an element is not only definite as to *kind*, but it is also definite as to the *quantity* of the elements which enter into combination. The quantitative characteristics are described by the " Laws of chemical combination."
4. The strength of the affinity varies with changes in the conditions of temperature, pressure, light, etc.
5. The effect produced by chemical affinity is modified by the relative concentrations—active masses—of the reacting substances.

Questions.

1. Explain the following terms: analysis, synthesis, mixture, compound, acid, neutral, alkaline.—*Science and Art Dept.*

2. Define the following terms, giving examples in each case: acid, base, acid oxide, basic oxide, basicity, normal salt, acid salt, basic salt.—*Sydney Univ.*

3. Describe a method for decomposing water by means of the electric current, showing what volumes of gases (and what gases) are produced.—*Cape Univ.*

4. Give careful descriptions of two chemical experiments requiring no other materials than at least two of the following: iron, sulphur, water. In each case state the object of the experiment, and give rough sketches of the apparatus you would employ. —*Cape Univ.*

5. Name two substances which when burnt in air or oxygen form basic oxides, two which produce acid-forming oxides, and two which give neutral oxides. Write the formulæ of the six oxides to which your answer refers.—*Science and Art Dept.*

6. What do you understand to be the difference between "equivalent" and "atomic weight"? How would you determine the equivalents of iron and copper?—*Science and Art Dept.*

7. Define the chemical terms "acid," "base," and "salt." Explain how you would ascertain to which of these classes a given substance belongs.—*London Univ. Matric.*

8. In what different ways can salts be obtained? Give illustrative examples.—*London Univ. Matric.*

9. What is meant by the equivalent of an element? In what sense can we use this term correctly with reference to a compound? —*London Univ.*

10. Define the following terms, giving an example in each case: (*a*) oxidation, (*b*) reduction, (*c*) neutralization, (*d*) basicity of an acid, (*e*) acid oxide, (*f*) basic oxide.—*Victoria Univ.*

CHAPTER XI

Chalk, and the Products of its Decomposition

§ 1. Chalk.

When a little wet chalk powder is placed on moist litmus paper, no change occurs, but if the chalk be first heated on a thick piece of platinum foil over a laboratory burner, as indicated in Fig. 82, it undergoes some change, for it will now turn the

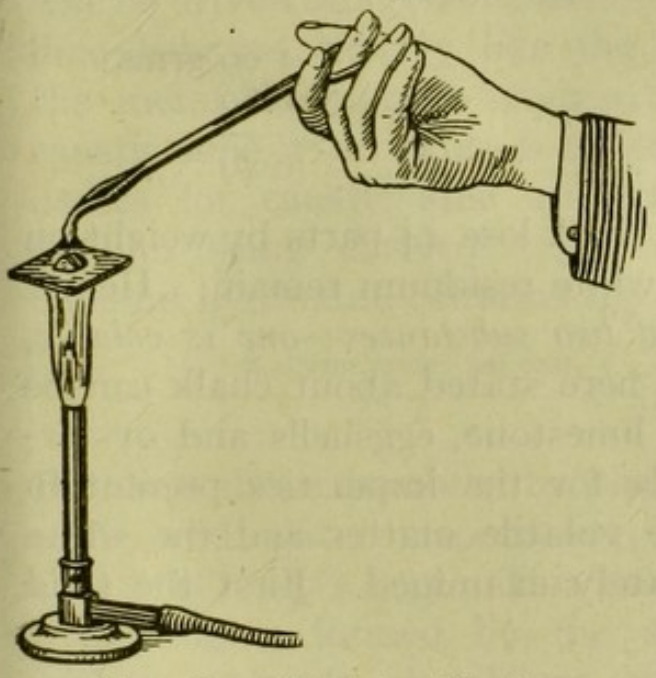


Fig. 82.—Calcining Chalk on Platinum Foil.



Fig. 83.—Desiccator for drying or cooling Substances in a Dry Atmosphere.

colour of the red litmus blue. Let the experiment be repeated on a larger scale. Roast a weighed amount—about a gram—at the high temperature of the Meker's gas flame, Fig. 16, for about half an hour. When the dish has cooled down just below red heat, put it in a **desiccator,** Fig. 83, which has a layer of fused calcium chloride on the bottom to keep the

atmosphere inside free from moisture, and thus prevent the contents of the dish from absorbing atmospheric moisture while cooling. When the dish is cold, weigh again. The following represents results which may be obtained:

Weight of dish and chalk	9·23 grms.
Weight of dish alone	8·14 ,,
Chalk weighs	1·09 ,,
Weight of dish and calcined chalk	8·74 grms.
Weight of dish alone	8·14 ,,
Calcined chalk	0·60 ,,

The dish and contents should be calcined again, and the whole reweighed to make sure that whatever change the chalk undergoes when heated has been completed. In the present case, the reweighing furnished 8·74 grms., showing that the substance was not changed by further heating. Hence,

Weight of uncalcined chalk	1·09 grms.
Weight of calcined chalk	0·60 ,,
Volatile matter	0·49 ,,

Hence, 100 parts by weight of chalk lose 44 parts by weight on calcination, and 56 parts of a white residuum remain. Hence, *chalk is a compound of at least two substances—one is volatile, and the other is not.* What is here stated about chalk can be repeated for calcspar, marble, limestone, eggshells and oyster-shells, when allowance is made for the impurities present in some of these materials. The volatile matter and the white residuum must now be separately examined. First the solid residue.

§ 2. The Solid Residue from the Decomposition of Chalk—Calcium Oxide.

The residue left after the calcination of chalk and related materials has been known to man for a very long time as **caustic lime**—"caustic," by the way, is a Greek term for burnt. Let a drop of water fall from a pipette on to some pieces of caustic lime in a dish, as illustrated in Fig. 84. The

hissing and crackling is followed by a swelling of the lime, which becomes indeed very hot. Clouds of steam arise, and the mass crumbles to a fine powder. The change which the caustic lime undergoes is called **slaking**. If large masses of lime are treated, enough heat is developed to make the water boil. Everything points to a chemical action. If sufficient water be added to "slake" the whole mass, and if the excess of water be driven off by heating the product at about 110° until the weight is constant, the lime will have increased in weight 24·3 per cent. If the slaked lime be heated, caustic lime is reproduced, for all the water will be driven off. The caustic lime behaves exactly like the product obtained by burning the metal calcium in oxygen. The product of the union of caustic lime with water is called **slaked lime**, and alternative names for caustic lime are **quicklime**, or **calcium oxide**—calcium being derived from a Latin word meaning lime. Calcium hydroxide contains the equivalent of :

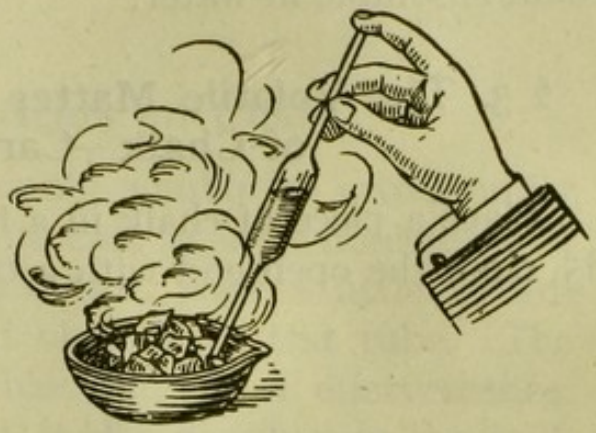


FIG. 84.—The Slaking of Quicklime.

Calcium oxide : per cent.	Water : per cent.
75·7	24·3

Dividing these numbers by the molecular weights of calcium oxide and water respectively, we get the molecular ratio : CaO 1·35 ; H_2O 1·35. This means that a molecule of calcium hydroxide is formed by the union of a molecule of water with a molecule of calcium oxide, and the reaction can be represented in symbols : $CaO + H_2O \rightarrow Ca(OH)_2$. We do not know the molecular weights of calcium oxide and of calcium hydroxide, and accordingly the simplest possible formulæ are used.

If an excess of calcium hydroxide be shaken up with water, the mixture is called **milk of lime** ; if the milk of lime be allowed to settle, and 100 c.c. of the clear liquid at, say, 20° be

evaporated to dryness in a weighed dish, a residual 0·11 grm. of slaked lime will be obtained. Hence, calcium hydroxide is soluble in water. The solution is called **lime-water.** If chalk be substituted for caustic lime in these experiments, no residue is obtained which would justify the inference that chalk is soluble in water.

§ 3. The Volatile Matter from the Decomposition of Chalk—Carbon Dioxide.

Place a piece of chalk in a hard glass or porcelain tube, Fig. 85, close the open end with a cork bored with a hole and fitted

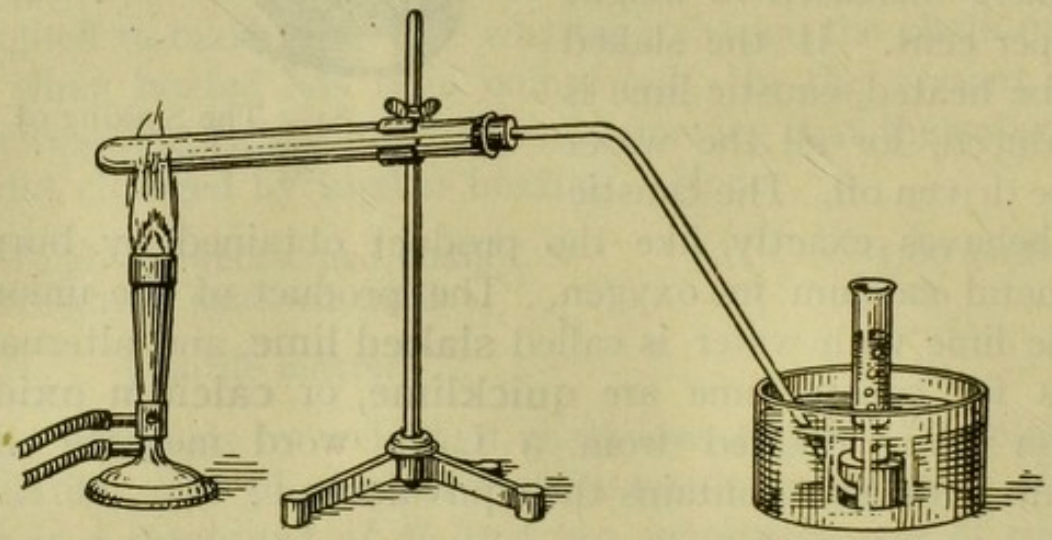


FIG. 85.—Collecting the Gas evolved when Chalk is calcined.

tightly with a delivery tube. Let the delivery tube dip in a gas collecting trough. Heat the porcelain tube with a blast gas flame. Air bubbles from the delivery tube, owing to its expansion inside the tube by the heat. When the chalk has attained a bright red heat, a gas commences to escape from the delivery tube. Place the gas collecting jar in the position (Fig. 85). When the speed of evolution of gas begins to slacken, disconnect the delivery tube, and examine the gas which has collected in the gas jar.

The gas is clear and colourless; a non-supporter of combustion; incombustible; like acids, it reddens a solution of blue litmus, and it renders clear lime-water turbid. These properties recall those of the residual gas obtained when

charcoal is burnt in oxygen; they are indeed characteristic of carbon dioxide. If a jar of the gas be placed over a solution of potassium hydroxide the gas is *all* absorbed. Hence, it is inferred that **during calcination chalk loses 44 per cent. of a volatile gas, which is mainly, if not wholly, carbon dioxide.**

§ 4. The Action of Acids on Chalk.

Although chalk is not appreciably soluble in water under the conditions described above, the case is very different if it be treated with an acid. For instance, pour a little hydrochloric acid upon a little crushed chalk in a test tube. The chalk dissolves with a considerable amount of effervescence. If caustic lime be similarly treated, it also dissolves in the acid, but without effervescence. If a lighted match be thrust into the test tube, the flame will be extinguished, indicating the presence of a colourless gas which—like nitrogen and carbon dioxide—does not itself burn. No such phenomena occur when calcined chalk is treated with the acid in the test tube. If a glass rod be dipped in a solution of clear lime-water, and a drop be held in the gas rising from the test tube, Fig. 86, the drop is rendered turbid, thus distinguishing between nitrogen and carbon dioxide. This result is in harmony with our preceding work. Hence, **carbon dioxide is expelled from chalk when it is calcined, or when it is treated with an acid.**

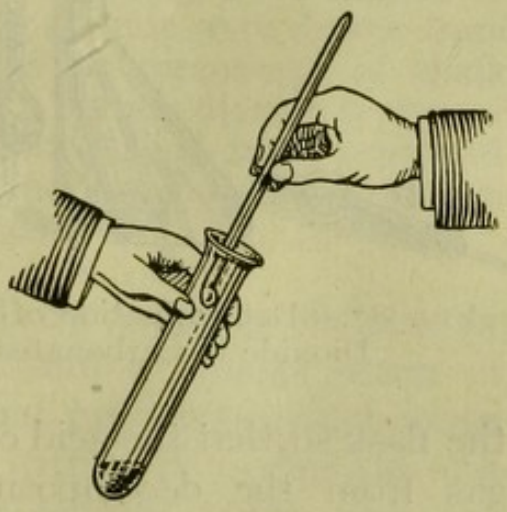


FIG. 86.—Testing the Gas evolved from Chalk and Acid with Lime-water.

Similar results are obtained with acids other than hydrochloric—*e.g.* sulphuric, nitric, and phosphoric acids, vinegar (acetic acid); and with substances other than chalk—*e.g.* powdered marble, limestone, calcspar, eggshells, oyster-shells. The same gas is obtained when several other carbonates are

treated in the same way—*e.g.* iron carbonate, lead carbonate (white lead), etc. Indeed, by arranging the experiment a little differently, the amount of carbon dioxide combined in any given mixture can be determined, because all carbonates are decomposed by acids, although all are not decomposed during calcination.

The amount of gas evolved when chalk decomposes.—A flask with a hollow leg, *a*, Fig. 87, is fitted with a two-hole stopper with tubes arranged as shown in the diagram. The tube on the right contains fused calcium chloride. Weigh the flask first empty and then with 2 to 5 grms. of chalk in the compartment *a*, but not in any other part of the flask. The chalk is best introduced by using a piece of wide glass tubing as if it were a funnel. Pour dilute hydrochloric acid into the larger compartment *b* by means of the bent funnel *A*, Fig. 59, so that no acid comes in contact with the chalk. Fit the tubes in the position shown in the diagram, and weigh. Tilt the flask so that the acid comes in contact with the chalk. The gas from the decomposing chalk must travel through the calcium chloride tube *c* before it leaves the flask, and, in consequence, no moisture is carried away by the escaping gas. When the chalk has ceased to effervesce, remove the glass rod *d*; attach a second calcium chloride tube *D* to the rubber tube *d*, and, by means of another rubber tube, attach *c* to an aspirator. A current of dry air is then drawn through the apparatus in order to expel any carbon dioxide retained by the solution in the flask and in the interior of the flask. In about half an hour, reweigh the flask and contents. The difference in the first pair of weighings represents the weight of the chalk introduced into the flask; and the difference in the second pair of weighings, the weight of the gas expelled

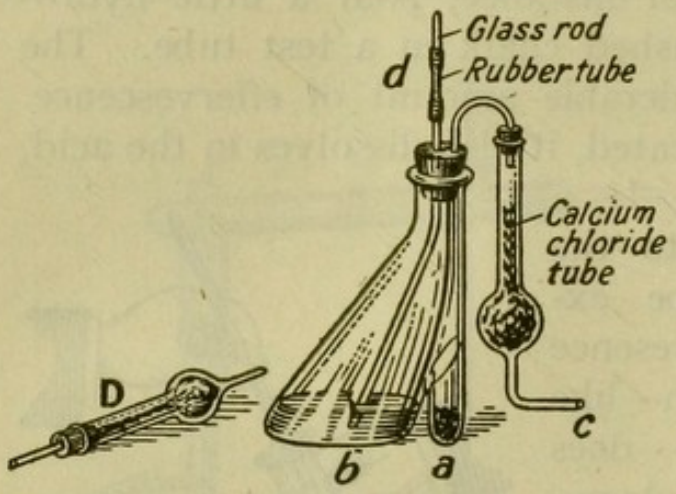


FIG. 87.—Determination of Carbon Dioxide in Carbonates.

from the chalk by the acid. Suppose that 2·77 grms. of chalk were used, and the loss due to the expulsion of gas, 1·22 grms. It follows that **100 grms. of chalk lose nearly 44 grms. of carbon dioxide when attacked by an acid.** Similar numbers were obtained when chalk was converted into caustic lime by calcination. In chemical language, chalk, a compound of carbon dioxide and calcium oxide, is called **calcium carbonate.**

The chemical symbol for carbon dioxide is CO_2, for calcium oxide CaO, and for calcium carbonate $CaCO_3$. The action of heat on calcium carbonate is therefore symbolized: $CaCO_3 = CaO + CO_2$. If marble be substituted for chalk, similar results are obtained, hence it is inferred that chalk and marble have probably the same chemical composition.

EXAMPLE.—Ten grams of dry calcareous clay were treated as just described, and 1·54 grms. of carbon dioxide were driven from the flask by the action of the acid. What percentage of chalk did the clay contain? Since 44 grms. of carbon dioxide represent 100 grms. of chalk, 1·54 grms. of carbon dioxide must represent 3·50 grms. of chalk. Hence 10 grms. of the clay contained 3·5 grms. of chalk. This is equivalent to 35 per cent.

Carbon dioxide is also obtained by treating sodium or potassium carbonate with the acid, and a similar series of experiments leads to the conclusion that **potassium carbonate** is a compound of potassium oxide with carbon dioxide, and **sodium carbonate** a compound of sodium oxide with the same gas. Unlike calcium carbonate, neither potassium nor sodium carbonate is decomposed by calcination.

The solution of chalk in hydrochloric acid can be evaporated to dryness, Fig. 28. The white solid which remains is deliquescent (p. 48), and it even liquefies when exposed to the air owing to the absorption of water vapour from the atmosphere. The salt must contain calcium, and the presence of chlorine can be demonstrated by the silver nitrate test. The salt is called **calcium chloride**, and it is represented by the formula $CaCl_2$.

The synthesis of chalk.—When a solution of carbon dioxide is passed into lime-water, a white precipitate is formed.

The precipitate can be filtered from the solution, Fig. 27, washed and dried. The resulting powder—called **precipitated chalk**—behaves just like chalk itself when treated as described above. A similar precipitate is obtained if sodium or potassium carbonate be added to a solution of calcium chloride. The filtrate from the precipitate when evaporated furnishes crystals of sodium or potassium chloride respectively. Chalk is also obtained if slaked lime or calcium oxide be exposed to the gas.

Mortar.—If clear lime-water be exposed to the air it will soon be covered with a film of calcium carbonate owing to the absorption of carbon dioxide present in the atmosphere. If quicklime be exposed to air it soon crumbles to powder, and it no longer becomes hot when water is poured upon it, the lime indeed is **air slaked** owing to the absorption of water vapour from the atmosphere. Hence, quicklime can be used for drying gases which exert no chemical action upon it. Slaked lime on exposure to the air acquires a hard, stony crust. This is due to the slow combination of the lime with the carbon dioxide of the air. Hence, the use of slaked lime for mortar used for binding bricks and stones in buildings. **The setting of mortar is due to the gradual combination of the lime it contains with the carbon dioxide of the air to form calcium carbonate.** The presence of calcium carbonate in old mortar is easily proved by the acid test. In making mortar, the object of mixing sand or cinders with the slaked lime is: (1) to prevent cracking and shrinkage as the mortar dries; and (2) to make the mortar more porous so that atmospheric carbon dioxide can penetrate the mass with greater facility.

§ 5. Calcium Chloride.—Water of Crystallization.

Crystallized calcium chloride.—If a concentrated aqueous solution of calcium chloride be placed in the desiccator, Fig. 83, and evaporated slowly, crystals will be formed. Let the crystals be carefully dried on blotting-paper and heated in a test tube, Fig. 24; a comparatively large amount of moisture

collects in the cooler part of the tube. This shows that water is probably combined with the crystals in some way. About a couple of grams of the crystals should now be weighed in a weighed dish, and gradually heated to redness ; the dish and contents cooled in a desiccator, and weighed again. The results of an experiment were :

Dried crystals	2·19 grms.
Calcined crystals	1·11 ,,
Water lost	1·08 ,,

Hence the crystalline salt contains 49·3 per cent. of water and 50·7 per cent. of calcium chloride. Divide each of the above numbers by the respective molecular weights of water and calcium chloride. We get 0·46 $CaCl_2$ and 2·74 H_2O. This is nearly equivalent to $CaCl_2.6H_2O$.

There can be little doubt that the water is combined chemically with the calcium chloride, since : (1) a *definite* amount of water combines with the salt ; (2) heat is evolved when the anhydrous (*i.e.* water-free) chloride is mixed with water ; and (3) the general physical properties of the crystalline and the anhydrous salt are different. When the water is expelled from the hydrated crystals, they lose their original crystalline form. The change is very marked with copper sulphate (blue vitriol). It separates from an aqueous solution in blue crystals, and these change to a white powder when the " combined water " is expelled. **The water which unites chemically with a substance in the act of crystallization is called water of crystallization.**

The conventional mode of writing the formulæ of crystalline salts—*e.g.* $CaCl_2.6H_2O$—suggests the idea that water exists in the crystals ready made. As a matter of fact, we have no evidence to show how the water is combined in the salt ; all we really know is that water is a product of the decomposition of the crystalline salt. Crystallization, however, is not necessarily dependent upon the presence of water. Common salt, for instance, is a crystalline salt with no water of crystallization. When crystalline calcium carbonate—calcspar—is calcined it changes to a white powder owing to the loss of carbon dioxide,

not water. Hence, **crystallization is not necessarily dependent upon the presence of water.** Indeed, the white powder which is produced by the decomposition of hydrated salts is in all probability a mass of very tiny crystals.

Questions.

1. Give the chemical composition of burnt lime, limestone, slaked lime, and show how burnt lime may be converted into calcium carbonate.—*Cape Univ.*

2. In what way may it be demonstrated that a profound change takes place when chalk or limestone is converted into lime by " burning " ?—*London Univ.*

3. What products would be obtained, and what weight of each when 10 grms. (*a*) of potassium chlorate, and of (*b*) white marble are separately heated to redness until no further change occurs ? (K=39, Cl=35·5, Ca=40, C=12, O=16).—*Board of Educ.*

4. Chalk weighing 1·09 grms. furnished 0·60 grm. of calcium oxide and 0·49 grm. of carbon dioxide on calcination. Hence compute the simplest possible chemical formula for chalk.

5. Hydrochloric acid containing 10 grms. of hydrogen chloride (HCl) act on zinc, and the same amount of acid acts on calcium carbonate ; what bulk of gas measured at the normal temperature and pressure is produced in each case ?—*Science and Art Dept.*

6. Quicklime is slaked with water, diffused through more water, and filtered. When carbon dioxide is passed through the filtered liquid, it becomes very turbid ; what is the composition of the substance which causes the turbidity ? Give equations.—*Science and Art Dept.*

7. I add sulphuric acid to a white salt, and effervescence occurs ; what may this be caused by, and what tests must I apply to ascertain the nature of the gas which is evolved ?—*Science and Art Dept.*

8. The gas formed by burning carbon in excess of air or oxygen is said to be identical with that which is evolved when an acid is poured on chalk ; in what different ways should these gases be compared in order to test the truth of this statement ?—*Science and Art Dept.*

9. How many grams of carbon dioxide will combine with 100 grms. of calcium oxide to form calcium carbonate ? (C=12, O=16, Ca=40).—*London Univ.*

10. When acids are poured upon either chalk or washing soda, effervescence is observed. Supposing that you were required to demonstrate that both substances yield the same gas, and that this is true whatever acid be used, what experiments would you

show ? Represent the action of some common acids on these substances by equations.—*London Univ.*

11. Describe all that is observed when quicklime is wetted with water. How much water is theoretically required to slake one hundredweight (112 lbs.) of pure lime ?—*Science and Art Dept.*

12. Describe in detail a method for determining approximately the density of carbon dioxide. State clearly how you would account for the value thus obtained in view of the fact that the molecular weight of this substance is 44.—*Board of Educ.*

13. Give the composition of quicklime, limestone, and slaked lime, and explain how you would find out which was which if you were given a sample of each.—*Madras Univ.*

CHAPTER XII

The Gaseous Oxides of Carbon

§ 1. Carbon Dioxide.

Laboratory method of preparing carbon dioxide.—Carbon dioxide is generally made in the laboratory by the action of hydrochloric acid upon calcium carbonate—marble, limestone, or chalk. The reaction has been studied in some detail, and it can be represented in symbols: $CaCO_3+2HCl=CaCl_2+CO_2+H_2O$. Fragments of marble are placed in a Woulfe's bottle, Fig. 42, p. 84, with a quantity of water. Concentrated hydrochloric acid is added by means of the funnel tube. The gas can be collected, like hydrogen over water; or, unlike hydrogen, it can be collected by placing the delivery tube in an empty gas cylinder, with its closed end downwards. The gas is so heavy that it displaces the lighter air upwards out of the jar—hence the term, **collecting gases by the upward displacement of air.** The gas so collected may contain a little air. It is easy to test if the jar is full of gas, because a lighted taper put down into the jar will be extinguished, when it meets the carbon dioxide, as completely as if it had been immersed in water.

Properties.—The gas is invisible; when breathed through the nostrils, it gives a tingling sensation; and it has an acid taste. As indicated above, carbon dioxide extinguishes the flame of burning bodies, and does not itself ignite. The gas can be poured on to the flame of a burning candle as indicated in Fig. 88. The flame will be extinguished. Carbon dioxide is an active agent in many portable "fire extinguishers." Some contain sodium carbonate and sulphuric acid or alum

solution so arranged that they can be mixed and the gases generated under pressure when desired. If enough carbon dioxide is forced on to the burning object the conflagration will be quenched. In " chemical fire engines " the pressure of the gas itself is utilized to force a stream of water on to the burning body.

If a jar of the gas be turned upside down for a minute, the heavy gas falls out and air takes its place. The gas is 1·53 times heavier than an equal volume of air, and it can be poured from

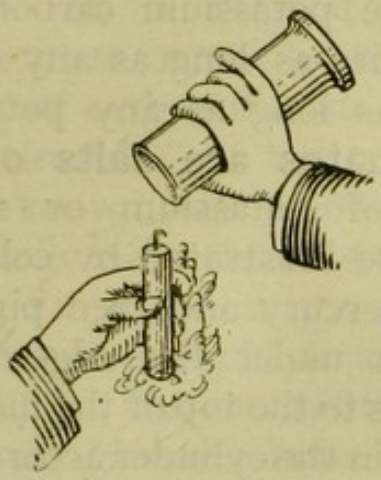


FIG. 88.—Pouring Carbon Dioxide on to the Flame of a Candle.

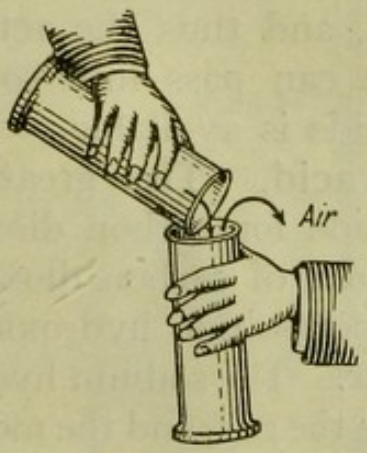


FIG. 89.—Pouring Carbon Dioxide from one Vessel to another.

one vessel to another as indicated in Fig. 89, and the fact that the gas has actually been transferred can be proved by testing each jar before and after the operation with a lighted taper.

The gas is easily liquefied by pumping the gas into steel cylinders kept cold during the process, and cylinders of the liquid are on the market. If the liquid evaporates rapidly solid snow-like carbon dioxide is formed. The solid vaporizes without melting.

A mouse placed in a jar of the gas will be suffocated in a very short time. Carbon dioxide is not particularly poisonous. Its harmful effects are mainly due to suffocation (absence of oxygen).

§ 2. Carbonic Acid and the Carbonates.

A solution of carbon dioxide in water reddens blue litmus (but it does not affect methyl orange), and it is supposed that a

small portion of the absorbed gas unites with the water, producing an acid—**carbonic acid**—which is symbolized H_2CO_3. The water does not dissolve very much gas, and in consequence there cannot be very much acid formed when the gas dissolves in water. If the water contains a base, say potassium hydroxide, a salt of carbonic acid is formed—**potassium carbonate**:

$$2KOH + H_2CO_3 \rightleftharpoons K_2CO_3 + 2H_2O$$

The base thus removes the carbonic acid from the solution, more gas therefore dissolves; more potassium carbonate is formed, and thus the action continues as long as any carbon dioxide can pass into solution or as long as any potassium hydroxide is available. The **carbonates are salts of carbonic acid.** The great avidity of potassium or sodium hydroxide for carbon dioxide may be illustrated by collecting a cylinder of carbon dioxide over mercury and then pipetting some potassium hydroxide solution under the edge of the cylinder. The sodium hydroxide rises to the top of the mercury, absorbs the gas, and the mercury rises in the cylinder accordingly.

How acids decompose carbonates.—When, say, hydrochloric acid is added to the solution of a carbonate, the carbonic and hydrochloric acids both compete for the base, when a certain amount of carbonic acid has been formed, the solution will be saturated, and any further liberation of carbonic acid from the carbonate will be followed by the escape of carbon dioxide from the solution. Hence acids which do not volatilize under the condition of the experiment can expel the carbonic acid from solutions of the carbonates. The carbon dioxide leaves the solution and thus ceases to compete against the hydrochloric acid.

The precipitation of insoluble carbonates.—Suppose now that solutions of potassium carbonate and calcium chloride be mixed together, calcium carbonate will be precipitated, and potassium chloride will remain in solution. Here, again, the two acids—carbonic and hydrochloric—are competing for the two bases—potash and lime—and the bases are distributed between the two acids. Calcium carbonate, however, is almost insoluble, and it is precipitated, and thus the lime and carbonic

acid cease to compete with or for the potash and hydrochloric acid respectively. We thus see how insoluble carbonates are formed as precipitates when soluble salts are treated with soluble carbonates.

The determination of carbon dioxide in a gas.—Solutions of potassium hydroxide are largely employed in analytical work as an absorbent for carbon dioxide. If air charged with carbon dioxide be drawn through a solution of potassium hydroxide in a weighed wash-bottle, the increase in weight represents the weight of carbon dioxide absorbed by the hydroxide. If the volume of the air be known, the amount of carbon dioxide in that volume of air follows at once. Similarly in gas analysis, the amount of carbon dioxide is determined from the contraction in volume which a given volume of the gas suffers after the gas has been in contact with potassium hydroxide. Hempel's burette has been previously described. The mercury in the measuring tube of the gas burette is raised to the zero mark by raising the levelling tube. The burette is then connected with the tube delivering the gas under investigation, and by lowering the levelling tube as much gas as is required can be introduced into the gas burette. Close the rubber tube with a pinch cork. The burette is fitted with a pipette, like that shown in Fig. 90, by means of a piece of glass capillary tube and two pieces of rubber pressure tubing. The cylindrical part of the pipette is filled with short cylindrical rolls of clean iron wire gauze 1 to 2 mm. mesh. The rolls are from 1 to 2 cm. long, and about 5 mm. thick. The cylinder is closed with a rubber stopper, and the pipette is then charged

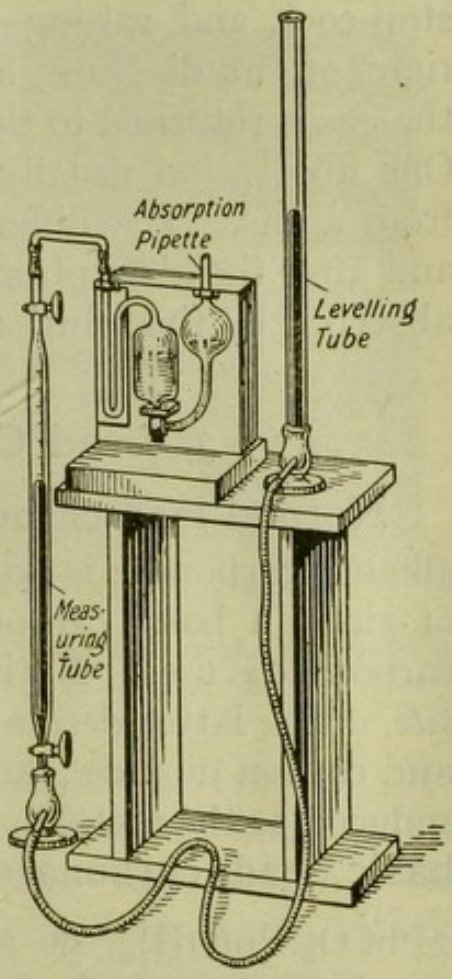


FIG. 90.—Analysis of Gases containing Carbon Dioxide.

with a 33 per cent. solution of potassium hydroxide in water. The iron does not oxidize during a determination, because it is protected by the adherent solution, which also helps to expose a large surface of the absorbent to the action of the gas. The level of the potash solution is adjusted to a fixed point on the U-capillary tube, and connected with the gas burette by thick rubber tubing as indicated above. The measured volume of gas is driven from the burette to the pipette by opening the stop-cock and raising the levelling tube as indicated on the right of the diagram, and, after standing for about a minute, the gas is returned to the burette by lowering the levelling tube. One absorption usually suffices to remove the carbon dioxide from a gas. The difference in the level of the burette before and after the absorption indicates the amount of carbon dioxide absorbed by the solution on the pipette.

§ 3. Lead Carbonates—White Lead.

Normal lead carbonate, $PbCO_3$, is precipitated when an alkali bicarbonate is added to a soluble lead salt as in the case of zinc; a basic carbonate is precipitated if a normal alkali carbonate is used. Native lead carbonate, $PbCO_3$, is called *cerussite*. The latter decomposes at about 200° into lead monoxide and carbon dioxide; and at the same temperature it is readily reduced to the metal by carbon monoxide. The most important **basic lead carbonate** has approximately the composition $2PbCO_3.Pb(OH)_2$, or graphically: $Pb\begin{matrix}CO_3—Pb—OH\\CO_3—Pb—OH\end{matrix}$; it is known as "white lead." White lead is largely employed as a pigment, and in the manufacture of pottery glazes. It is made by a number of different processes.

Stack or Dutch process of manufacturing white lead.—The old so-called Dutch vinegar process—said to have been "old" in 1662—is supposed to give a better product than any other process. There are several modifications, for instance, in Cookson's works, a layer of dilute—3 per cent.—acetic acid is placed in the bottom of a large number of earthenware pots. The pots are placed upon a bed of spent tan bark from the

leather tanning yards. Straps of corrugated sheet lead are placed on the pots, and, above this, boards are rested on the supports *A*, Fig. 91. A layer of tan bark is placed on the boards, and then a second row of pots, "lead straps," etc. The room is nearly filled with pots in this manner. The lead acid pots and tan bark are thus confined in a series of little chambers. In about twelve weeks most of the lead will have been transformed into compact masses of white lead. The stacks are then unloaded and the white lead is crushed in a mill, any lumps of unchanged lead are removed. The white lead is then ground up with water, passed into settling tanks, and finally dried.

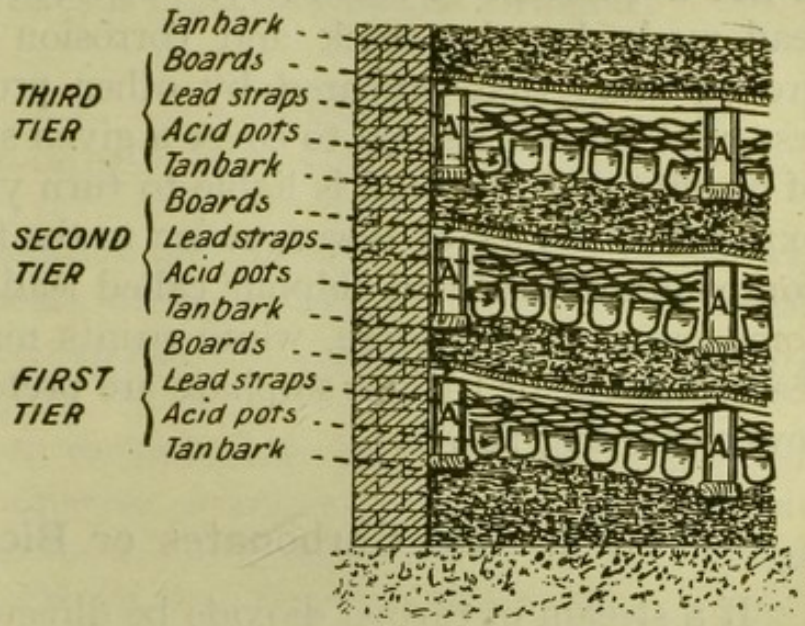


FIG. 91.—Section through Lower Corner of a White-lead Stack (Diagrammatic).

The reactions which occur in each chamber are probably as follows: The heat developed by the decomposition of the tan bark volatilizes the acetic acid which forms a basic lead acetate. The decomposing tan bark furnishes carbon dioxide, which attacks the basic lead acetate to form a basic lead carbonate, and liberates acetic acid. The acid attacks the lead, forming more basic acetate. Thus the cycle continues over and over again.

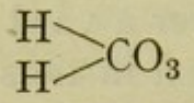
The chamber corrosion process.—In this process straps of metallic lead—about six inches wide and over a yard long—are hung on a series of horizontal bars arranged in tiers. Air, acetic acid vapour, steam, and carbon dioxide are admitted into the chamber maintained at the most favourable temperature for rapid reactions. These are probably similar to those which occur in the stack process. In about forty-five

days the chambers are "drawn," and the corroded lead is washed, etc., as before.

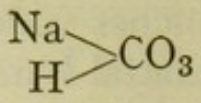
Many other more rapid processes have been proposed. These may furnish a product of equal chemical purity with the stack processes, but the consumer frequently prefers white lead made by the older more expensive stack process. The difference between white lead made by the different processes is not a question of chemistry. The covering power of white lead made by the stack and corrosion processes is usually greater than that prepared by other processes. As a result less white lead is needed to cover a given surface a given degree of opacity. White lead is liable to turn yellow or brown when exposed to the air of towns, owing to the formation of a brown compound of lead and sulphur called lead sulphide, PbS. For some purposes, therefore, white paints made from zinc oxide, lead sulphate, or barium sulphate are preferred in spite of their lower covering power.

§ 4. Acid Carbonates or Bicarbonates.

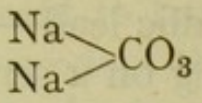
If a stream of carbon dioxide be directed through a concentrated solution of sodium carbonate, crystals of a white solid separate. These can be filtered off, washed in cold water, and dried by placing them on porous earthenware. The composition of the crystals corresponds with the formula $NaHCO_3$. This substance is called **acid sodium carbonate, or sodium bicarbonate.** Anhydrous sodium carbonate has the formula Na_2CO_3, and if crystalline, $Na_2CO_3.10H_2O$. The anhydrous salt is commercial **soda ash,** and the crystalline salt **washing soda.** The relation between carbonic acid, sodium carbonate, and sodium acid carbonate can be represented by the graphic formulæ:



Carbonic acid—
H_2CO_3.



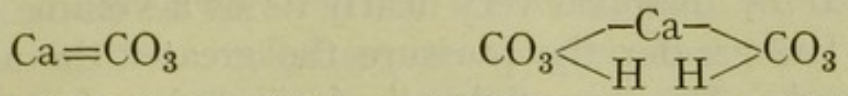
Acid sodium carbonate—
$NaHCO_3$.



Normal sodium carbonate—
Na_2CO_3.

Again, when a stream of carbon dioxide is sent through a solution of clear lime-water, the solution becomes turbid owing

to the separation of calcium carbonate: $Ca(OH)_2+CO_2=CaCO_3+H_2O$. If the current of gas be continued, the precipitate redissolves, and the solution becomes clear again. The phenomenon is explained by assuming that the normal calcium carbonate is but very sparingly soluble, and that a more soluble **calcium acid carbonate** is formed by the prolonged action of carbon dioxide. The composition of the normal and of the acid carbonates is indicated by the formulæ:



Normal calcium carbonate—$CaCO_3$. Calcium acid carbonate—$Ca(HCO_3)_2$.

(*a*) If the clear solution of the acid carbonate be boiled, the precipitate reappears owing to the decomposition of the bicarbonate and the escape of the carbon dioxide $Ca(HCO_3)_2=CaCO_3+H_2O+CO_2$.

The bicarbonate is so very unstable that it cannot be isolated by evaporating the aqueous solution. The sodium acid bicarbonate is a little more stable. It is converted into the normal salt by calcination: $2NaHCO_3=Na_2CO_3+H_2O+CO_2$.

If clear lime-water be poured into the solution, the calcium carbonate is precipitated again, owing to a reaction which can be symbolized: $Ca(OH)_2+Ca(HCO_3)_2=2CaCO_3+2H_2O$.

Sodium bicarbonate is one ingredient of baking powder, and it is hence called **baking or cooking soda.** When mixed with acid sodium tartrate (cream of tartar), which has a feeble acid reaction, carbon dioxide is evolved, this puffs up the dough, hence the term "saleratus" is sometimes applied to this salt—the salt which aerates, from the Latin *sal*, salt; *aer*, air or gas. Effervescent powders like "Seidlitz powder" are mixtures of sodium bicarbonate with tartaric acid, acid sodium tartrate, or some similar acid or salt. The constituents of the mixture react when moistened, liberating carbon dioxide. Sodium bicarbonate is used in medicine for neutralizing the acidity of the stomach.

Sodium carbonate and bicarbonate are hydrolyzed in aqueous solution: $Na_2CO_3+H_2O\rightleftharpoons NaOH+NaHCO_3$, and the latter: $NaHCO_3+H_2O\rightleftharpoons NaOH+H_2CO_3$; and the carbonic

acid dissociates: $H_2CO_3 \rightleftharpoons H_2O + CO_2$. The condition of equilibrium is therefore somewhat complex. As a result of the hydrolysis, aqueous solutions of both carbonates react alkaline towards red litmus, and lose carbon dioxide when warmed, and even on exposure to air.

§ 5. The Effect of Pressure on the Solubility of Gases.

Water at 15° dissolves very nearly its own volume of carbon dioxide. The greater the pressure the greater the amount of gas dissolved. The "sparkling" of aërated waters, like soda water, is due to the fact that these waters have been charged with carbon dioxide at high pressures, and the gas escapes with effervescence when the pressure is reduced by opening the bottle. The bottles are made thick to resist the internal pressure. W. Henry found that for **gases which exert no chemical action on the solvent, water will dissolve the same volume of compressed gas as it dissolves when the gas is under ordinary pressure** (temperature constant). This relation is sometimes called **Henry's law.** Imagine a cylinder, *A*, Fig. 92, graduated into five equal divisions, one division filled with water and the other four with carbon dioxide. The cylinder is closed by a tightly-fitting piston under a pressure of one atmosphere. The water absorbs one volume of carbon dioxide and the piston moves down one division as shown at *B*, Fig. 92. Now start again by placing two atmospheres' pressure on the piston: According to Boyle's law, the gas will be compressed to half its former volume, and the piston will move down to the second division. The water

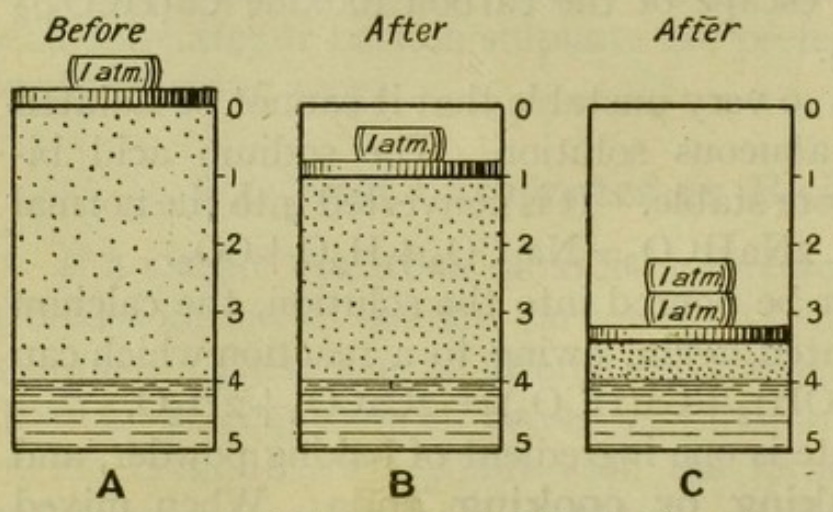


FIG. 92.—Diagrammatic Illustration of Henry's Law.

still absorbs its own volume of gas (Henry's law), and the piston accordingly moves down one division, and *C*, Fig. 92, will represent the equilibrium condition. As a kind of corollary to Henry's law, J. Dalton discovered that **in a mixture of gases which exert no chemical action on the solvent nor on one another, the amount of each gas dissolved will be proportional to its partial pressure.** This is **Dalton's solubility law.**

Application to air.—When air containing, say, 79 volumes of nitrogen and 21 volumes of oxygen, and 0·04 volume of carbon dioxide, is shaken up with water, the amount of each gas absorbed by the water can be approximately computed in the following manner: The relative solubilities are: nitrogen, 0·02; oxygen, 0·04; and carbon dioxide, 1·79. The partial pressure of each gas is proportional to the relative amount of that gas present in a given volume of air. If the pressure of air be just one atmosphere, the partial pressure of the nitrogen will be proportional to $0{\cdot}79 \times 1$; of oxygen, $0{\cdot}21 \times 1$; and of carbon dioxide, $0{\cdot}0004 \times 1$. Hence, the relative amounts of these gases absorbed by the water will be: nitrogen, $0{\cdot}79 \times 0{\cdot}02 = 0{\cdot}0158$; oxygen, $0{\cdot}21 \times 0{\cdot}04 = 0{\cdot}0082$; and carbon dioxide, $0{\cdot}0004 \times 1{\cdot}79 = 0{\cdot}00072$. Hence, 1 c.c. of water dissolves 0·0158 c.c. of nitrogen; 0·0082 c.c. of oxygen; and 0·00072 c.c. of carbon dioxide. The composition of the dissolved gases, if removed from the air by boiling, or exposure to a vacuum, will be: nitrogen, 63·9 per cent.; oxygen, 33·2 per cent.; carbon dioxide, 2·9 per cent. The relatively large solubility of carbon dioxide is counterbalanced by its low partial pressure, otherwise we might expect a heavy rainstorm to remove a great part of the carbon dioxide from the atmosphere.

§ 6. Carbon Dioxide in Nature.

Occurrence of carbon dioxide.—Atmospheric air contains about 0·03 per cent. of its volume of carbon dioxide; and on account of the occurrence of this gas in air, T. Bergmann (1774) called it "acid of air." It issues from the ground in many places both as a gas and in aqueous solution (mineral water)—*e.g.* the water of the Geyser Spring (Saratoga), at Neiderselters

(Hesse-Nassau), Seidlitz (Bavaria), etc. Selters water is, in England, called "Seltzer Water." "Apollinaris" is a natural water from a spring in the valley of Aar near the Rhine, which has carbon dioxide in solution, and it has an acid reaction; if the water has an alkaline carbonate as well as the gas in solution, it will have an alkaline reaction, *e.g.* the waters of Vichy, Neuenahr, etc. The natural waters are often bottled and exported. Apollinaris and other natural mineral waters are imitated artifioially. Soda water, *i.e.* water saturated with carbon dioxide, in the stomach acts as an aperient. Beverages are sometimes "revived" by saturating them with carbon dioxide under pressure.

J. B. Boussingault (1844) estimated that Cotopaxi emitted more carbon dioxide per annum than was generated by life and combustion in a city like Paris. Owing to the fact that carbon dioxide is nearly one and a half times as heavy as air, this gas is inclined to collect as a gas in old deep wells, in valleys, and in depressions in the ground near lime-kilns; and in certain neighbourhoods where carbon dioxide is evolved from volcanoes and fissures in the ground—*e.g.* the Valley of Death (Lake of Laach, Java), where one traveller says the whole bottom is strewn with the skeletons of human beings, animals, and birds which have been asphyxiated in an atmosphere overloaded with carbon dioxide; in the Grotta del Cane (Naples) there is said to be a constant depth of about 18 inches of carbon dioxide on the floor, so that dogs entering the cave are suffocated, while men are safe; and it is also said that grizzly bears have been found suffocated to death by the carbon dioxide which issues from the ground and accumulates in the valley at Death's Gulch (Yellowstone Park, Cal.). If the supply of gas were not kept up, the gas which collects in the low levels would gradually be diffused through the atmosphere. Tremendous deposits of calcium and magnesium carbonates—chalk, limestone, dolomite—as well as smaller deposits of other carbonates, occur in various parts of the world.

Rain-water holding carbon dioxide in solution when percolating through the ground, attacks the magnesian and limestone rocks, and in the water chooses the path of least resistance,

gradually widening courses for itself. Tremendous caves appear to have been cut in limestone rocks in this way in various parts of the world—Manifold Valley (Staffs.), Peak Cavern (Derbyshire), Luray Cavern (Virginia), Mammoth Cave (Kentucky), Adelsberg Cavern (Carniola, Austria), etc. Rain-water percolating through limestone rocks becomes charged with dissolved calcium bicarbonate ; such water in dripping through the roof of a cave or subterranean cavern will be exposed to the air. As a result, some carbon dioxide escapes from the solution, and a certain amount of calcium carbonate is deposited. Each drop of water adds its own little share of calcium carbonate. The deposit grows—maybe on the roof, where it is called a **stalactite** ; maybe on the floor, when it is called a **stalagmite.** All depends upon the time occupied by each drop in gathering and dropping, how fast the carbonate is deposited. Measurements of a stalactite in the Ingleborough Cavern (Yorkshire)—made in 1839 and in 1873—show that it grew at the rate of nearly 0·3 inch per annum. The stalagmite grows upwards from the ground, and the stalactite grows downwards, like an icicle, from the roof. In time, the two may meet and form a pillar. Fig. 93 conveys but little idea of the beauty of some limestone caverns in which stalactites and stalagmites have been growing. The photograph shows stalactites, stalagmites, and pillars which have no doubt been formed in this manner. The San Filippo spring (Tuscany) is said to deposit " lime " at the rate of 12 inches a month, and the spring has formed a bed of limestone rock 250 feet thick, $1\frac{1}{4}$ miles long, and $\frac{1}{3}$ mile wide. The building stone called *travertine* (Tiberstone) is probably a limestone deposited from a mineral spring. The Colosseum and much of ancient and modern Rome were built with this stone.

Hard and soft water.—Add a few drops of a solution of soap in dilute alcohol to distilled water and shake the mixture. A lather is formed which persists for some time when the mixture is allowed to stand. Try the same experiment with a clear solution of calcium bicarbonate, and with a solution of calcium chloride. A lather is formed in these solutions only *after* a considerable amount of the soap solution has been added.

Repeat the experiments with the two last-named solutions, but first boil the solutions; a lather forms quite readily in the calcium bicarbonate solution after it has been boiled, but boiling makes no difference to the calcium chloride solution. **Water in which soap lathers easily is said to be soft water,** and if a lather is produced only after the addition of much soap, the water is said to be **hard water.** Water in which the



FIG. 93.—Stalactites and Stalagmites in the Aranui Caves, N.Z.

hardness is not removed by boiling is said to be **permanently hard water**; and if it is removed by boiling, **temporary hard water.**

Soap is a compound of a fatty acid—chiefly palmitic, oleic, and stearic acids—with a base. So-called **soft-soap** is a potassium salt of the fatty acid, ordinary soap is a **sodium salt, lead plaster** is a lead soap. Both these salts are soluble in water. If a solution of ordinary soap in water is added to a calcium or magnesium salt—say calcium chloride—water, sodium chloride, and an insoluble calcium salt of the fatty acid

is precipitated as a curdy matter. Let NaS represent the composition of ordinary soap, then the reaction with calcium salts can be represented symbolically :

$$\underbrace{2NaS}_{\text{Soluble soap.}} + CaCl_2 = 2NaCl + \underbrace{CaS_2}_{\text{Insoluble curd.}}$$

When all the soluble calcium or magnesium salts have been removed by precipitation, the alkali introduced by the subsequent addition of soap solution is available for cleansing purposes. Hence, hard waters are objectionable in domestic work, because more soap is needed to produce a given result than when soft water is used. The insoluble curd is a *magnesium* or *calcium soap*, and it represents *wasted soap*. Hence the need for removing calcium and magnesium salts from water before it is employed for cleansing purposes. The use of soap for the purpose is too expensive if the water is appreciably hard. By using a soap solution of definite strength, it is possible to compare the hardness of different samples of water by finding how much of the standard soap solution is needed to give a lather which after one minute's shaking persists after the solution has stood for five minutes.

The process of removing lime salts from hard water is called **softening the water.** If the hardness of the water be due to the presence of acid carbonates of calcium or magnesium, mere boiling will soften the water because, as indicated above, the acid carbonates are then decomposed, and the normal carbonates are precipitated. In **Clark's process for softening water** (1841), the necessary amount of milk of lime or lime-water is added to convert all the acid carbonates of lime and magnesium into the normal carbonate. We have here the curious paradox—"add lime to remove lime." The theory of the action has been previously discussed, p. 205.

Hard water may be wholly or partially softened by boiling. Temporary hardness is due to the presence of calcium and magnesium bicarbonates ; permanent hardness is due to the presence of calcium and magnesium chlorides or sulphates. The temporary hardness, if present, can be removed by Clark's lime process, and the permanent hardness may be removed by

the addition of sodium carbonate. The sodium carbonate precipitates the calcium and magnesium as insoluble carbonates : $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$. The water still contains sodium sulphate and sodium chloride, but the presence of a small quantity of these salts is not considered objectionable. Sodium carbonate will remove temporary as well as permanent hardness. The processes used for softening potable hard water may thus be summarized : (1) Distillation ; (2) Boiling ; (3) The addition of lime with or without soda, ash, or other chemicals. The two former are usually too expensive or inconvenient on a large scale. There are other processes in use.

Boiler scale.—The " furring " of kettles, and the formation of " boiler scale," is due to the precipitation of calcium and magnesium salts. Boiler scale is a poor conductor of heat, and hence the efficiency of a boiler which has " scaled " is seriously impaired. The boiler scale and the metal have different rates of contraction and expansion by heat. If the water in the boiler gets low, and the metal overheated, the " scale " separates from the metal. If cold water now runs into the boiler, the scale quickly cools, contracts, and cracks. Water pours through the cracks on to the hot metal ; a large volume of steam is generated, and the sudden pressure may be great enough to burst the boiler. Hard water in steam boilers not only produces " boiler scale," but it may corrode the boiler shell, and cause " foaming " and " bumping." The corrosion and pitting of boilers is usually produced by soft waters from swampy districts which contain organic acids in solution ; by water from mining districts containing mineral acids in solution (*e.g.* sulphuric acid from the oxidation of pyrites, *q.v.*) ; and by water containing magnesium or calcium chlorides and nitrates. A great many nostrums for preventing boiler scale and corrosion have been proposed. In some, the water is treated before it enters the boiler ; in others, the water is softened in the boiler itself. Whatever agent be used, it must be cheap ; easily applied ; yield no acid when used ; and precipitate the salts which make the water hard in a flocculent powdery condition easily blown from the boiler.

§ 7. The Composition of Carbon Dioxide.

1. Composition by weight.—A weighed amount of carbon —diamond, graphite, etc.—is burnt at a red heat in a platinum boat, placed in a porcelain tube, *C*, Fig. 145. The tube also contains a layer of hot copper oxide. A stream of oxygen purified from carbon dioxide by passing through wash-bottles, *B*, containing potassium hydroxide and sulphuric acid, is led over the hot carbon. The resulting gas, on passing through the hot copper oxide, is all oxidized to carbon dioxide. The carbon dioxide which is absorbed in weighed potash bulbs, *D* and a tube *E* containing soda lime in one leg, and calcium chloride in the other. The platinum boat containing the carbon is weighed before and after the experiment, so that due allowance can be made for any ash present in the original sample of carbon. One gram of charcoal required 2·6662 grams oxygen to burn it all to carbon dioxide. Hence, the combining ratios of carbon and oxygen in carbon dioxide are 8 grams of oxygen per 3·001 grams of carbon; or 11·001 grams of carbon dioxide; or, 32 grams of oxygen require 12·003 grams of carbon to form 44·003 grams of carbon dioxide.

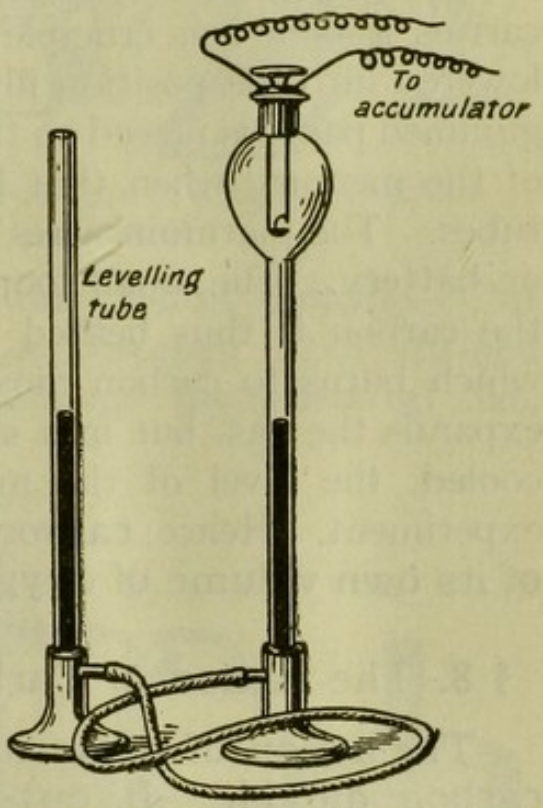


FIG. 94.—Volume Synthesis of Carbon Dioxide.

2. Relative density of carbon dioxide.—This constant, determined by weighing an empty globe, and then the globe filled with gas (Fig. 94), shows that if the density of oxygen is 32, that of carbon dioxide is 44·26. Hence, the molecular weight of carbon dioxide is nearly 44·26. This is only possible if 12 parts of oxygen are combined with 32 parts of oxygen by weight. With the atomic weight of oxygen 16, and carbon 12·003, it follows that the formula of carbon dioxide must be CO_2.

3. Composition by volume.—The volume of a solid is negligibly small in comparison with the volume of the same substance in the gaseous state. Hence, if solid carbon dioxide be burnt in oxygen, Avogadro's hypothesis would lead to the inference that one volume of oxygen will form an equal volume of carbon dioxide :

$$\underset{\text{(Solid)}.}{C} + \underset{2\text{ vols.}}{O_2} = \underset{2\text{ vols.}}{CO_2}$$

This is best illustrated experimentally by means of the eudiometer, Fig. 94, charged with mercury. The bulb of the right tube, Fig. 94, is charged with oxygen ; and the stopper which carries a bone-ash crucible containing a chip of charcoal, is lowered into the position illustrated in the diagram. A slip of gummed paper is placed on the right tube, indicating the position of the mercury when that liquid is at the same level in both tubes. The platinum wires are connected with an accumulator or battery. The small loop of platinum wire in contact with the carbon is thus heated red hot. This ignites the carbon, which burns to carbon dioxide. The heat of the combustion expands the gas, but in a short time, when the apparatus has cooled, the level of the mercury is the same as before the experiment. Hence, **carbon dioxide contains the equivalent of its own volume of oxygen.**

§ 8. The Action of Carbon Dioxide on some Metals.

The action of potassium, calcium, and magnesium on carbon dioxide.—If carbon dioxide be heated in contact with metallic potassium, sodium, calcium, or magnesium, the metals are oxidized, and the carbon of the gas separates in a solid condition. Pass carbon dioxide from a suitable apparatus, *A*, Fig. 95, through a washing bottle, *B*, containing sulphuric acid, and then into a bulb of hard glass, *C*, containing a few shavings of metallic magnesium, potassium, or calcium. When all the air has been expelled from the apparatus, the bulb is heated. The metal burns vigorously in an atmosphere of carbon dioxide, and the gas is decomposed, forming black carbon, and calcium carbonate. The reduction of the carbon

dioxide is symbolized by the equation: $CO_2 + 2Ca \rightarrow 2CaO + C$; and the calcium oxide combines with the excess of carbon dioxide, if the temperature is not too high, forming the carbonate, $CaO + CO_2 = CaCO_3$. Is the black deposit really carbon? Clean the tube *C* from carbon dioxide by means of a current of air, then heat the bulb while the air is still passing. The formation of carbon dioxide by the combustion of the black carbon answers the question.

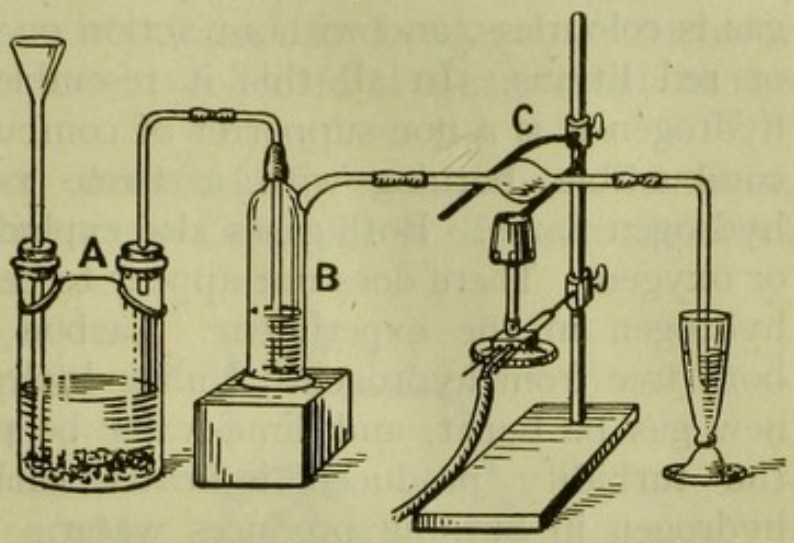


FIG. 95.—The Action of Metals on Carbon Dioxide.

The action of zinc, iron, carbon, and copper on carbon dioxide.—Put a plug of asbestos, Fig. 96, in a porcelain or a vitrified quartz tube, *C*, Fig. 96, introduce some fragments of zinc,

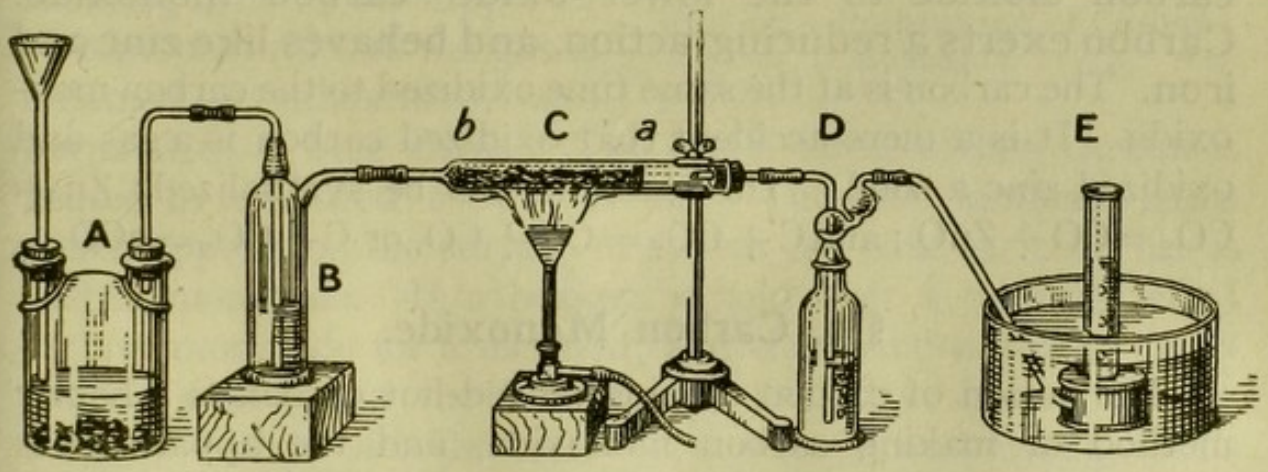


FIG. 96.—The Action of Carbon Dioxide on Iron, Zinc, and Carbon.

and introduce another asbestos plug, *a*. Connect the tube with the carbon dioxide generator *AB* used in the preceding experiment. When the air has been expelled from the tube, connect a wash-bottle, *D*, charged with a solution of potassium hydroxide so as to prevent the passage of any carbon dioxide which may travel through the tube *C*. Heat the metal, and

collect any gas which bubbles through the potash solution by the gas trough *E* in the usual way. Transfer the gas into a series of smaller tubes (the method is shown, Fig. 5) and examine each tube with the object of identifying the gas. The gas is colourless, and without action on lime-water, or on blue or red litmus. In all this it resembles hydrogen, and like hydrogen it is a non-supporter of combustion, and yet is itself combustible, burning with a flame rather bluer than the hydrogen flame. Both gases also explode when mixed with air or oxygen. There does not appear to be any possible source of hydrogen in the experiment. Carbon dioxide and zinc are both free from hydrogen. Unlike hydrogen, if a tube of this new gas be burnt, and lime-water be poured into the vessel, the turbidity produced indicates carbon dioxide, whereas hydrogen in burning produces water. The new gas is called **carbon monoxide**. Zinc is oxidized at the time carbon dioxide is deoxidized. If carbon dioxide is represented by the formula CO_2, it is probable that the new gas is representable by CO. **The metals magnesium, calcium, and potassium reduce carbon dioxide to free carbon; zinc and iron reduce carbon dioxide to the lower oxide—carbon monoxide. Carbon exerts a reducing action, and behaves like zinc and iron.** The carbon is at the same time oxidized to the carbon monoxide. It is a mere accident that oxidized carbon is a gas and oxidized zinc a solid. The reactions can be symbolized: $Zn + CO_2 = CO + ZnO$; and $C + CO_2 = CO + CO$, or $C + CO_2 = 2CO$.

§ 9. Carbon Monoxide.

The action of carbon dioxide on red-hot carbon is a handy method of making carbon monoxide, and the apparatus is illustrated in Fig. 96. The common laboratory method of making carbon monoxide is to heat formic acid, HCOOH, with concentrated sulphuric acid to about 100° in a flask (Fig. 97), fitted with a double-bored rubber stopper; one hole of the stopper is fitted with a gas delivery tube, and the other with a tap funnel containing concentrated (98 per cent.) formic acid. Each drop of formic acid produces some bubbles of carbon monoxide. The reaction is simple: $H.COOH + H_2SO_4$

$= H_2SO_4.H_2O + CO$. There is no frothing, and the velocity of the stream of gas can be regulated by the rate at which formic acid is dropped on to the sulphuric acid. Concentrated sulphuric acid can also be mixed with sodium formate in a flask provided with a safety funnel, and very gently warmed. The carbon monoxide evolved is collected in a gas trough in the ordinary manner.

Properties.—Carbon monoxide is a colourless, tasteless, and odourless (poisonous) gas. One volume of water dissolves about 0·023 volume at 20°. The gas condenses to a colourless transparent liquid at −190°, at atmospheric pressure; the liquid solidifies at −203°. Carbon monoxide is an active poison. Less than one per cent. in an atmosphere is said to cause death. When a lighted taper is plunged into the gas, the flame is extinguished (non-supporter of combustion), but the gas is inflamed (combustible), and burns with a blue flame. The gas is formed when carbon is heated in a limited supply of air. The blue lambent flame which appears on the surface of a clear red coke (or coal) fire is carbon monoxide. If a beaker be held over a burning jet of carbon monoxide for a moment, and clear lime-water be afterwards poured into the beaker, the turbidity shows the presence of carbon dioxide. Carbon monoxide, on burning, forms carbon dioxide: $2CO + O_2 = 2CO_2$. Collect a mixture of two volumes of carbon monoxide and one volume of oxygen in a soda-water bottle; apply a lighted taper to the mouth of the jar; the mixture explodes with some violence.

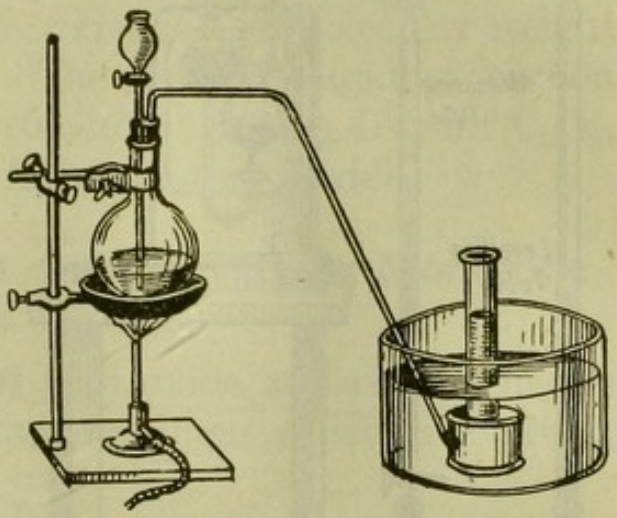


FIG. 97.—Preparation of Carbon Monoxide.

Carbon monoxide unites directly with chlorine: $CO + Cl_2 = COCl_2$. The resulting compound is called **phosgene** or **carbonyl chloride**; it also unites with sulphur vapour, forming **carbonyl sulphide**, COS. Carbon monoxide unites with some

of the metals forming the so-called metal carbonyls, *e.g.* **nickel carbonyl,** $Ni(CO)_4$; **iron carbonyl,** $Fe(CO)_5$; etc.

Composition.—A mixture of carbon monoxide and oxygen can be exploded in the apparatus illustrated in Fig. 98. The Hempel's gas burette is charged with mercury up to the zero mark. 20 c.c. of carbon monoxide and 20 c.c. of oxygen are introduced by connecting the end of the measuring tube with the tube delivering the required gas. Connect the measuring tube with the explosion pipette by means of a piece of glass capillary tube, *C*, and two pieces of thick-walled rubber pressure tubing. The explosion pipette consists of a thick-walled glass bulb in which are fused two platinum wires with tips about 2 mm. apart. This explosion bulb is connected with another bulb by means of a glass tube and stopcock. The upper end of the explosion bulb ends in a U-shaped gauge tube. The explosion pipette is charged with mercury in such a way that the upper bulb is empty when the lower bulb is full of mercury, and the mercury extends to a mark on the gauge tube. Open the two stopcocks and raise the levelling tube of the burette so as to transfer the mixture of gases from the burette to the explosion pipette. Allow a little mercury to pass into the pipette from the burette to make sure that all the gas has been transferred to the pipette. Close both stopcocks, and pass a spark across the platinum terminals. After the explosion, open both stopcocks, and transfer the gas from the pipette to the burette by depressing the levelling tube until the level of the mercury in the burette is in its former position. Bring the

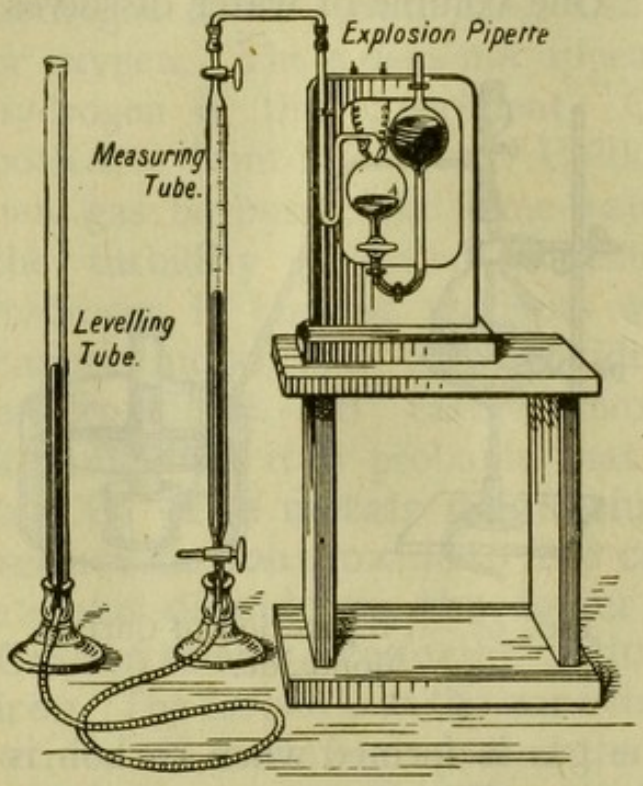


FIG. 98.—Analysis of Gases by Explosion.

mercury to the same level in both tubes and read the volume of the gas in the measuring tube. It will be found that the 30 vols. of carbon monoxide with 30 vols. of oxygen give 45 vols. of gas. When the gaseous product of the explosion was treated with a solution of potassium hydroxide, 15 vols. of oxygen remained. The absorption was conducted as indicated on p. 201, Fig. 90. This shows that 30 vols. of carbon monoxide combined with 15 vols. of oxygen to form 30 vols. of carbon dioxide. By Avogadro's hypothesis, this agrees with the equation: $2CO+O_2=2CO_2$. The density of the gas is nearly fourteen times that of hydrogen. Hence the molecular weight of the gas is 28 (oxygen=32). The atomic weight of carbon is 12, and oxygen 16, and 12+16=28. Hence, CO, not C_2O_2, C_3O_3 . . . is the correct formula for carbon monoxide.

§ 10. The Action of Carbon and of Carbon Monoxide on some Oxides.

Heat an intimate mixture of lead oxide and carbon in the tube shown in Fig. 99, and examine any gas which is evolved. After the air has all been expelled, it will be found that carbon dioxide issues from the tube, and renders the lime-water turbid. Grey beads of metallic lead remain in the tube. Similar results are obtained with tin, zinc, and several other metallic oxides. Under the conditions of this experiment, the carbon is able to take the oxygen from the metallic oxide; in other words, the carbon is oxidized, and the oxide is reduced: $C+2CuO=2Cu+CO_2$. Heating an organic compound with copper oxide will show whether carbon is or is not present—if present, carbon dioxide will be evolved, and this is recognized by its effect on lime-water.

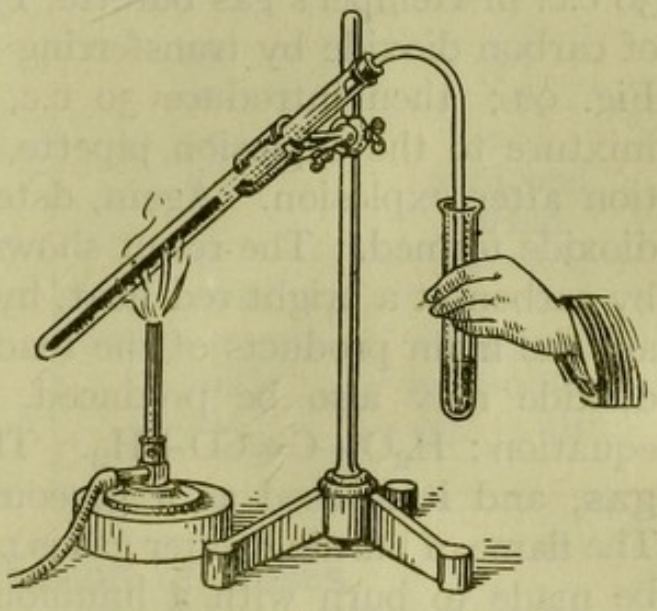


FIG. 99.—The Action of Carbon on Metallic Oxides.

In passing it may be noted that somewhat similar results are obtained when the metallic oxides are heated with hydrogen —page 121, thus, copper oxide is reduced and the hydrogen oxidized: $CuO+H_2=Cu+H_2O$. Zinc oxide, by the way, is not reduced by hydrogen (except under special conditions), although it is by carbon. Carbon monoxide also will reduce many metallic oxides in the same way as hydrogen. The apparatus indicated on page 121 will do for the experiment if the bottle *A* be replaced by an apparatus for making carbon monoxide.

The action of steam on red-hot carbon.—The similarity in the action of hydrogen and carbon on the metallic oxides, and the fact that we have now discovered that carbon dioxide and water are reduced by red-hot metals, leads us to try to reduce hydrogen oxide—steam—by red-hot carbon. The experiment can be conducted in the apparatus shown in Fig. 64. A gas collects in the gas jar. The gas is really a complex mixture. It gives a turbidity with lime-water, and yet burns with a blue flame, showing that it contains carbon dioxide, and possibly hydrogen and carbon monoxide. Introduce about 30 c.c. in Hempel's gas burette, Fig. 90, determine the amount of carbon dioxide by transferring it to the potash pipette as in Fig. 90; then introduce 30 c.c. of oxygen and transfer the mixture to the explosion pipette, Fig. 98. Note the contraction after explosion. Again, determine the amount of carbon dioxide formed. The result shows that when steam is reduced by carbon at a bright red heat, hydrogen and carbon monoxide are the main products of the reaction, while a trace of carbon dioxide may also be produced. This is symbolized by the equation: $H_2O+C=CO+H_2$. This mixture is called **water gas,** and it is used as a gaseous fuel for heating purposes. The flame of burning water gas is non-luminous, it can, however, be made to burn with a luminous flame by charging it with the products of the decomposition of hot oils which do not condense when the gas is cold.

The action of air on red-hot carbon.—If air is forced through a thick bed of coke, the oxygen all burns to carbon monoxide and the nitrogen remains unaffected. The resulting gas contains about 63 per cent. of nitrogen and the remainder

carbon monoxide with a little hydrogen and carbon dioxide. The mixture, called **producer gas,** is largely used as a gaseous fuel in the industries. Producer gas is thus partially burnt carbon. The air used in the producer for converting the carbon into carbon monoxide is, for convenience, called **primary air,** and the air subsequently needed for completing the combustion of the producer gas is called **secondary air.**

§ 11. Summary.

Carbon forms two gaseous oxides: the monoxide CO, and the dioxide CO_2. The former may be regarded as partially burnt carbon, the latter is the ultimate product of the oxidation. The properties of the two gases are compared side by side in Table XA.

TABLE XA.—A COMPARISON OF THE PROPERTIES OF THE GASEOUS OXIDES OF CARBON.

Property.	Carbon monoxide.	Carbon dioxide.
Colour and smell	nil	nil
Combustible ?	yes	no
Supporter of combustion ? . .	no	no
Action of litmus solution . .	nil	reddened
Action of lime-water . . .	nil	turbid
Action of aqueous potash . .	nil	absorbed
100 vols. of water dissolve at 20°	2·3 vols.	110 vols.
One litre weighs	1·250 grms.	1·964 grms.
Liquefies	−190°	−79° (sublimes)
Solidifies	−203°	−57° (5 atm.)

§ 12. The Diffusion of Gases.

Owing to the fact that air is 14 times as heavy as an equal volume of hydrogen under the same physical conditions, if a jar of hydrogen be placed mouth upwards under a jar of air mouth downwards, most of the hydrogen will flow upwards into the upper cylinder, and air will flow downwards into the lower cylinder, Fig. 100. The action is analogous with what would

occur if the lower cylinder contained an oil and the upper cylinder water. The oil and water would change places. The two liquids can be left an indefinite time without mixing, for the two liquids—oil and water—are immiscible. On the contrary, the two gases—hydrogen and air—will spread throughout the two vessels in a short time, and in such a way that the two cylinders will enclose a homogeneous mixture of air and hydrogen. The gases are miscible in all proportions. Had the two liquids been soluble in one another—say, alcohol and water instead of oil and water—these also would have diffused one into the other so as to form a homogeneous solution of alcohol and water.

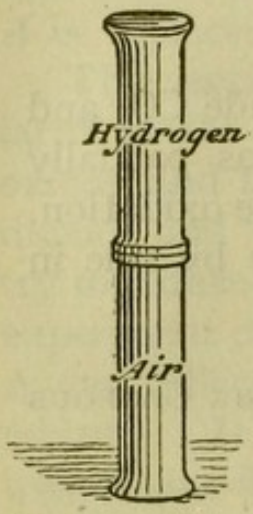


FIG. 100.—Diffusion Experiment.

The process of diffusion in the case of liquids appears to be very much slower than with gases. The molecules of gases seem to lead a more or less independent existence. This is illustrated by the rapidity with which the molecules of, say, ammonia can travel from one end of a room to the other and affect the sense of smell. In liquids, however, the molecules are much less mobile. This can easily be proved by dropping a small grain of aniline dye into a tumbler of clear still water. The water will be uniformly coloured in a few weeks. The molecules of solid substances have practically lost their mobility. But not all. Carbon laid in contact with pure, hot, solid iron will diffuse into the mass of the metal; gold in contact with lead will in a few years, diffuse into the lead in appreciable quantities; carbon will diffuse into the body of hot vitrified porcelain; and metallic silver will diffuse into hot "solid" glass, staining it yellow.

The transfer of gases in bulk from one vessel to another is an effect of gravitation, whereas diffusion is not an effect of gravitation. Thomas Graham (1832) showed that the speed at which the molecules of a gas can diffuse or travel through thin porous membranes—indiarubber, porous earthenware, etc.—is related to the specific gravity of the gas. Thus we have **Graham's law of diffusion: the relative speeds of diffusion of gases**

are inversely proportional to the square roots of their relative densities. For example, hydrogen diffuses nearly four times as fast as oxygen ; the relative densities of oxygen and hydrogen are nearly as 16 : 1 ; and the relative rates of diffusion of the two gases are nearly as $\sqrt{1} : \sqrt{16}$; *i.e.* as 1 : 4.

To find the relative density of a gas by comparing its speed of diffusion with that of another gas of known density.—Let D_1 and D_2 represent the relative densities of two gases, one of which, D_1, is known, the other, D_2, is unknown. Suppose that the relative speeds of diffusion of the two gases V_1 and V_2 are known. Then, it follows from Graham's law : $V_1\sqrt{D_1} = V_2\sqrt{D_2}$, or, for two gases A and B,

$$\frac{\text{Speed of diffusion of gas A}}{\text{Speed of diffusion of gas B}} = \frac{\sqrt{\text{Density of gas B}}}{\sqrt{\text{Density of gas A}}}$$

Given any three of these numbers, the fourth can be calculated by arithmetic.

EXAMPLE.—The speeds of diffusion of carbon dioxide and of ozone were found by Soret (1868) to be as 0·29 (V_1) is to 0·271 (V_2). The relative density of carbon dioxide is 22 (D_1) H = 1. What is the relative density of ozone (D_2) ? From the preceding relation, it follows that $\sqrt{D_2} = 0{\cdot}29 \times \sqrt{22} \div 0{\cdot}271 = 0{\cdot}29 \times 4{\cdot}69 \times 3{\cdot}69$; or $D_2 = (5{\cdot}02)^2 = 25$ nearly.

Advantage has been taken of the different speeds of diffusion of different gases to devise several pleasing experiments. The simple facts can be illustrated by fixing porous pots (such as are used for ordinary battery cells) to the ends of bent tubes as shown in the Figs. 101, 102. The porous pots contain air. Bring a cylinder of hydrogen over the one porous pot, Fig. 102. Hydrogen diffuses through the walls of the pot faster than the air can diffuse outwards. Consequently, the pressure of the gas inside the porous pot will increase. This is shown by the motion of the coloured liquid in the U-tube away from the porous pot. Before the cylinder of hydrogen was placed over the porous pot, the air diffused inwards and outwards through the pot at the same rate. Repeating the experiment, Fig. 102, with a cylinder of carbon dioxide instead of hydrogen, the air

moves outwards from the porous pot faster than the carbon dioxide can pass inwards. Consequently, there is a reduction in the pressure of the gases in the porous pot. This is shown by the motion of the liquid in the U-tube towards the porous pot.

If the liquid in the leg of the U-tube be connected with a battery and electric bell, and if a wire be fused in the leg of the U-tube so that when the liquid rises electric contact is made, the bell will ring. A device based on this principle has been suggested as an alarm indicator for the escape of coal gas in rooms, or fire-damp in coal mines. These gases, like hydrogen, diffuse through the walls of the porous pots faster than air can escape. The experiments, Fig. 101, can be modified so that the liquid is sprayed from the tube like a miniature fountain ; or the outward pressure of the gas can be made to blow a soap bubble if a film of soap solution be placed across the widened mouth of the tube. The ready diffusion of gas through the walls of buildings plays a part in ventilation. Most building materials are porous, and permit the passage of gases through them in both directions. The diffusion does not take place so readily when the walls are saturated with moisture—*e.g.* new buildings, etc.

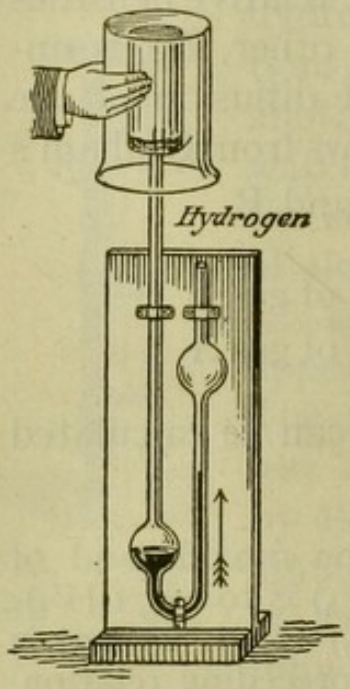


FIG. 101.

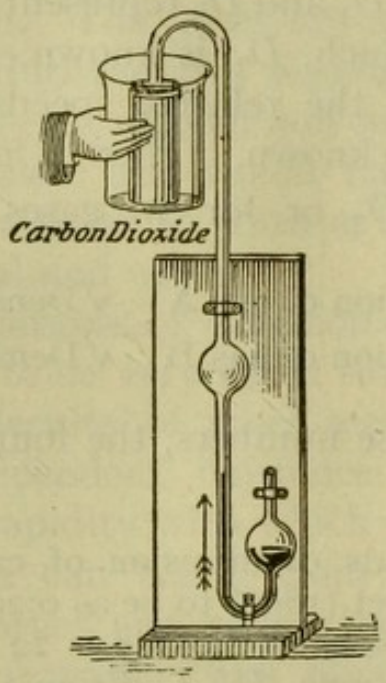


FIG. 102.

Diffusion Experiments.

If a slow current of electrolytic gas, that is, the mixture of hydrogen and oxygen obtained by the electrolysis of water, be allowed to pass through the stem of a " church-warden " clay pipe, and the gas issuing from the pipe be collected in a gas trough, the gas thus collected will no longer explode when

brought in contact with a flame. On the contrary, it will rekindle a glowing chip of wood, showing that a relatively large proportion of oxygen is present. In passing through the porous pipe, hydrogen escapes by diffusion through the porous walls of the " clay tube " much more rapidly than the heavier oxygen. This phenomenon—the separation of one gas from another by diffusion—has been called, by Graham, **atmolysis**—from the Greek words ἀτμός (atmos), vapour ; and λύω (lyo), I loosen.

Questions.

1. A bottle is supposed to contain one of the following three gases : air, nitrogen, or carbon dioxide. How would you propose to determine which gas is present ?

2. Separate quantities of calcium carbonate, each in fine powder, are submitted to (1) strong heat, (2) the action of dilute hydrochloric acid, and (3) the action of a solution of carbon dioxide in water. State what happens in each case.—*Cape Univ.*

3. What chemical changes do you suppose will take place when burnt lime is exposed to the air ? Give the name and formula of the substance which will be left after the lapse of a considerable time. How must this residual compound be treated so as to yield slaked lime, and how can it be utilized in the preparation of a sample of water which has temporary hardness ?

4. If you were told that four given powders were sodium chloride, sodium carbonate, sodium bicarbonate, and quicklime, by what practical tests would you be able to decide whether the substances were correctly labelled ?—***Cape Univ.***

5. Name and describe the products resulting from the following operations :—(*a*) burning magnesium ribbon in air ; (*b*) heating chalk to bright redness ; (*c*) passing steam over red-hot iron filings ; (*d*) passing carbon dioxide through lime water.—*Tasmania Univ.*

6. The gas which accumulates in the Grotto del Cane near Naples is said to be carbon dioxide. Describe how you would test by experiments the correctness of the assertion.—*London Univ. Matric.*

7. What substances are produced when charcoal is heated to redness with (*a*) steam, (*b*) carbon dioxide, (*c*) litharge ? Explain by equations, and state any changes of volume which may be noticed.—*Science and Art Dept.*

8. By what experiments can you render it probable that chlorine is derivable from common salt, and carbon dioxide from washing

soda ? How do you know that the chlorine or carbon dioxide does not come from something else used ?—*Science and Art Dept.*

9. A white powder is either quicklime or chalk, or a mixture of chalk and quicklime. How would you determine, experimentally, which it is ?—*Coll. Preceptors.*

10. How many c.c. of carbon dioxide are produced by the complete combustion of 12 grms. of carbon in oxygen ? How many c.c. of carbon dioxide can be generated from 100 grms. of marble by an aqueous solution of hydrogen chloride ? (Ca=40, O=16, C=12, H=1.) How could you distinguish carbon dioxide from nitrogen ?—*London Univ. Matric.*

11. State fully what is denoted by the symbol CO_2, and describe briefly how the facts implied by that symbol have been ascertained. —*London Univ. Matric.*

12. Describe what you would observe, and state the nature of the changes that would take place, on passing carbon dioxide gas (*a*) over heated potassium, (*b*) over red-hot charcoal, (*c*) into lime-water. Give equations.—*London Univ. Matric.*

13. How would you prepare and collect jars of practically pure carbon monoxide and carbon dioxide respectively from solid carbon ? Sketch the necessary apparatus in each case.—*London Univ. Matric.*

14. How many compounds does carbon form with oxygen ? What are their names and formulæ ? How can they be (*a*) distinguished, (*b*) separated from each other, (*c*) converted into each other ?—*London Univ. Matric.*

15. State what you have observed to take place on passing carbon dioxide into lime-water, giving explanatory equations. What are the salient properties of the products ?—*London Univ.*

16. A particular gas has a diffusion rate=0·81 referred to air=1·0. Find the density of the gas.—*London Univ.*

17. Carbonic acid is said to be a dibasic acid. Explain the meaning of basicity, and give reasons why this acid must be regarded as dibasic.—*London Univ.*

18. What determines whether a gas should be collected (*a*) over water, (*b*) over mercury, (*c*) by the downward displacement of air, (*d*) by the upward displacement of air ?

19. If 50 c.c. of hydrogen take ten minutes to diffuse out of a vessel, how long will 20 c.c. of nitrogen take to diffuse under the same conditions ? (H=1, N=14.)—*Board of Educ.*

20. A bottle of hydrogen gas is brought mouth downwards in close contact with the mouth of another containing carbon dioxide ; how would you ascertain whether any, and if so how much, of the heavy gas passes into the upper jar after ten minutes' contact ? State any principle involved in such an experiment.—*Science and Art Dept.*

21. Describe the characters and properties of six of the more important carbonates, and write their formulæ.—*Science and Art Dept.*

22. Lime-water is shaken up in a jar filled with carbon monoxide; what occurs? The carbon monoxide is then inflamed, and the lime-water once more shaken up with the contents of the jar. What now takes place?—*Science and Art Dept.*

23. A colourless gas fills a bottle containing clear lime-water. A burning taper ignites the gas, which burns with a blue flame. The bottle is shaken and the lime-water becomes turbid. Name the gas and explain the change which has taken place in it.

24. Air is passed through a tube full of common charcoal and heated to redness; how would you find out whether the air is changed in volume or in properties? Would it make any difference if, in one experiment, you use a very long tube of charcoal, and, in another, a very short tube?—*Science and Art Dept.*

25. One gram of carbon is burnt to carbon dioxide. What volume of gas will be produced at 0° and 760 mm.? How much caustic soda will be required to form sodium carbonate with it? and how much of sodium bicarbonate were produced instead? (C=12, H=1, O=16, Na=23. One gram of hydrogen occupies 11·1 litres at 0° and 760 mm.)—*Cambridge Junr. Locals.*

26. What volume of gas measured at 18° and under a pressure equal to that exercised by a mercury column 720 mm. high would you expect to be evolved on dissolving in an acid 100 grms. of the white substance obtained on exposing lime-water to the air?—*London Univ. Matric.*

27. How may it be shown that the gases named carbon monoxide and carbon dioxide contain different proportions per cent. by weight of carbon?—*London Univ. Matric.*

28. Describe two methods by which pure carbon monoxide can be obtained. What are the proofs that it has the composition assigned to it? How can it be oxidized? And how can it be recovered from the oxidized product? Carbon monoxide and nitrogen are both colourless gases having the same density; how could you distinguish between them?—*London Univ.*

29. Air is shaken with recently boiled distilled water. What will be taken out of the air? The water is then boiled, and the escaping gas collected. What will be the constituents of this gas, and their approximate proportions? What difference in the result will there be made if the water is made alkaline before boiling?—*London Univ.*

30. What happens when (1) hydrogen is passed over heated iron oxide; (2) limestone is heated in an iron tube; (3) carbon dioxide is passed over heated charcoal; (4) steam is passed over heated iron? Explain as fully as you can.—*Panjab Univ.*

31. Distinguish between potassium carbonate and bicarbonate. How can each of these bodies be obtained from the other ? How can the percentage of carbon dioxide in one of them be determined ? —*Cambridge Univ.*

32. What is marble ? What experiments would you make in order to show that marble contains three elements ?—*Cambridge Univ.*

33. Why does soap often form a scum when it is used with spring water but not with rain water ? Indicate why rain water is preferable to spring water for washing.

34. How is the earthy crust produced which is often found coating the inside of a kettle after long use ?

35. What is meant by the " hardness " of a water. Distinguish between temporary and permanent hardness. Show how hard water may be softened.—*Sydney Univ.*

36. The well water at Canterbury can be rendered soft by the addition of an aqueous solution of lime. Explain why lime is able to render some kinds of hard water soft.—*London Univ.*

37. A teacher of chemistry wishes to show his class the explosiveness of a mixture of hydrogen and oxygen in suitable proportions. Accordingly, in the morning he prepares the mixture, puts it in a thin indiarubber bladder, sets it aside, and in the evening brings it forth to the class and applies a lighted taper. State and explain what will happen.—R. H. Jude and H. Gossin, *Physics*, London, 1899.

38. What tests would you use to distinguish :—(*a*) between a jar containing carbon dioxide and one containing carbon monoxide ; (*b*) between a saturated solution of sodium sulphate and a supersaturated solution of the same substance ; (*c*) between a solution of chlorine and a solution of hydrogen chloride ?—*Dept. of Educ. Ontario.*

CHAPTER XIII

Combustion and Flame

§ 1. Is Combustion Oxidation?

Lavoisier's work in 1774, on the composition of air, and on the increase in weight which occurs when a metal is calcined in air, has already been described in outline. During the next two years, Lavoisier proved that carbon dioxide is the product of the oxidation of carbon, and that carbon dioxide and water are the products of the combustion of organic compounds containing carbon, hydrogen, and possibly oxygen. In 1777, Lavoisier published his oxidation theory of combustion: (1) Oxygen is necessary for combustion; (2) Oxygen is consumed during combustion, and the increase in weight of the substance burnt is equal to the decrease in weight of the atmospheric air. The origin of the water formed during combustion was completely explained by Cavendish's synthesis of water in 1783. Consequently, **combustion is a process of oxidation which is attended by the development of light and heat.** When carbon burns in air, carbon dioxide is formed; when hydrogen is burnt in air, water is formed; when phosphorus burns in air, phosphorus pentoxide is formed; sulphur furnishes sulphur dioxide, etc.

Combustible substances must be heated to a certain temperature before they can ignite, and this temperature must be maintained if they are to continue burning. **The ignition or kindling temperature is the temperature to which the substance must be heated in order to start combustion or explosion.** With oils, in air, the ignition temperature is usually called the **flash point.**

It must be added that many other chemical reactions which furnish light, heat, and flame, are now also included under the term "combustion," even though oxygen be absent. Hence **combustion is not always oxidation, for the term is applied generally to any chemical process which is attended by the development of heat and light.** For instance, the "combustion" of brass in chlorine; of hydrogen in chlorine; of magnesium in steam; of potassium in carbon dioxide; of aluminium in nitrogen; etc. The development of flame, light, and heat during combustion is quite an accidental feature of the process of oxidation. The speed of the oxidation may vary from the slow decay of organic matter occupying maybe centuries, to the rapid explosion travelling at the rate of 10,000 feet per second.

The relation between the combustible and the supporter of combustion.—It has been found convenient in our previous studies to call the burning substance the **combustible,** and the atmosphere surrounding the burning substance the **supporter of combustion.** Under ordinary conditions the atmosphere is the enveloping medium, and the terms "combustible" and "incombustible," without further amplification, refer to the burning or non-burning of substances in air. Conventionally too, other gases are said to be supporters or non-supporters of combustion if they behave towards ordinary combustibles like air. These terms, however, are purely *conventional* because, from the chemical point of view, it is a matter of indifference whether hydrogen burns in air, or air in hydrogen. If the atmosphere be hydrogen, the flame must be fed with atmospheric air. In this case, the meaning of the conventional terms is reversed, for air is then the combustible, and hydrogen the supporter of combustion. There are several ways of showing this **reversed or reciprocal combustion,** as it is called. The idea is illustrated by the following experiment with coal gas, which, like hydrogen, is styled a combustible gas and a non-supporter of combustion.

An ordinary lamp cylinder, *A*, Fig. 103, may be closed at one end with a cork perforated to fit over a Bunsen's burner, and also with a hole in which a glass tube *C*—about 10 cm.

long and 1 cm. diameter is fitted The top of the cylinder is covered with a sheet of asbestos *D*—6 or 7 cm. square, and perforated with a round hole about 2 cm. diameter. The air holes of the gas burner are closed; the gas is turned on and the opening in the asbestos is closed by laying a piece of cardboard loosely on the hole. In a few minutes, the apparatus will be filled with coal gas. Light the gas as it issues from *C*, and simultaneously remove the cardboard which was closing the hole in the asbestos. The flame will pass up the tube drawing the air after it. The upward current of gas causes an upward current of air in the tube *C*, which burns with a feebly luminous flame in the atmosphere of coal gas. The excess of coal gas issuing from the opening in the asbestos may be ignited, and the two flames show air burning in coal gas, and coal gas burning in air. By modifying the arrangement, Fig. 103, it is easy to show hydrogen and coal gas supporters of combustion; and oxygen, and chlorine, as combustibles.

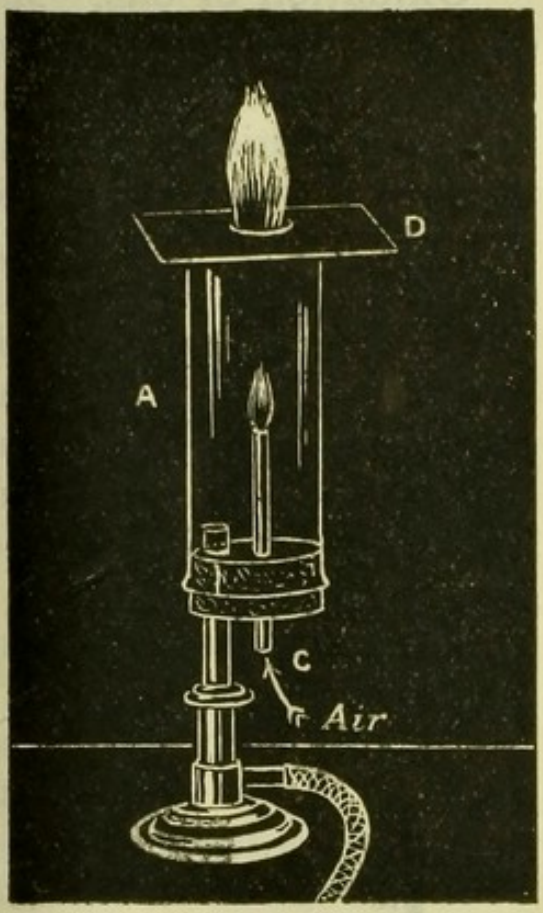


FIG. 103.—Reciprocal Combustion.

Pyrophoric powders.—Finely divided lead is prepared by heating lead tartrate, at as low a temperature as possible, in a glass tube sealed at one end. When the evolution of gas has ceased either close the open end with a cork, or seal it up hermetically while hot. If the cold powder be allowed to fall through the air on to the floor, the oxidation of the powder proceeds so rapidly that the temperature is raised and the falling powder becomes red hot. Hence, the term *pyrophoric lead*. Finely divided iron oxalate, nickel oxide, etc., reduced at a low temperature in a stream of hydrogen, also furnish pyrophoric powders.

Spontaneous combustion.—The so-called spontaneous ignition of coal which takes place in gob, in coal stacks, in coal bunkers, etc., may be caused by the rapid oxidation of pyrites in the coal, or the coal itself. Some kinds of small coal and coal dust mixed with air are said to ignite in the vicinity of 200°.

Oxidation of oils.—Many oils—linseed oil, nut oil, poppy oil, hemp oil—absorb oxygen. Linseed oil used for paint, for instance, absorbs oxygen and forms a tough resinous skin as the paint "dries." This skin holds the colouring matters in suspension and protects the material underneath. The paint oils, therefore, do not "dry," in the ordinary sense of the word, by evaporation, but by oxidation. If rags, etc., greasy with oil, be left in a badly ventilated place, or if a heap of greasy material be left for some time undisturbed under such conditions that the mass is not well enough ventilated to keep it cool, the temperature may rise high enough for spontaneous inflammation. The oxidation of the paint oils is facilitated by the addition of lead and manganese salts.

Eremacausis.—The decay of wood is a process of oxidation, very slow, it is true. The process of slow oxidation without the application of heat is sometimes called **slow combustion** or **eremacausis**—from two Greek words meaning to burn quietly. The rusting of iron is another example of a slow oxidation, although the end-product is not the same as in the combustion of iron in oxygen. In the former case a hydrated ferric oxide—$Fe_2O_3.nH_2O$—is formed, and in the latter case magnetic iron oxide—Fe_3O_4. The absorption of oxygen by rusting iron is generally illustrated by inserting a plug of steel wool, *A*, Fig. 104, into a 100 c.c. eudiometer tube *B*, resting in a dish of water *C*. The level of the water *B* is adjusted, and the apparatus examined after about twenty-four hours. The iron will be coated with rust, and the enclosed air will have decreased in volume.

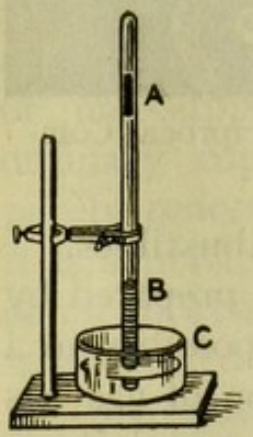


FIG. 104.—Iron Rusting.

Sewage.—In the one method of sewage treatment, the sewage is mixed with a large volume of water. The oxygen

dissolved by the water, assisted by bacteria, quickly renders the organic matter innocuous, mainly by converting it into carbon dioxide and water—and possibly nitrogen compounds.

§ 2. Respiration involves Oxidation.

John Mayow (1674) demonstrated that the respiration of animals is a process of oxidation analogous with combustion. Mayow placed a mouse in a cage under a vessel standing over water, Fig. 105, and noticed that the water rose in the jar as respiration continued just as if a burning candle had been placed under the jar—p. 95, owing to the withdrawal of what he called "nitro-aëreal particles" (oxygen). He found that the mouse died after a time, and it was impossible to ignite a combustible body in what he called the residual "aëreal" gas (nitrogen).

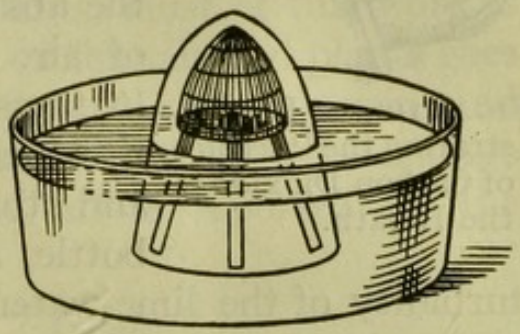


FIG. 105.—Mayow's Experiment showing the Abstraction of Oxygen from Air during the Respiration of Animals.

The respiration of animals.—All living organisms are continually wasting tissue as a result of muscular or other forms of work. The air during respiration loses about 4 to 5 per cent. of oxygen, and gains 3 to 4 per cent. of carbon dioxide. Oxygen, taken in by the lungs, is absorbed by the blood. The blood contains **hæmoglobin,** this unites with oxygen, forming **oxyhæmoglobin**—the former predominates in blue venous blood; the latter, in red arterial blood. The oxyhæmoglobin gives up its oxygen very readily, and it thus oxidizes the waste products—partly to carbon dioxide. The carbon dioxide held in solution by the venous blood is pumped by the heart to the lungs, and the gas is finally exhaled in the breath. Hence, as one writer puts it, "a living being is at work. Work means waste. Waste means decay. Decay is combustion. Combustion is oxidation."

By breathing into a beaker, and then adding clear lime-water; or better, by blowing through a glass tube into a beaker

containing clear lime-water, it is easy to demonstrate the presence of carbon dioxide in the breath—Fig. 106. The precipitation of calcium carbonate causes the clear lime-water to become turbid, etc. The experiment can be modified by drawing a stream of air through pieces of "soda-lime" in a tower, *A*, Fig. 107, to remove carbon dioxide from the air; then through a wash bottle, *B*, with clear lime-water. The clarity of the lime-water demonstrates the absence of carbon dioxide in the stream of air. The air after passing the *temoin* (witness) tube, *B*, enters a glass chamber, *C*, which holds a mouse or a couple of mice, and then passes through another wash bottle, *D*, containing clear lime-water. The turbidity of the lime-water in *D*, and the clarity of the lime-water in *C*, can only be explained by assuming that the mice are giving off carbon dioxide during respiration. The same vessel *C* can be used for trying the effect of different gases on mice.

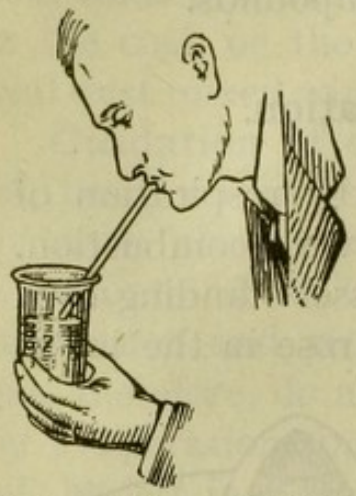


FIG. 106.—Demonstrating the Presence of Carbon Dioxide in the Breath.

The respiration of plants.—Just as Mayow's experiment, Fig. 105, proves that animals use up the oxygen of air during respiration, so the apparatus, Fig. 108, can be employed to show that plants behave in a similar way. Here a freshly-cut spray of green leaves is placed in a flask fitted on to

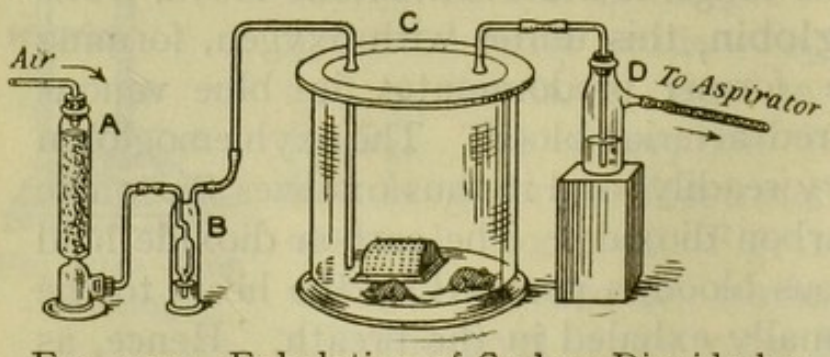


FIG. 107.—Exhalation of Carbon Dioxide by Animals.

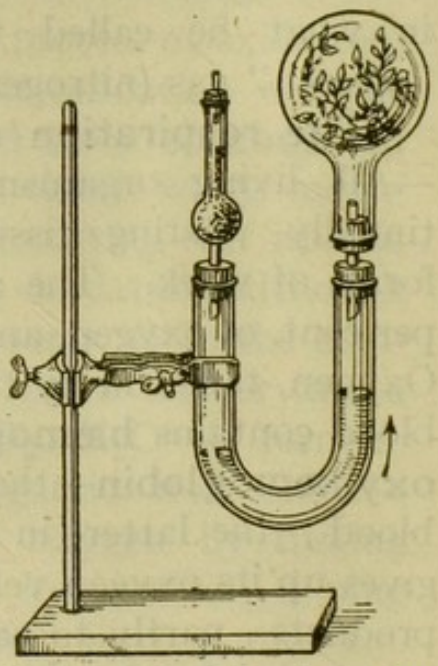


FIG. 108.—Showing the Abstraction of Oxygen from Air during the Respiration of Plants.

the right limb of a U-tube containing some clear lime-water; the other limb is fitted with a tube packed with sticks of caustic potash to protect the lime-water from the carbon dioxide in the air. After standing over twenty-four hours in a shady place, the lime-water will appear turbid, and have risen in the right limb of the tube. Oxygen and not nitrogen has been abstracted from the air in the flask by the plant.

Less carbon dioxide is exhaled during sleep, because less waste products are formed. The heat evolved during the oxidation processes in the body maintains the body at the necessary temperature. In the case of plants, most of this work is done by the leaves. The respiration of animals and plants goes on continuously, night and day—oxygen (air) is taken in, and returned to the air as carbon dioxide and water. The percentage composition of inhaled and exhaled air is reported by the bio-chemists as follows:

	Nitrogen.	Oxygen.	Carbon dioxide.	Moisture.
Inhaled air . .	79·15	21·00	0·04	varies
Exhaled air . .	79·59	16·00	4·38	nearly saturated

The consequent loss in weight in both animals and plants is made good by assimilation or feeding. Fish abstract dissolved oxygen from water by the aid of their gills. Fish quickly die for want of oxygen when placed in cold water which has been deprived of "dissolved air" by boiling. Aerated water furnishes the oxygen necessary for their sustenance.

The assimilation of carbon dioxide by plants.—The respiration of plants must not be confused with the process of assimilation. In daylight, plants absorb carbon dioxide from the air, fix the carbon, and give off oxygen. In sunlight, the process is very active, so that the respiration process, though at work, is masked because more carbon dioxide is taken in and oxygen given out by assimilation (feeding), than oxygen is taken in and carbon dioxide given out by respiration (breathing). The decomposition of the carbon dioxide (feeding) only occurs in daylight, and plant life is thus dependent upon this process for nourishment. This action of light may be readily shown by loosely packing a two-litre flask with green leaves, and filling

up the flask with water through which carbon dioxide has been allowed to bubble. Fit the flask with a stopper and funnel as shown in the diagram, Fig. 109. Also fill the flask and part of the funnel with water. A test tube inverted over the funnel will collect sufficient oxygen to allow the usual tests being made. The experiment can be modified by burning a candle under a bell jar until the flame is extinguished, and then placing a freshly-cut spray of leaves under the jar. When exposed to sunshine, the carbon dioxide is abstracted and oxygen takes its place, so that after a few hours' exposure a candle will burn in the confined air.



FIG. 109.—Assimilation of Carbon Dioxide and Evolution of Oxygen by Plants.

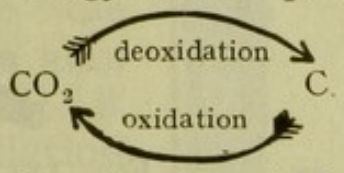
The energy required for the decomposition of the carbon dioxide is derived mainly from the solar light and heat. There is thus a transformation of the sun's energy into chemical energy which is stored up as vegetable tissue. The heat of combustion of burning wood is believed to be equivalent to the solar energy used in its formation. At night, in darkness, feeding stops, but breathing—the absorption of oxygen and the evolution of carbon dioxide—continues. The net result of both processes—assimilation and respiration—is to remove carbon dioxide from the air, and restore oxygen. There is probably a kind of equilibrium pressure between plants and the carbon dioxide of the air. If the amount of carbon dioxide exceeds a certain limit, this would be followed by greater activity in vegetable life, and thus the normal proportion of carbon dioxide would be restored. Similarly, if the amount of carbon dioxide were reduced below the normal, vegetable life would be impoverished until equilibrium was restored.

The proportion of carbon dioxide present in the gases dissolved by sea-water is about 27 times as great as the proportion of this gas in air. Since carbon dioxide is very soluble in water, it follows that if a large surplus of carbon dioxide were introduced into the atmosphere, say, from volcanic sources, the sea would dissolve a still greater proportion. Hence, *the sea must be an*

important means of regulating the amount of carbon dioxide in the atmosphere.

It will be noticed that all animal and vegetable life is dependent upon the carbon dioxide → carbon reaction, which in turn is dependent upon the sun's energy ; and further, that the energy dissipated during the carbon → carbon dioxide reaction renders a further supply necessary for the carbon dioxide → carbon reaction. There is a kind of closed cycle, an alternation of oxidations and deoxidations :

Sun's energy stored—plants feed.



Energy dissipated—animals and plants breathe, etc.

maintained by a continuous supply of energy from the sun. If the supply should cease, the deoxidation of carbon dioxide would stop, and the present conditions of life on the earth would come to an end because the available carbon would be transformed into unavailable carbon dioxide.

§ 3. The Safety Lamp.

If a helical coil of cold copper wire be placed on a candle flame as in Fig. 110, the flame will be extinguished, but if the coil be first heated, the flame is not quenched. Again, a stout glass tube, *B*, Fig. 111, about 3 cm. diameter and 60 cm. long, is fitted at one end *A* with a perforated rubber stopper and bent glass tube ; the other end *C* is fitted with a perforated stopper and copper tube about 6 mm. in diameter and 30 cm. long. The tube is clamped to make an angle of about 30° with the horizontal. Fill the tube with coal gas by connecting *C* with the gas supply ; light the gas at *C* and remove the stopper at *A*. Air enters at *A* and makes an explosive mixture of air and gas in the tube. The flame at *C* will retreat down the *C* tube and explode the gas in *B*. Repeat the experiment, using a copper tube 3 mm. in diameter at *C*. The flame will be extinguished in *C* before it reaches the gas in *B*. That *B* does contain an

explosive mixture of air and gas can be shown by applying a lighted taper at *A*. Consequently, the flame is cooled below the ignition temperature of the mixture, during its passage down the narrower copper tube ; but not with the wider copper tube.

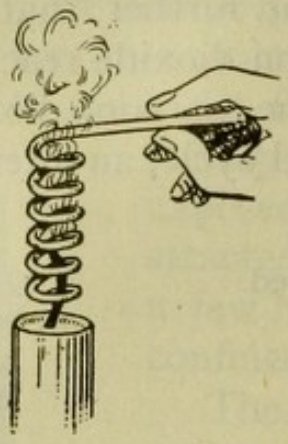


FIG. 110.—Candle Flame extinguished by Cold Coil of Copper Wire (not by Hot Coil).

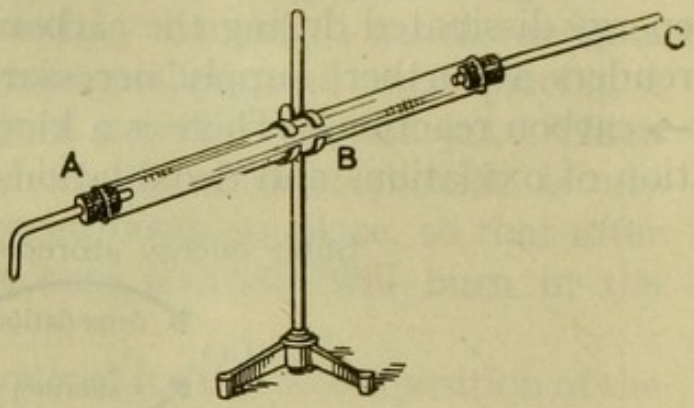


FIG. 111.—Gas Explosion.

Again, fix a piece of wire gauze over an unlighted Bunsen's burner, turn on the gas, bring a lighted taper above the gauze ; the gas above the gauze is ignited, but the flame does not pass through the gauze, Fig. 112. Conversely, if the gas be ignited below the gauze, the flame will not pass through, although the passage of inflammable gas through the gauze can be demonstrated by bringing a lighted taper above the gauze. If the gauze be heated red hot, the flame will pass through and burn on both sides.

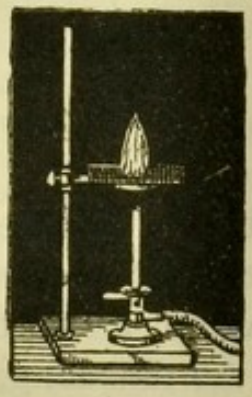


FIG. 112.—Effect of Wire Gauze on Flame.

Experiments not unlike these led Humphry Davy, in 1815, to the idea of "flame sieves," and finally to the "safety lamp for miners." In Davy's safety lamp, Fig. 113, an oil lamp is surrounded by a cylinder—$1\frac{1}{3}$ inches in diameter, and 6 inches high—made of iron wire gauze, having 28 meshes per linear inch. The cylinder is closed at the top with a double layer of gauze *A*, Fig. 113. The lamp is provided with a socket lock to prevent it being opened in the mine, and there is a ring at the top to allow the lamp to be carried or suspended. The lamp is ventilated by air passing through the mesh of the gauze near

the flame. The air impinges on the flame, and the products of combustion escape through the gauze in the upper part of the cylinder. When such a lamp is taken into an atmosphere containing a mixture of marsh gas and air, the explosive mixture passes through the gauze and is ignited inside the cylinder. The cylinder may even be heated red hot by the combustion of the explosive gases inside. The flame, however, is unable to pass through the gauze and ignite the mixture outside the cylinder. **The gauze acts as a "flame sieve"; it permits a free circulation of gas and air, but it obstructs the passage of the flame.** Prior to the invention of Davy's lamp, the risk of explosion in "fiery mines" was very serious, and two notable attempts had been made to deal with the difficulty—by Clanny and by Stephenson. The Davy lamp considerably lessened the danger, but it was not "fool-proof," because miners were emboldened to take unnecessary risks in dangerous atmospheres. Mr. Buddle, one of the first users of Davy's lamp, in a report on Accidents in Mines (1835), stated, *inter alia :*

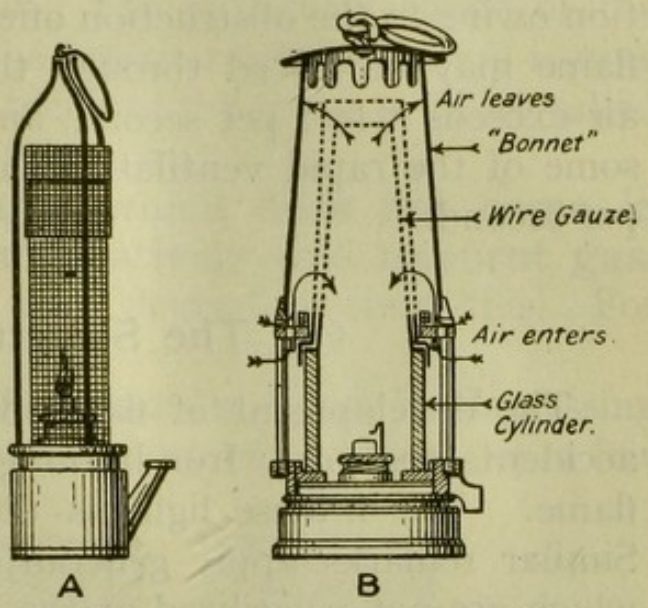


FIG. 113.—Safety Lamps (old and new).

> I first tried it in an explosive mixture on the surface, and then took it into a mine ; and, to my astonishment and delight, it is impossible for me to express my feelings at the time when I first suspended the lamp in the mine and saw it red hot ; if it had been a monster destroyed, I could not have felt more exultation than I did.

If the gauze should happen to be heated locally above the ignition temperature of the mixture outside ; or if the lamp is exposed in a strong current of air, say, a ventilating shaft, or a "wave" of air sometimes generated in the operations of blasting, the flame may be driven through the meshes of the

gauze. Considerable improvements have been made on the original *Davy's lamp*, *A*, Fig. 113. The modern forms of safety lamp—*e.g.* the *Marsaut's lamp*, *B*, Fig. 113—allow the lamp to be used under conditions of great danger with a minimum risk of igniting an explosive mixture of firedamp and air. The old Davy's safety lamp is obsolete. It gives a very poor illumination owing to the obstruction offered by the wire gauze, and the flame may be forced through the gauze when the current of air exceeds 5 feet per second, and in modern mines, the air in some of the rapid ventilating shafts may attain 20 to 30 feet per second.

§ 4. The Structure of Flame.

The development of flame during combustion is quite an accidental feature. Iron burning in oxygen gives no perceptible flame. The intense light is due to the incandescent solid. Similar remarks apply generally to the combustion of solids which are not volatilized at the temperature developed during the combustion. For this reason, also, copper, carbon, etc., do not usually show any appreciable flame. On the other hand, phosphorus, sulphur, bitumen, fat, wax, etc., burn with a flame because these solids are volatilized at the temperature of combustion. The flame of most of the combustible gases has quite a characteristic appearance—sulphur burns in air with a lavender blue flame ; burning hydrogen is scarcely visible in bright daylight, provided the gas and air are free from dust ; carbon monoxide has a rich blue flame ; potassium burns with a violet flame ; sodium with a golden yellow flame ; calcium with an orange red flame ; etc.

It will be obvious that when a stream of gas issues from a tube, the gas can only burn at its surface of contact with the air. The shape of the flame, issuing from, say, a circular jet, is due to the fact that as the gas issues from the jet, a ring of gas, so to speak, next to the tube burns first ; before any more gas can come in contact with the air and burn, it must rise past the first ring of flame, and each successive layer of gas has to pass higher and higher before it can find the supply of air

necessary for combustion. The flame thus assumes the form of a cone. Of course, there are no real " rings of gas," but this mode of expression helps us to understand the phenomenon. The upward direction of the flame, even if the gas be directed horizontally or downwards, is due to the increased buoyancy of the hot air in immediate contact with the flame producing a strong upward current of air. The particular shape of the flame is also conditioned by the pressure behind the gas issuing from the tube, and on the character of the jet—*e.g.* the so-called " bat's-wing," and " fish-tail " burners.

The interior of the flame which does not come in contact with the air is comparatively cold unburnt gas. Numerous experiments have been devised to show this. For instance :

(1) Cross sections of the flame can be shown by depressing thin sheets of asbestos paper (say, 15 cm. square) for a few



FIG. 114.—Flame Sections (A and B, Coal Gas ; C, Hydrogen).

moments on the flame of, say, a Bunsen's burner protected from draughts. The hotter portions of the flame where the gases are burning char the paper, producing a dark ring when the paper is held horizontally, Fig. 114, *B* ; and a more or less elongated cone, if the paper be held vertically in the flame *A*, Fig. 114. The particular " flame figure " produced depends on the part of the flame in which the paper is held. Grease or oil is used in making the asbestos paper. Well-glazed white writing paper can also be used. The upper side of the paper can also be dusted with red mercuric iodide. This turns yellow where the flame is hottest. Copper foil also furnishes an interesting modification of the experiment.

(2) A narrow glass tube—say, 20–30 cm. long—held in the centre of the flame will draw off a portion of the unburnt gas

from the interior, and the unburnt gas can be lighted at the end of the tube, Fig. 115.

(3) A pin pushed at right angles through the stem of a

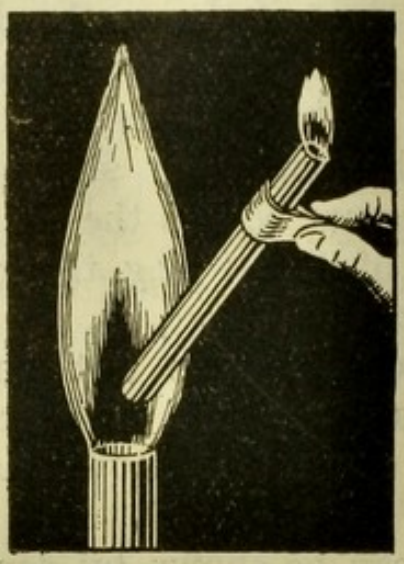


FIG. 115.

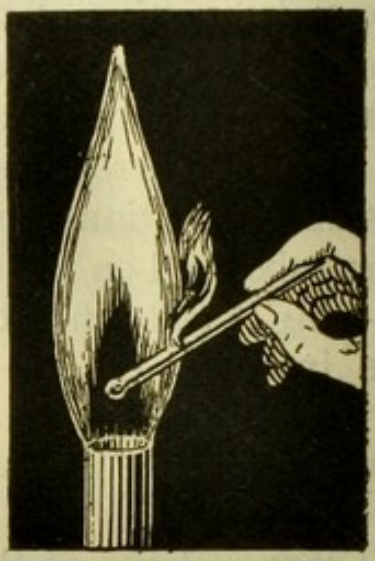


FIG. 116.

Experiments on the Interior of Coal Gas Flames.

match about 3 cm. from the tip, enables the tip of the match to be supported about 3 cm. above the jet of, say, a Bunsen's burner. The gas can be lighted. The match will remain in the centre of the flame without inflaming. The experiment can be modified by thrusting the match into the centre of the flame as illustrated in Fig. 116.

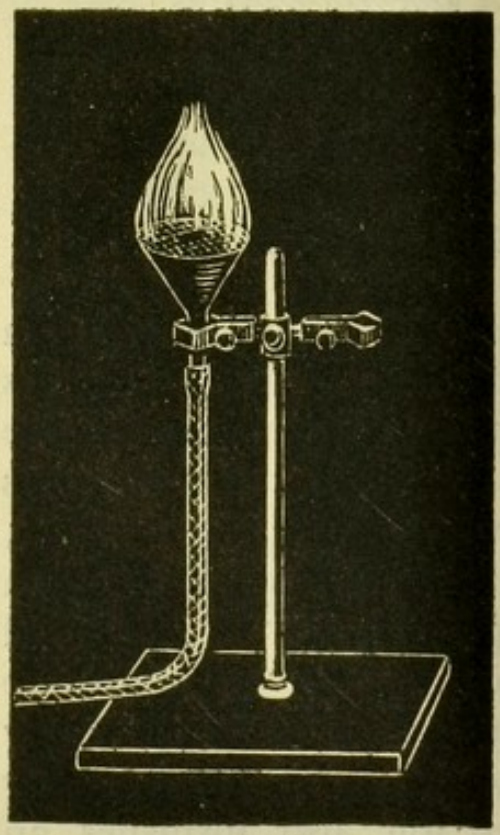


FIG. 117.—Hollowness of Flame.

(4) The preceding experiment can be modified by connecting a 5–7 cm. funnel with the gas supply as illustrated in Fig. 117. The broad mouth of the funnel is covered with a piece of fine copper or brass wire gauze. A small conical heap of gunpowder (1½ cm. base) is placed on the middle of the gauze.[1] The gas is turned on, and a lighted taper slowly depressed from above

[1] Gunpowder must not be placed on the *hot* wire gauze, and it must be kept in a compact heap so that no particles are scattered about.

downwards to the funnel until the gas is ignited. The gunpowder remains on the gauze unconsumed. Ordinary matches can be thrust through the flame and laid on the heap of gunpowder without being ignited.

Single-mantled flames.—The nature of the chemical actions which occur in the flame during the burning of gases like hydrogen in air and in chlorine are probably much simpler than is the case with gases like water gas and coal gas, which

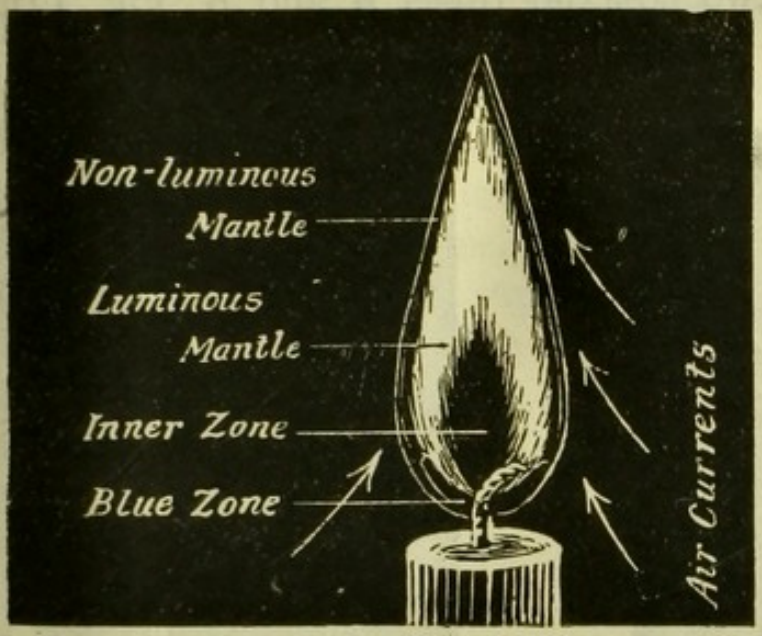


FIG. 118.—Structure of the Candle Flame.

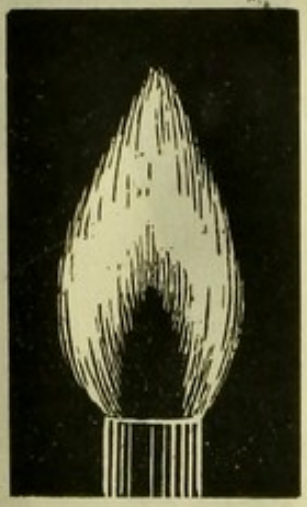


FIG. 119.—Hydrogen Flame.

furnish complex decomposition products. This is evidenced to some extent by the structure of the hydrogen flame, which is a cone with a uniform sheath of the burning gas as is illustrated in Fig. 119. The interior contains unburnt gas. A section of the flame is illustrated by *C*, Fig. 114.

Double-mantled flames.—Burning coal and water gases, burning candles, and burning oils also furnish double-sheathed flames, Figs. 118, 120. The inner mantle is bright yellow, more or less opaque and luminous; the outer mantle is but faintly luminous. Sections are illustrated by *A* and *B*, Fig. 114. In addition, there is a bluish non-luminous zone of incomplete combustion at the base of the flame. With the flame of oil lamps and candles, the hydrocarbons are drawn up the wick by capillary action and vaporized near the top of the wick; in the

case of a candle, the wax is melted by the heat of the flame. The wick is so plaited that it curls over and exposes the tip to the air. The tip of the wick is thus gradually burnt, and " snuffing " is not needed. Fig. 120 shows the structure of the non-luminous Bunsen's flame.

Smithells' flame separator.—A. Smithells has designed an apparatus (1891) which illustrates in an interesting manner the presence of the two mantles in an ordinary coal gas flame. The apparatus consists of two co-axial tubes *A* and *B*, Fig. 121.



FIG. 120.—Structure of the Flame of Coal Gas.

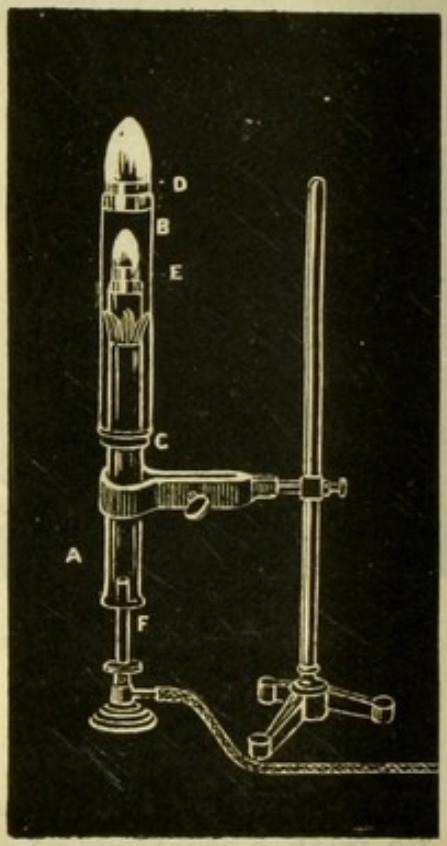


FIG. 121.—Smithells' Experiment.

The outer wider tube is shorter than the inner tube, and fitted with a rubber union *C*, and a brass tube *D* to permit the outer tube to be slid up and down. The upper ends of the co-axial tubes fire fitted one with a mica *D* and the other with an aluminium *E* cylinder. The narrower tube is clamped over an unlighted Bunsen's burner and a loose packing of cotton wool *F* placed between the burner and the glass tube. Adjust the tops of the co-axial tubes at the same level. Close the air-holes of the Bunsen's burner ; turn on the gas ; light the gas at the

top of the outer tube. The gas burns with the usual luminous coal gas flame. Gradually open the air holes of the burner until the flame appears non-luminous. Slide the outer tube upwards, and the two-coned structure of the flame will be obvious, for the outer cone ascends with the wide tube while the inner cone, after the tube has been pushed upwards about 10 cm., remains burning at the top of the inner tube.

§ 5. The Bunsen's Burner.

1. Structure of the burner.—The gas burner devised by Robert Bunsen about 1855 will be very familiar to chemical students. Its construction is easily understood. Unscrew the burner tube from the base. The burner consists of three parts. (1) The base *A*, Fig. 122, supplied with gas by means of a rubber tube connected with the main. The gas ecapes from a small opening in the base, which may or may not have a screw "pin-hole" nipple. By lighting the gas issuing from the base, a long thin pencil of flame is obtained.

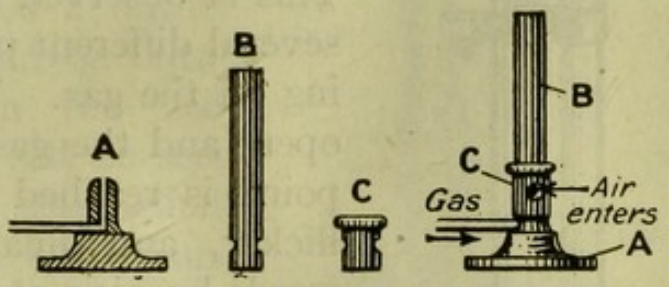


FIG. 122.—Parts of Bunsen's Burner.

(2) The burner tube, *B*, has a couple of openings near the base, and these can be closed, partially closed, or opened by turning the air regulator. (3) The air regulator, *C*, is a short cylindrical tube fitted with holes to correspond with the holes in the burner tube. There are numerous modifications, that just described may be taken as typical. Some are provided with an attachment for forcing in air under pressure, forming the so-called *blast burners* (see Figs. 31 and 58). Replace the air regulator and burner tube.

2. How the burner does its work.—If the air-holes are closed, an ordinary luminous gas flame is obtained. If the air-holes are opened, the jet of gas from the small orifice produces a partial vacuum in the neighbourhood of the jet, and, in consequence, air is drawn into the air-holes and mixes with the gas in the burner tube. The reduction in pressure is

conveniently shown by closing one of the air-holes with a piece of gummed paper, and affixing a small manometer, Fig. 123, to the other air-hole by means of a perforated cork. When the manometer is charged with a liquid—coloured to enable it to be seen better—and the gas is turned on, the movement of the liquid towards the burner shows that the air-holes exert a slight suction. When the gas is turned off, the liquid in the manometer returns to its former position.

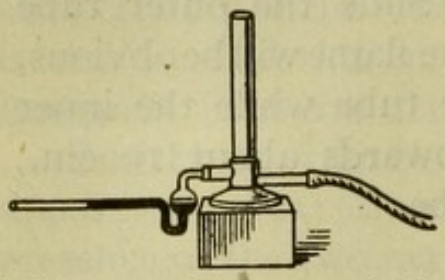


FIG. 123.—Pressure at Air-holes of Bunsen's Burner.

A certain ratio must exist between the proportion of air and gas in the burner tube in order to get the gas to burn quietly with a blue flame—the so-called **Bunsen's flame.** This is observed by placing the regulator in several different positions and gradually turning off the gas. When the air-holes are fully open, and the gas is gradually turned off, a point is reached when the flame begins to flicker, and finally "strikes back," afterwards burning at the bottom of the tube. As a matter of fact, the mixture of air and gas burning in the Bunsen's burner is explosive when the gas is burning quietly, the rate at which the flame travels in the explosive mixture of air and gas is less than the rate at which gas is issuing from the burner; when more air or less gas is introduced, the speed at which the explosive flame can travel is increased; when the rate of the explosive flame and the speed of the gas issuing from the burner are nearly equal, the flame reaches the unstable condition; any further increase in the amount of air or decrease in the amount of gas gives an explosive mixture in which the explosive flame can travel faster than the issuing gas, the flame then "strikes back." This phenomenon is best studied

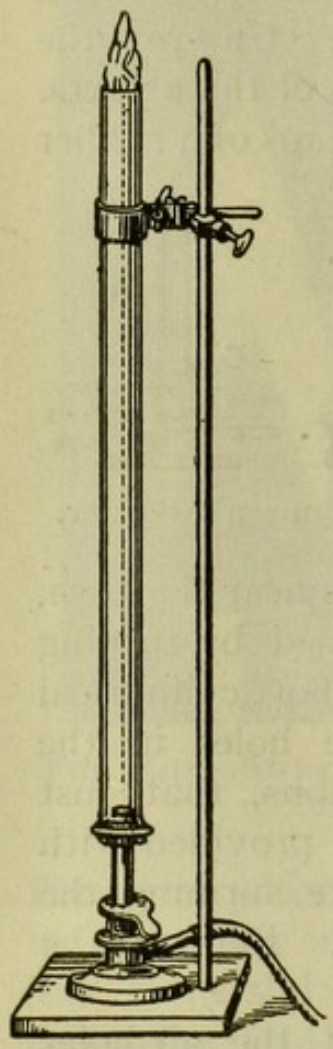


FIG. 124.—Striking back of Bunsen's Flame.

by clamping a long tube—5 or 6 feet long, and about 1½ inches wide—vertically over a Bunsen's burner, Fig. 124. Plug the space between the Bunsen's burner and the glass tube with cotton wool. Close the air-holes of the former, and light the gas (Fig. 124). Gradually remove the cotton wool until a large blue Bunsen's flame is obtained. Then open the air-holes of the Bunsen's burner gradually, and a point will be reached when the flame "strikes back" with a loud though harmless report.

In the Bunsen's burner, the proportion of air to gas is between 2 and 3 volumes of air per one volume of gas, but for complete combustion of the gas, about 6 volumes of air are needed. If such a mixture were sent through an ordinary Bunsen's burner, the flame would "strike back"—for the reasons indicated above. G. Méker, however, has designed a burner in which such a mixture can be burnt—**Méker's burner.** From the sectional diagram, Fig. 125, it will be seen that the air-holes are larger than usual, and a deep grid hinders the flame "striking back." Since the gas issuing from the burner has enough air for complete combustion, the flame is practically a "solid cone" of burning gas, and there is no "inner cone of unburnt gas." In consequence, the temperature of the interior of the flame is rather greater than the temperature near the outside.

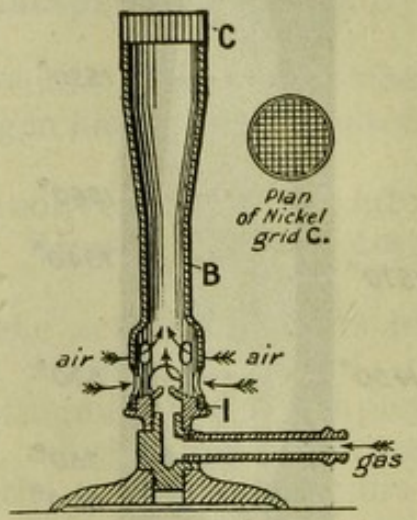


FIG. 125.—Méker's Burner.

3. Why is the flame non-luminous?—A general explanation of the cause of luminosity of flames has not been developed. In a great many cases, the luminosity of a flame is due to the presence of solid incandescent particles. With ordinary coal gas, the particles are probably carbon. The carbon is formed by the decomposition of the hot unburnt gas in the inner cones. (*a*) *Oxidation.* It was formerly taught that the non-luminosity of the Bunsen's flame was exclusively due to the influence of the admixed oxygen bringing about rapid and complete combustion, so that instead of the gas decomposing

with the production of free carbon, it was assumed that the gas was burnt directly to carbon bioxide and water. It is quite true that oxygen intimately mixed with the coal gas exerts a rapid oxidizing action, facilitates rapid combustion, and the production of a non-luminous flame. (*b*) The cooling *of the flame by different gases.* This, however, is not all the story. Inert gases like nitrogen, carbon dioxide, and steam produce non-luminous flames by chilling the reacting gases. (*c*) *The raising of the temperature of the decomposition of coal gas by admixture with inert gases.* Other things being equal, coal gas, when mixed with nitrogen, is probably more stable when heated in the inner cone than when nitrogen is absent; and accordingly, the mixture of gas and air entering the Bunsen's flame does not decompose at so low a temperature, and in consequence does not liberate free carbon so readily as the gas alone would.

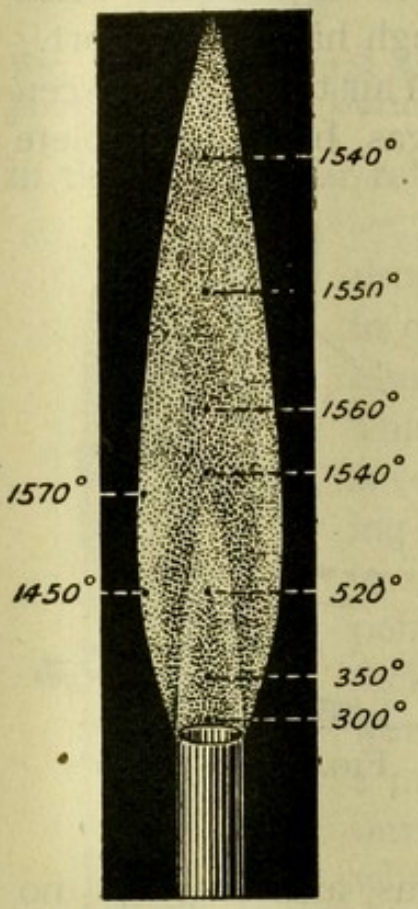


FIG. 126. — Temperatures of Different Parts of the Bunsen's Flame (Féry).

4. Oxidizing and reducing flames. —The outer mantle of the flame, where there is an excess of oxygen, is oxidizing; and the inner region, where combustion is not complete, is reducing. This can be confirmed by holding a piece of copper wire across different parts of the flame. Advantage is taken of this in qualitative analysis where oxidizing and reducing "flame reactions" furnish valuable indications of the composition of a mixture.

5. The temperature of the Bunsen's flame.—The temperature of different parts of the Bunsen's flame, as recorded by a thermocouple inserted in different parts of the flame (C. Féry) is shown in Fig. 126. The maximum temperature is somewhere between 1800° and 1870°.

Valuable information respecting the composition of certain mixtures can be obtained by taking advantage of the different

volatility of salts, and the different temperatures of the Bunsen's flame. For instance, potassium salts can be volatilized so as to give the flame reaction for potassium, before the sodium has begun to volatilize, if the mixture of the two salts be held in the cooler part of the Bunsen's flame near the burner.

Questions.

1. Carbon dioxide is constantly pouring into the atmosphere from many different sources. Why, then, has the air not become thoroughly bad during the many thousands of years since living beings came on this earth ?

2. Name the sources from which the atmosphere is constantly receiving carbon dioxide.

3. In the experiment, Fig. 108, how would you test if the statement is correct : " Oxygen and not nitrogen has been abstracted by the plant " ?

4. About 400 B.C., Plato taught that the conversion of iron into rust is attended by the loss of something. How would you test the truth or falsity of this assertion ?

5. Describe an experiment illustrating the action of plants in sunlight on carbon dioxide.—*London Univ. Matric.*

6. By what experiments could you distinguish three samples of water—one of which may be rain water, another water from a well, and the third sea water ? How may the presence of air dissolved in water be demonstrated ?—*London Univ. Matric.*

7. It is said that " the gas produced during the burning of a candle is also present in air." How would you proceed to test the truth or falsity of this statement ?

8. In the light of later investigations, explain the following statement made by J. Priestley about 1771 : " A sprig of mint vegetating for a few days in an air vitiated by a burning candle restored the purity of that air sufficiently to allow the candle to be burnt in it again."

9. A small box, containing a live guinea-pig is placed on the pan of a delicate balance, and the instrument then exactly equipoised. If the whole be now allowed to remain at rest, it will soon be seen that a distinct diminution of the weight of the box and its contents occurs. Explain this fact.—*London Univ. Matric.*

10. Explain how it is that fish can obtain sufficient oxygen for their respiration. What experiment can you suggest for the purpose of proving the correctness of your explanation ?—*London Univ. Matric.*

11. 300 vols. of carbon monoxide are mixed with 300 vols. of oxygen, an electric spark is passed through the mixture, and then

a solution of caustic potash is added ; what volume of gas will be absorbed, and what will the residue, if there be any, consist of ?—*Science and Art Dept.*

12. If you place a burning candle in a closed bottle the flame will soon be extinguished. Why does the candle not continue to burn ? How is the composition of the air affected by the flame ?—*London Univ.*

13. Give a general account of the physical and chemical processes which are taking place in the flame of a candle. Describe the structure and properties of flame.—*London Univ.*

14. Give some account of the structure of flame and explain the principle of the Davy lamp.—*London Univ.*

15. Explain the blue flame seen upon a blacksmith's fire. What effects, if any, would be produced by blowing steam together with air into the fire ?—*London Univ.*

16. Describe any experiment you may have witnessed proving that air is concerned in the combustion of substances such as are ordinarily burnt to afford heat or light. Sketch the apparatus that was used. Define combustion.—*London Univ.*

17. How may oxygen be caused to burn in either hydrogen or coal gas ? Explain the terms *complete combustion* and *incomplete combustion.—London Univ.*

18. Wet iron filings are confined with air in a glass tube. Describe all that may be learned from this experiment.—*London Univ.*

19. Describe the difference in the appearance and in the products of a candle flame burning in air and in chlorine.—*Science and Art Dept.*

20. What substances are produced when charcoal is heated to redness with (*a*) steam, (*b*) carbon dioxide, (*c*) litharge ? Explain by equations, and state any change of volume which may be noticed.—*Science and Art Dept.*

21. Make a sketch of a Bunsen burner. Mention experiments which show that the inside of the flame (*a*) is comparatively cool, (*b*) contains unburnt gas.—*Adelaide Public Exam. Board.*

22. What is lime-water, what is its appearance, how is it prepared, and what happens when we blow air from our lungs through it ?—*Madras Univ.*

23. Make a large drawing of a candle flame and describe its different parts and what is going on in them.—*Madras Univ.*

24. Why is a candle flame luminous, and the flame of a Bunsen burner non-luminous ? What is the construction of a Bunsen burner ?—*Science and Art Dept.*

25. What reasons do you give for the greater brilliancy of combustion of a candle, for example, in oxygen as compared with air ?—*Science and Art Dept.*

CHAPTER XIV

Energy and Matter

§ 1. Matter and Energy.

Matter has been conventionally defined to be that which occupies space and possesses weight (p. 1). Matter may be found under different conditions of temperature, electrification, motion, etc.; and daily experience teaches us that changes are continually taking place in the conditions of bodies around us. Change of position, change of motion, of temperature, volume, and chemical combination are but a few of the myriad changes associated with bodies in general. As a first approximation, every change in the condition of the bodies around us is supposed to be due to the action of energy. In other words, **energy is that which has the power of changing the conditions of bodies.** Whenever a body is changing its condition, there energy is in action. Energy is the cause, change of condition the effect. Work can be done only at the expense of energy, and accordingly energy is sometimes defined as the capacity for doing work; or, as W. Ostwald puts it, energy is work and all else that can be produced from or converted into work.

Energy and matter are inseparable.—We can therefore describe our knowledge of the material world in terms of two entities or abstractions: 1. Energy; 2. Matter. It is sometimes convenient to keep these two concepts distinct; although energy and matter are separable in thought, in reality they are indissolubly joined together. Energy is not matter, nor matter energy; there can be no matter without energy, nor energy without matter. **Matter is that which possesses weight and occupies space.** Matter is a convenient name for those

two qualities which all material things have in common. Air, water, glass, copper, etc., are forms of matter; heat, light, electricity, and magnetism are forms of non-matter—energy; colour, odour, etc., are specific properties of particular forms of matter.

Energy, like matter, is indestructible.—Whenever it has been possible to make accurate measurements it has been proved that when any quantity of one form of energy is made to disappear, an equivalent quantity of another form or forms of energy appears. **No gain or loss of energy has ever been observed in an isolated system.** This is the famous **law of conservation or persistence of energy.** We have no means of measuring the absolute or total amount of energy which a body possesses. Air confined in a closed vessel at atmospheric pressure might appear to possess no energy because it can do no work. But reduce the pressure of the surrounding air, and the air confined in the vessel is capable of performing work. In the study of natural phenomena, we are only concerned with that portion of the total energy which can be utilized for doing work. This is called the **available energy.**

A raised stone can do work in falling to a lower level, and it is therefore said to possess more available energy than a similar stone in a less elevated position. Again, water in an elevated position can do work in virtue of the law that "all liquids will flow to the lowest level that circumstances will permit." Consequently, water at the top of a hill possesses available energy. A bent spring, a raised hammer, compressed air, and a piece of iron in the vicinity of a magnet, all have available energy. Substances which in virtue of their relative condition, or the motions of their molecules, are capable of entering into chemical actions, are also said to possess available energy. Such is gunpowder, a mixture of metallic zinc and sulphuric acid, etc. The light, heat, sound, and mechanical motion which attend the explosion of guncotton are equivalent to the chemical energy stored in the explosive.

§ 2. The Degradation or Dissipation of Energy.

The transformations of energy.—Water may be transported from the top of a mountain to the valley beneath in a

variety of ways : it may come down in underground channels, rivers, and rain ; or in the form of snow, glaciers, or an avalanche. So may energy pass from a state of high to a state of low potential in many and various ways, giving rise to mechanical, thermal, actinic, chemical, electrical, or magnetic phenomena. In reality, the so-called " different forms of energy " correspond with the tendencies which any given system may have to change in particular directions. If there is a tendency for the different parts of a system to come into closer contact, we have gravitation or cohesion ; if there is a tendency to an equalization of temperature, thermal energy ; and when there is a tendency to undergo transformation into another substance, chemical energy. Hence, the definition : **a chemical reaction is one mode by which energy can be transferred from one state to another.** We have seen many examples of the liberation of energy—heat, light, electricity—during chemical reactions. **To avoid the assumption that this energy comes from nothing, it is postulated that the original system contained a definite amount of available energy—chemical energy.**

If a substance can unite with another, it is said to possess chemical energy, because it can do chemical work ; and conversely, substances which cannot combine chemically with other substances have no available chemical energy, for they can do no chemical work. During a chemical reaction, the chemical energy is transformed into an equivalent amount of some other form of energy, which is usually, though not always, heat (see p. 71). Hence, the relation between chemical energy and heat (thermal energy) is an important subject, which, for convenience, is called **thermochemistry.** Chemical energy may also be transformed into electrical energy during a chemical reaction. That branch of chemistry which deals with the relation between chemical energy and electricity (electrical energy) is called **electrochemistry.** Just as chemical changes which are accompanied by an evolution of heat are called " exothermal reactions," so reactions which are accompanied by an evolution of electrical energy have been called " exo-electrical reactions," and conversely for " endothermal " and " endo-electrical " reactions.

The degradation of energy.—Just as water will always run down from a high to the lowest level that circumstances will permit, so **in all processes with which we are acquainted, every known form of energy at a high potential always runs down to energy at the lowest potential circumstances will permit,** and one of the most interesting facts in connection with all natural changes is this constant running down or degradation of energy. Energy becomes less available for doing work. **Every change which takes place in nature does so at the cost of a certain amount of available energy.** When we inquire whether or not a transformation can take place, the question to be answered is: Will the occurrence involve the degradation of energy? If not, the transformation will not take place under the given conditions. An ancient philosopher—Heracleitus of Ephesus—said that "all things are in motion," and we might add that that motion always involves the degradation of energy. The transformation of energy in a given system only ceases when the available energy has run down to the level of its surroundings. The system is then said to be in a **state of stable equilibrium.**

§ 3. Thermochemistry.

It has just been emphasized that we have no acquaintance with matter apart from energy. Isolated matter and energy are pure abstractions. Each one completes and presupposes the other. The element chlorine, for instance, must be regarded as a form of matter which is always associated with a certain amount of available energy, because it is able to do chemical work, and we cannot conceive of energy coming from nothing. We cannot answer: How much energy is associated with the chlorine? The actual amount available possibly depends upon the nature of the substance with which it is brought in contact. Similarly with hydrogen. When these two elements—hydrogen and chlorine—are brought in contact, under the right conditions for the degradation of energy, chemical action sets in, and the chemical energy is degraded or transformed into heat or light. The resulting compound—hydrogen chloride—still contains some chemical energy, for if it be mixed with water,

a great amount of heat is developed, chemical energy is degraded, and hydrochloric acid results. The hydrochloric acid still contains chemical energy because more energy is degraded in the form of heat when the acid is brought into contact with sodium hydroxide, and sodium chloride is formed. **Every chemical reaction involves a change both in the form of the matter and in the form of the energy of the system.** What is generally understood by "descriptive" or "material" chemistry deals with the former, not with the latter. The chemistry of to-day is not materialistic, for it is concerned with both energy and matter.

Law of Lavoisier and Laplace.—The free or available chemical energy of different substances is usually degraded in the form of heat during chemical action. The system gets hotter because heat is evolved by the reacting substances—such reactions are said to be **exothermal reactions** in contrast with **endothermal reactions** which absorb heat and thus cause the system to become cooler. That branch of chemistry which deals with the relation between thermal and chemical energy is called **thermochemistry.** Experiment shows that every compound has a definite heat of formation, which is numerically equal to the heat required for the decomposition of the compound back into its elements, but of opposite sign. If it were not so, heat would be gained or lost when a compound is formed and then decomposed back into its original constituents. Such a result is at variance with the principle of the persistence or conservation of energy. The fact that **every compound has a definite heat of formation which is numerically equivalent to its heat of decomposition but of opposite sign,** is sometimes called the **law of Lavoisier and Laplace,** because A. L. Lavoisier and P. S. de Laplace first pointed out this generalization between 1780–84.

The symbols used in thermochemistry.—The unit of heat is called the **calorie,** and it has been agreed that a calorie is to represent the amount of heat required to raise the temperature of one gram of water through 1° C. Consequently, 100 cals. will raise the temperature of 100 grams of water 1°, or of 1 gram of water 100°. In chemistry, it is convenient to

represent the thermal value of a reaction by reference to the formula weights of the substances concerned in the reaction. Thus the heat of formation of phosphorus pentoxide is 370,000 cals. This means that 370,000 cals. are generated when 142 grams of phosphorus pentoxide are formed by burning 62 grams of phosphorus in oxygen. To avoid dealing with large numbers it will be more convenient to consider a **calorie** as the amount of heat required to raise the temperature of 1000 grams of water 1° C. This is the so-called " kilogram-calorie," or the " big calorie," and it is here written with a capital " C." Thus " cal." refers to the gram-calorie, " Cal." refers to the kilogram-calorie. Hence, the energy degraded in the form of heat when phosphorus burns in oxygen is equivalent to 370 Cals. This is represented in symbols :

$$2P+5O=P_2O_5+370 \text{ Cals.}$$

If the state of aggregation of the initial and final products of the reaction are not self-evident, the state of aggregation must be represented in the equation, otherwise latents of fusion or vaporization may lead to ambiguity. Thus :

$$2H+O=H_2O_{gas}+59{\cdot}4 \text{ Cals.}$$

means that the union of 2 grams of hydrogen with 16 grams of oxygen is attended by the evolution of 59·4 big Calories when the water is in the form of steam ; if the steam is condensed to a liquid,

$$2H+O=H_2O_{liq}+68{\cdot}4 \text{ Cals.}$$

The extra 9·0 Cals. represent the heat given out when 18 grams of steam are condensed to a liquid. Again, if the reacting substances are in aqueous solution, a certain amount of heat may or may not be dissipated in the act of solution. For example, 13·7 Cals. are evolved when a dilute solution of sodium hydroxide is mixed with a dilute solution of hydrochloric acid. The dilute solution is represented by a suffix " aq." Thus :

$$NaOH_{aq}+HCl_{aq}=NaCl_{aq}+H_2O+13{\cdot}7 \text{ Cals.}$$

If the sodium chloride were prepared by passing hydrogen chloride gas into a dilute solution of sodium hydroxide, more

heat is evolved, because 17·4 Cals. are evolved when 36·4 grams of hydrogen chloride are dissolved in water :

$$NaOH_{aq}+HCl_{gas}=NaCl_{aq}+H_2O+31{\cdot}1 \text{ Cals.}$$

§ 4. Ozone.

The preparation of ozone.—When a series of electric sparks pass in air there is a curious smell in the neighbourhood. This smell has been traced to the formation of a kind of oxygen —called ozone—different from that which is prepared by

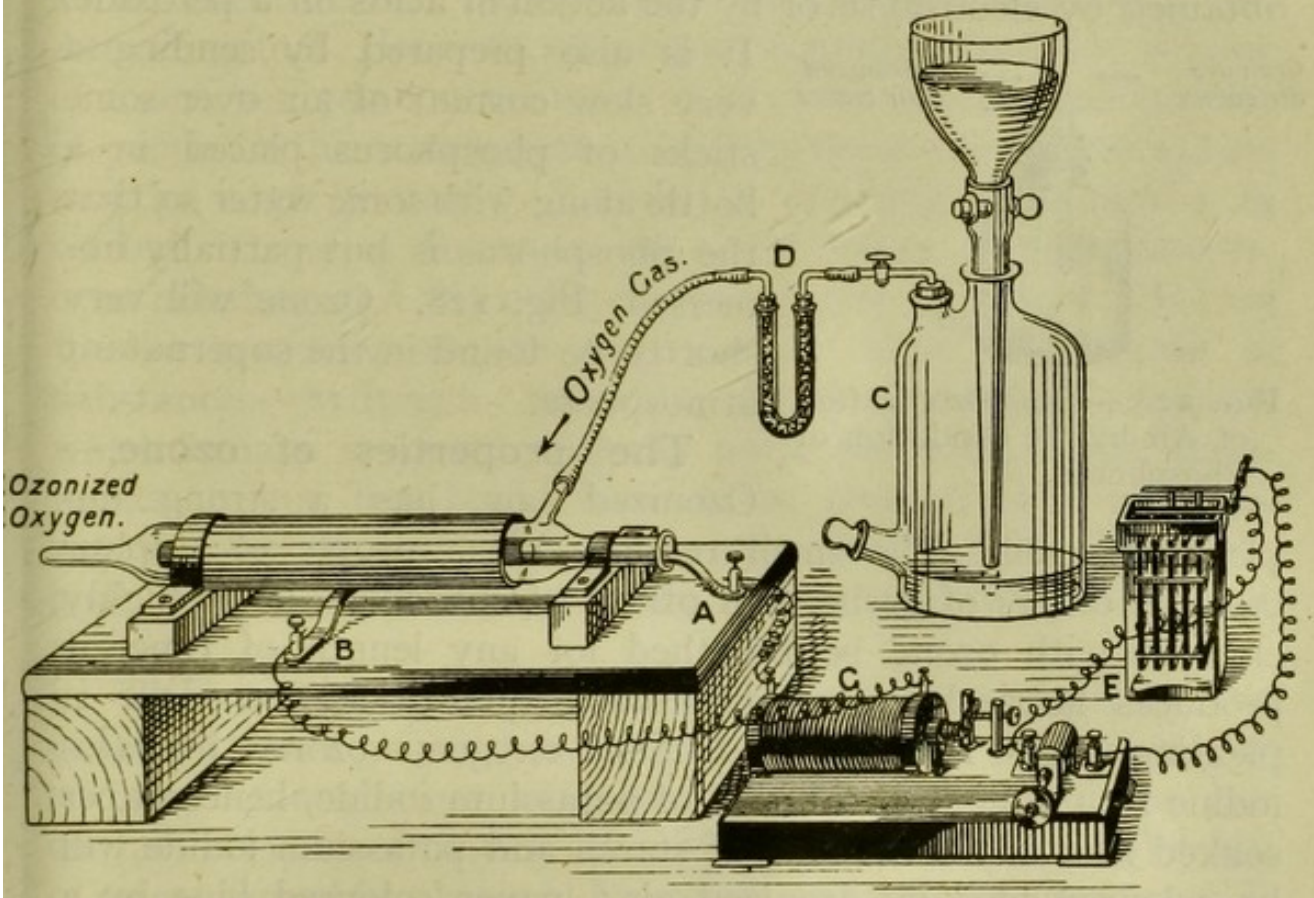


FIG. 127.—Preparation of Ozone by Exposing Oxygen or Air to an Electric Discharge.

ordinary processes. One of the most convenient ways of making ozone is to pass an electrical discharge through oxygen. The apparatus illustrated by Fig. 127 may be used. It consists of two concentric tubes. The inner tube is coated on its inner surface with tinfoil in metallic contact with the terminal *A* ; and the outer tube is coated on its outer surface with tinfoil in metallic contact with the terminal *B*. The two terminals are

connected with an induction coil. A slow stream of oxygen is led from the gasholder *C* through the calcium chloride drying tube *D*, and then through the annular space between the concentric tubes, and is there exposed to a discharge of electricity which passes from one tinfoil surface to the other, and is operated by the induction coil and battery *E*. The gas issuing from the ozone tube or ozonier is charged with 3 to 8 per cent. of ozone. Air can be used in place of oxygen, but the ozone is then contaminated with nitrogen.

Ozone is also formed in small quantities when oxygen is obtained by electrolysis or by the action of acids on a peroxide. It is also prepared by sending a very slow current of air over some sticks of phosphorus placed in a bottle along with some water so that the phosphorus is but partially immersed, Fig. 128. Ozone will very shortly be found in the supernatant atmosphere.

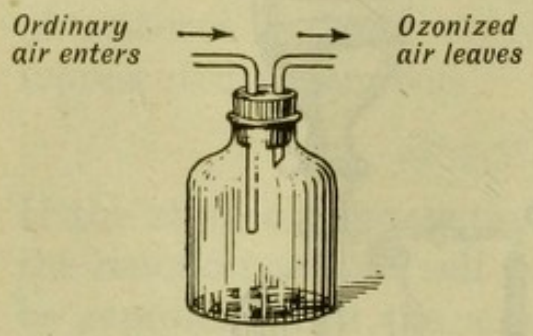


FIG. 128.—The Ozonization of Air by the Oxidation of Phosphorus.

The properties of ozone.—Ozonized air has a strong unpleasant smell. The smell reminds some people of sulphur dioxide, others of garlic, and others of chlorine. If air highly charged with ozone be breathed for any length of time, it produces headache; but in minute quantities the odour is pleasing and refreshing. Unlike oxygen, ozone liberates iodine from a neutral solution of potassium iodide, hence paper soaked in a mixed solution of starch and potassium iodide will be coloured blue by ozonized air; paper coloured blue by a solution of indigo or by litmus is bleached. A globule of mercury shaken in a flask containing ozonized air loses its lustre and spreads a film over the walls of the flask. The globule of mercury is restored by shaking with water. Metallic silver also is oxidized by ozone. Ozone is absorbed by turpentine, cinnamon, and similar oils. Ozone is rapidly decomposed into ordinary oxygen when heated, and by exposure to organic substances like cork, indiarubber, etc.; and also catalytically by exposure to finely divided platinum, to silver oxide, Ag_2O,

manganese dioxide, MnO_2, etc. Paper dipped in a solution of lead acetate and exposed to the fumes of hydrogen sulphide is blackened owing to the formation of lead sulphide. The blackened paper becomes white again on exposure to ozonized air owing to the conversion of black lead sulphide, PbS, into white lead sulphate, $PbSO_4$.

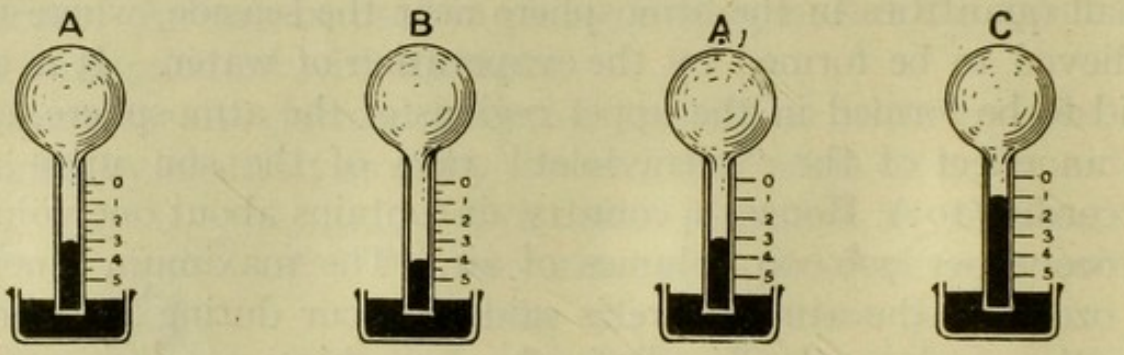
The occurrence of ozone.—Ozone is supposed to occur in small quantities in the atmosphere near the seaside, where it is believed to be formed by the evaporation of water. It is also said to be formed in the upper regions of the atmosphere, etc., as an effect of the "ultraviolet" rays of the sun upon air. According to A. Houzeau, country air contains about one volume of ozone per 700,000 volumes of air. The maximum amount of ozone in the atmosphere is said to occur during the spring months, and gradually diminishes, reaching a minimum in winter. Ozone is absent in the air of towns, dwelling-houses, over marshes, and wherever organic matter is present. Owing to the confusion of the reactions of ozone with those of substances—hydrogen peroxide, chlorine, nitrogen oxides—which behave in many respects quite similarly, many statements in our text-books have to be revised. For instance, many doubt if ozone has ever been detected in air at all, and they say that ozone has been confused with other things.

The constitution of ozone.—(1) Since ozone can be obtained from purified oxygen without the withdrawal or addition of any other kind of matter to oxygen, ozone can contain no form of matter other than oxygen. (2) The density of ozone cannot be obtained by weighing because oxygen as well as ozone are always mixed together. A sample of ozonized oxygen is introduced into two flasks, A and A_1, Fig. 129. (*a*) The vessel A is heated so as to decompose the ozone. The gas now occupies a greater volume than before, B, Fig. 129. The expansion is measured when the gas is cooled to its former temperature. The vessel A_1, containing the same mixture of ozonized oxygen, is treated with cinnamon oil; the contraction due to the removal of ozone can be measured, C, Fig. 129.

Soret found the following data, Fig. 129, with measured volumes of a sample of ozonized oxygen :

Expansion after heating . . . . . 1 c.c.
Contraction after treatment with cinnamon oil. 2 ,,

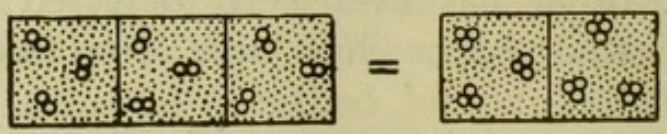
Hence the ozonized oxygen contained 2 c.c. of ozone ; and 2 c.c. of ozone becomes 3 c.c. of ordinary oxygen when heated.



(A) Ozonized oxygen. (B) After the ozone has been converted into oxygen by heat. (A) Ozonized oxygen. (C) After removal of ozone with cinnamon oil.

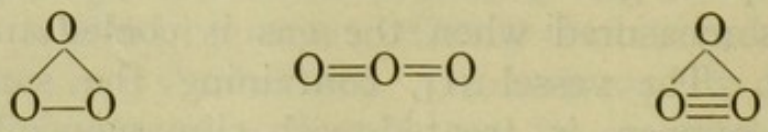
FIG. 129.—Soret's Experiments with Ozone (Diagrammatic).

This is interpreted by Avogadro's hypothesis to mean that **three volumes of oxygen form two volumes of ozone.** This idea is diagrammatically represented by



3 Volumes of Oxygen give 2 Volumes of Ozone.

This interpretation would make the density of ozone 48 when oxygen is 32. The deduction has been confirmed by comparing the rates of diffusion of ozone with oxygen whose density is known (p. 223). Accordingly, **the molecular formula of ozone is written O_3** ; but we do not know whether to write the graphic formula :



The available energy of ozone.—When ozone is converted into oxygen, heat is liberated ; and when oxygen is converted

into ozone, heat is absorbed. **Energy equivalent to 34·1 Cals. is absorbed in the production of one molecule of ozone from ordinary oxygen.** Otherwise expressed :

$$3O_2 = 2O_3 - 68{\cdot}2 \text{ Cals. ; or } 3O_2 + 68{\cdot}2 \text{ Cals.} = 2O_3$$

Hence, when oxygen is associated with this extra energy, its properties are quite different from those of ordinary oxygen. So far as we can see, therefore, the molecule of ozone contains three atoms of oxygen while the molecule of ordinary oxygen contains two atoms of oxygen ; and the three-atom molecule has the equivalent of 34·1 Cals. more of available energy associated with it than the two-atom molecule. It may be said that in virtue of this extra energy, the ozone is more active chemically.

Uses.—Ozone is used for the purification of water. Its function is to oxidize the organic matter and sterilize the water. Ozonized air is also used in ventilation, for bleaching oxidizing oil in the manufacture of linoleum, etc. The industrial applications have stimulated inventors, and accordingly, a number of fairly efficient ozonizers have been placed on the market. In most of these, a high-tension alternating electric discharge is sent across a space through which the air to be ozonized passes.

Questions.

1. How would you demonstrate the presence or absence of ozone in a given sample of air ?

2. Compare the properties of ozone with those of oxygen.—*Science and Art Dept.*

3. What is the action of ozone upon each of the following substances : (*a*) Turpentine, (*b*) indiarubber, (*c*) manganese dioxide, (*d*) silver oxide, (*e*) lead sulphide, (*f*) finely divided silver ?—*Science and Art Dept.*

4. The formula for ozone is O_3, describe fully experiments the results of which support this formula.—*Science and Art Dept.*

5. How is ozone produced in nature, and by what means can its presence in air be detected ?—*Science and Art Dept.*

6. What is the action of ozone upon potassium iodide, and how would the effect be distinguished from that which is produced upon the same salt by nitrogen peroxide ? Calculate the weight

of potassium iodide equivalent to one gram molecule of ozone. (K=39·1, I=126·8, O=16.)—*Science and Art Dept.*

7. Define the terms electrolysis, anion, endothermal reaction. Give two examples of each.—*Cape Univ.*

8. State the law of diffusion of gases. Soret found that 0·227 c.c. of chlorine diffused in the same time as 0·2708 c.c. of ozone. Calculate the density of ozone assuming that the density of chlorine is 36 (nearly).—*Cambridge Univ.*

9. What do the following expressions mean: (*a*) basic salt, (*b*) equivalent of an element, (*c*) unstable compound, (*d*) exothermic compound?

CHAPTER XV

The Relations of Chlorine—Iodine, Bromine, and Fluorine

§ 1. Commercial Processes for Making Chlorine.

Weldon's process.—Chlorine is prepared on a large scale by the action of manganese dioxide on hydrochloric acid, but to cheapen the process the solution of manganese chloride is mixed with slaked lime to about 55°, and agitated by blowing air through the solution. A precipitate of lime and manganese oxide separates as a brown mud—*Weldon's mud*. Weldon's mud can be used over again to oxidize more hydrochloric acid.

Deacon's process.—If a mixture of air and hydrogen chloride be passed through a hot tube, a little free chlorine is formed owing to the oxidation of a small percentage of the hydrogen chloride; but if the hot tube contains pumice stone saturated with a salt of copper, a considerable proportion of the hydrogen chloride is oxidized to chlorine: $4HCl+O_2=2H_2O+2Cl_2$. The copper salt seems to act as a catalytic agent, and in this respect it resembles the action of manganese dioxide on decomposing potassium chlorate. The process can be illustrated by the apparatus, Fig. 130, where a gentle current of air is driven through a flask containing warm concentrated hydrochloric acid. The mixture of air and hydrogen chloride is passed through a wash bottle containing water, and then through a hard glass tube containing pumice stone which has been soaked in a solution of copper chloride and dried. Chlorine gas mixed with nitrogen, etc., issues from the tube, and it may be collected in a jar by the upward displacement of air.

Electrolytic process.—If an electric current from an accumulator, Fig. 41, be sent through a U-tube containing a

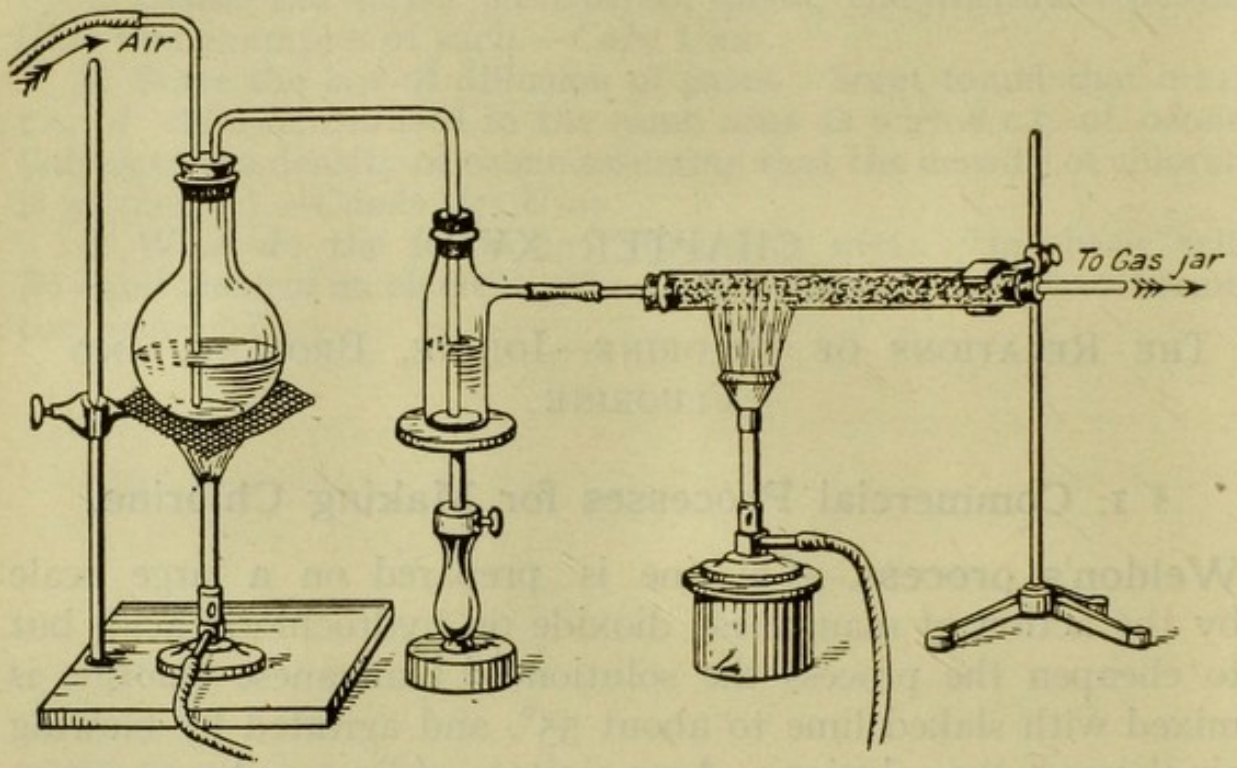


FIG. 130.—Illustration of Deacon's Process for Chlorine.

concentrated solution of zinc chloride and with side tubes, as shown in Fig. 131, and also with a platinum wire cathode and a carbon rod as anode, metallic zinc will precipitate on the cathode; no gas will be evolved from the side tube, but chlorine gas will be given off at the other side. The action is probably: $ZnCl_2 \rightarrow Zn + Cl_2$.

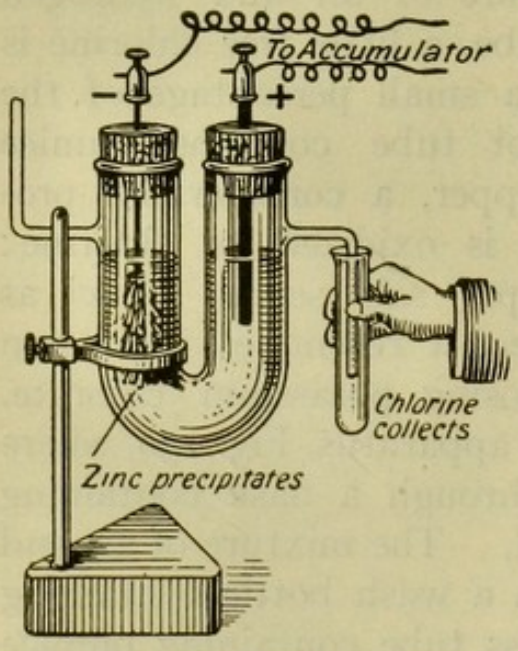


FIG. 131.—The Electrolysis of Zinc Chlorides.

If the U-tube be charged with a concentrated solution of sodium chloride, chlorine will be given off at the anode as before, but hydrogen gas will be given off at the cathode. By analogy it is inferred that the sodium chloride is decomposed into sodium and free chlorine: $2NaCl \rightarrow 2Na + Cl_2$; and that the metallic sodium which separates at the cathode immediately reacts with the water

(p. 123), forming hydrogen and sodium hydroxide: $2Na+2H_2O \rightarrow 2NaOH+H_2$. If the solution of salt had been mixed with red litmus, the colour would be bleached about the anode and coloured blue about the cathode. Several modifications of this reaction are employed on a manufacturing scale for converting a solution of sodium chloride into: (1) chlorine gas; (2) sodium hydroxide; and (3) hydrogen as a by-product. To hinder the diffusion of the sodium hydroxide to the solution of chlorine which accumulates about the anode, porous diaphragms of various kinds are used. The carbon anode is here used because it is not attacked by chlorine, as is the case if platinum be used.

When concentrated hydrochloric acid is electrolyzed in place of zinc chloride, hydrogen is given off at the cathode, and chlorine at the anode. The reaction is represented: $2HCl \rightarrow H_2+Cl_2$.

§ 2. Bromine.

Discovery.—While studying the mother liquid which remains after the crystallization of salt from the water of the salt marshes of Montpellier, A. J. Balard (1826) was attracted by the intense yellow coloration developed when chlorine water is added to the liquid. Balard digested the yellow liquid with ether; decanted off the yellow supernatant ethereal solution; and treated this with potassium hydroxide. The colour was destroyed. The solution was evaporated to dryness. The residue resembled potassium chloride, but, instead of chlorine, it furnished, when heated with manganese dioxide and sulphuric acid, red fumes which condensed to a dark brown liquid with an unpleasant smell. Balard called this substance "muride," but afterwards changed the name to "bromine"—from a Greek word meaning stench. Balard demonstrated the elementary nature of bromine, and showed that it is closely related to chlorine.

Occurrence.—Bromine does not occur free in nature. Small quantities occur combined in many silver ores; and it occurs associated with potassium, sodium, magnesium, or

calcium, in many mineral waters, salt springs, and sea-water. The water of the Atlantic is said to contain 0·007 per cent. of magnesium bromide ; the water of the Dead Sea, 9 per cent., the mineral water of Ohio, from 3·4 to 3·9 per cent. of magnesium bromide. Bromine is also found in marine animals and plants, in rock salt, etc. The saline deposits of Stassfurt contain about one per cent. of magnesium bromide. From this latter source, the main supply of the bromine in commerce is derived.

Manufacture.—The mother liquid remaining after the separation of the potassium salts from carnallite, p. 133, contains about 0·25 per cent. of bromine in the form of magnesium bromide. The hot liquid is allowed to percolate down a tower packed with earthenware balls ; here the descending liquid meets an ascending stream of chlorine gas. The magnesium bromide is decomposed: $MgBr_2+Cl_2=MgCl_2+Br_2$. The bromine vapours leave the top of the tower through an exit pipe, and are liquefied in a suitable condenser. In the electrolytic process of manufacture, the mother liquid from the carnallite is electrolyzed. The magnesium bromide can be decomposed by the electric current before the magnesium chloride, and even if some chlorine is formed it attacks the magnesium bromide, as just indicated, thus it is possible and practicable to separate the bromine.

Preparation.—Bromine is prepared in the laboratory by the action of sulphuric acid and manganese dioxide upon potassium bromide as in the preparation of chlorine from potassium or sodium chloride, Fig. 73.

Properties.—At ordinary temperatures, bromine is a heavy mobile reddish-brown liquid, nearly three times as heavy as water. It freezes to a yellowish-brown crystalline mass at $-7°$, and boils in air at 59°. It is very volatile, and gives off a dark reddish-brown vapour at ordinary temperatures. Bromine separates in the form carmine-red needle-like crystals, when a solution of bromine in carbon disulphide is cooled to $-90°$. The solid is almost colourless at $-252°$. Bromine has a disagreeable irritating smell, and it irritates the eyes, causing a copious flow of tears, and it also attacks the mucous membrane of the throat and nose. It is poisonous, and attacks the skin,

producing troublesome sores. 100 grams of water dissolve 3·2 grams of bromine at 20°. The solution is called *bromine water*. Bromine is also fairly soluble in chloroform, carbon disulphide, etc. Bromine resembles chlorine in general chemical properties, but is not quite so energetic. Bromine combines directly with many elements—phosphorus, antimony, copper, iron, etc.—forming bromides analogous with chlorides. It unites slowly and incompletely with hydrogen in sunlight, forming hydrogen bromide.

Uses.—Bromine is used in metallurgy, photography, and the chemical industries. It is also used as a disinfectant, for which purpose it is sold under the name "bromum solidificatum" (solid bromine), which is kieselguhr—a siliceous earth, p. 593—saturated with bromine. Bromine is also used as an oxidizing agent.

§ 3. Hydrogen Bromide—Hydrobromic Acid.

Preparation.—From the analogy of bromine with chlorine, it might be expected that hydrogen bromide would be prepared by the action of sulphuric acid on potassium or sodium bromide, just as hydrogen chloride is prepared by the action of the same acid on sodium chloride. When the attempt is made, it is true that colourless hydrogen bromide is at first given off, but the issuing gas immediately acquires a yellow and then a brown tinge characteristic of bromine. The hydrogen bromide, in fact, is oxidized by the sulphuric acid, and the sulphuric acid is reduced. A dilute solution of the acid can be made with dilute sulphuric acid, but the action is very slow.

This gas can be obtained directly from its elements. If a stream of hydrogen be bubbled through warm bromine, the hydrogen which passes along is highly charged with bromine vapour, and, when ignited, dense clouds of hydrogen bromide are formed. If a mixture of hydrogen and bromine be passed through a red-hot tube containing platinized asbestos, or a hot platinum spiral, the elements rapidly combine. The platinum acts as a stimulant or catalytic agent.

The following is the method employed in the laboratory: Mix, say, 10 grams of red phosphorus with 80 grams of fine

sand, and place the dry mixture in a dry distillation flask, *A*, Fig. 132. Add about 20 c.c. of water. Close the flask with a rubber stopper fitted with a tap funnel, *B*, and delivery tube as indicated in Fig. 132. The end of the tap funnel is drawn to a fine point. Connect the delivery tube with a tower or a U-tube, *D*, containing glass wool and slightly damp red phosphorus. The gas may be collected by the upward displacement of air, or absorbed in water, or collected over mercury. The absorption vessels for water are best arranged as indicated in Fig. 132. Two wash bottles, *E*, *F*, are arranged so that if there is a back suction in the flask, water is drawn from *F* to *E*; and when the gas issues from the gas generator, the liquid is forced on to *F*, and the gas bubbles through in the usual way. One wash-bottle, *F*, is one-third filled with water, the other, *E*, at the start, is empty. About 60 grams of bromine are placed in the tap funnel, and allowed to fall, drop by drop, on the red phosphorus. As each drop of bromine comes in contact with the phosphorus, a flash of light is produced. Some prefer to keep the flask immersed in cold water during the early stages of the reaction, and to wrap a towel round the flask in case of an explosion. The heat of the reaction volatilizes some bromine, which is retained by the phosphorus in the U-tube; when all the bromine has been run into the flask, a further quantity of hydrogen bromide may be obtained by gently warming the flask. If gaseous hydrogen bromide is required, it can be dried by means of a tube packed with calcium bromide.

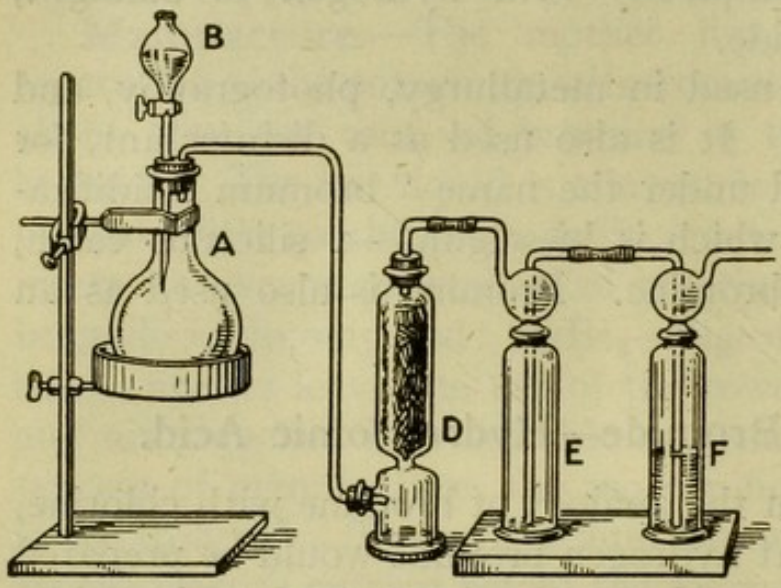


FIG. 132.—Preparation of Hydrogen Bromide and Hydrobromic Acid.

The chemical reactions which occur during the preparation of hydrogen bromide by the action of bromine on phosphorus

and water, are probably somewhat as follows: Phosphorus bromide, PBr_3, is first formed, this reacts with the water: $PBr_3+3H_2O=H_3PO_3+3HBr$. The whole reaction is usually represented on the supposition that phosphorus tribromide is formed: $2P+6H_2O+3Br_2=2H_3PO_3+6HBr$. Several other side reactions occur.

Properties.—Hydrogen bromide is a colourless gas with a strong penetrating smell. It fumes in air. The gas condenses to a liquid at $-73°$; and solidifies to a colourless solid at $-87°$. It is very soluble in water. The aqueous solution is called **hydrobromic acid.**

Dry hydrogen bromide has no action on litmus. Hydrogen bromide resembles hydrogen chloride very closely in chemical properties, but is less energetic. Hydrobromic acid forms **bromides** in the same way that hydrochloric acid forms chlorides. Hydrogen bromide is more easily decomposed than hydrogen chloride. At 800° decomposition is quite appreciable. The gas is also slightly decomposed by exposure to sunlight.

§ 4. Iodine.

Discovery.—In 1812, B. Courtois used an aqueous extract of varec or kelp in the manufacture of saltpetre. (*Varec* or *kelp* is the ash obtained from dry seaweed burnt at as low a temperature as possible.) Courtois noticed that the copper vats, in which the kelp solution was used, were rapidly corroded by the liquid, and he traced the effect to a reaction between the copper and an unknown substance in the lye obtained by extracting the kelp with water. On evaporating the aqueous extract of the kelp, crystals of potassium sulphate first separate, then follow crystals of sodium sulphate, sodium chloride, and afterwards sodium carbonate. The remaining liquid is heated with sulphuric acid in a retort. "A vapour of a superb violet colour" is obtained which condenses in the tube of the retort and receiver in the form of brilliant crystalline plates. In 1814, Gay-Lussac published an extensive and remarkable memoir on this new substance, which was called iodine—from a Greek word meaning violet. Gay-Lussac established the elementary

nature of iodine, and demonstrated its relationship to chlorine.

Occurrence.—Varec or kelp contains from 0·1 to 0·3 per cent. of iodine. The kelp derived from deep seas is richer in iodine than that from shallower parts. Iodine also occurs in small quantities in sea-water ; sea plants ; sea animals ; in some land plants and animals ; in cod-liver oil ; in the thyroid gland of animals ; and in many mineral springs. It occurs combined with silver in some Mexican ores, and in some South American lead ores. Much of the iodine of commerce is extracted from the mother liquid remaining after the separation of sodium nitrate from " caliche " in Peru, etc.

Manufacture.—The mother liquid remaining after the crystallization of the sodium nitrate from the aqueous extract of caliche is treated with sodium bisulphite, which first reduces the sodium salt to free iodine. The solid iodine which separates is allowed to settle, washed, and pressed into blocks. The impure iodine so obtained is sublimed in iron retorts and the vapours condensed in a series of earthenware receivers.

Iodine is extracted from the ash of seaweed by concentrating the aqueous extract so as to remove alkaline carbonates, chlorides, and sulphates by crystallization. The mother liquid containing the iodides and some bromides is treated first with sulphuric or hydrochloric acid, and then with manganese dioxide. On heating the mixture, iodine is liberated : $2NaI+Cl_2 = 2NaCl+I_2$. This is condensed in earthenware receivers arranged so that any water distilled over is condensed and drained off. A ton of kelp is said to furnish 10 to 12 lbs. of iodine.

Preparation.—In the laboratory iodine can be prepared by a process analogous with that used for chlorine and bromine, but using potassium iodide in place of the corresponding chloride or bromide, Fig. 22.

Properties.—At ordinary temperatures, iodine is a dark bluish-black crystalline plate with a metallic lustre. Iodine vaporizes slowly at ordinary temperatures, and it has a slight smell resembling chlorine. It is very sparingly soluble in

water : 100 volumes of a saturated solution at 25° contain about 0·32 gram of iodine, and is coloured a faint brown. The iodine is much more soluble if potassium iodide be also present. Iodine is fairly soluble in many organic solvents—alcohol, ether, acetone, chloroform, carbon disulphide, benzene, etc. The colours of the solutions differ with different solvents : chloroform and carbon disulphide give violet solutions ; while alcohol, water, aqueous solutions of potassium iodide, and ether give brown solutions. This is illustrated by the following experiment : Place a layer of carbon disulphide, *A*, at the bottom of a glass cylinder, Fig. 133 ; on this a layer of water, *B*, and above all, a layer of ether, *C*. Drop some crystals of iodine into the cylinder. The lowest layer will form a violet solution ; water will give a yellowish-brown solution, and the ether a brown solution. It is supposed that the violet solutions contain free iodine, and the brown solutions a tri-iodide—HI_3.

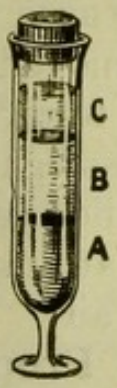


FIG. 133.—Colours of Iodine Solutions.

Iodine resembles chlorine and bromine in its chemical properties, but it is rather less energetic. Chlorine can displace bromine from bromides, and both chlorine and bromine can displace iodine from iodides. Iodine, like chlorine and bromine, combines with many elements, forming **iodides.** When yellow phosphorus and iodine are placed in contact, the phosphorus melts and inflames, forming phosphorus iodide. Antimony powder inflames spontaneously when it is shaken with iodine vapour ; iodine and mercury also combine energetically when heated.

When in contact with starch, iodine forms an intense blue coloration. The reaction is delicate enough to reveal the presence of 0·0000001 grm. of iodine per c.c. The blue colour disappears when heated to about 80°, but returns on cooling. The " blued " starch is supposed to be either a " solid " solution of iodine in the starch, or else an " addition " compound of iodine with starch.

Uses.—Iodine is used in medicine, the manufacture of dyes and organic compounds, in photography, and in analytical chemistry.

§ 5. Hydrogen Iodide—Hydriodic Acid.

Preparation.—As in the case of the corresponding bromine compound, hydrogen iodide can be made by the direct combination of iodine and hydrogen. It cannot be made satisfactorily by the action of sulphuric acid upon potassium iodide. Gaseous hydrogen iodide is usually made by the decomposition of phosphorus iodide by the action of water. This is done by mixing red phosphorus and iodine in a dry flask, and gradually adding water from a dropping funnel to the products of the reaction. This is a modification of the process employed for the preparation of hydrogen bromide rendered necessary, because bromine is liquid, and iodine solid. Free iodine is removed from the gas by passing the hydrogen iodide through a tower of red phosphorus, and the gas can be dried by passing it through a tube containing calcium iodide. Hydrogen iodide cannot be collected over mercury because the mercury is attacked ; it is usually collected by the upward displacement of air.

Properties.—Hydrogen iodide is a colourless gas which fumes strongly in air. It condenses to a colourless liquid at 0° under 4 atmospheres pressure. This boils at −34·14°, and freezes to a white solid which melts at −50·8°. The term "hydrogen iodide" is reserved for the gas, and **hydriodic acid** for the aqueous solution. The gas is very soluble in water. The solution fumes strongly in air, and it has acid properties. Hydriodic acid is colourless when freshly prepared, but the solution soon turns brown owing to the oxidation of the hydrogen iodide with the separation of iodine: $4HI+O_2=2H_2O+2I_2$. Gaseous hydrogen iodide is decomposed when exposed to light. The easy reduction of hydrogen iodide: $2HI=I_2+H_2$ corresponds with the energetic reducing qualities of this acid. It is used as a reducing agent in organic chemistry.

§ 6. Calcium Fluoride.

Calcium fluoride, *fluorspar*, or *fluorite*, occurs in veins very frequently associated with lead ores, and sometimes by itself.

In the limestone caves of the Matlock district, Derbyshire, veins of fine crystals of this mineral are exposed. In Derbyshire the mineral is called "blue john" or "Derbyshire spar." Fluorspar also occurs in many other districts. The mineral occurs in cubic and octahedral crystals. The crystals may be colourless, or tinted red, brown, yellow, green, blue, or violet by traces of contaminating metallic oxides, etc. Some of the crystals are very pleasing, and such are used for ornamental purposes, jewellery, etc.

When heated to about 902°, fluorspar melts to an opaque greyish-white enamel. This property of fluorspar was mentioned by G. A. Agricola in 1529, and he called the mineral *fluor lapis*, literally "fluxing stone"—from the Latin *fluere*, to flow. The German miners apply the term "spath" to all transparent or translucent minerals with a well-marked cleavage, hence, the German term for this mineral—"fluss-spath." Fluorspar is used as a flux in metallurgy; and in the manufacture of glass, enamels, and glazes.

No gas is evolved when fluorspar is melted, but if fluorspar be strongly heated in an oxidizing flame, on charcoal, a pungent acrid smell, resembling hydrogen chloride, can be detected by bringing the nose near to the charcoal. The fumes redden blue litmus, and if the residue be moistened with water and tested with red litmus, the paper will turn blue. When fluorspar is mixed with sulphuric acid in a test tube, no perceptible action occurs, but if the mixture be heated, a gas is given off and the glass is strongly corroded, showing that the gas developed by the action of hot sulphuric acid on fluorspar decomposes glass. The gas also attacks porcelain, and many of the metals, but it does not act very markedly upon lead, gold, platinum, wax, paraffin, and rubber. The three latter will not stand heating, and consequently the further investigation of this gas—the "spirit of fluorspar"—hydrogen fluoride, must be conducted in lead, gold, or platinum vessels.

§ 7. Hydrogen Fluoride—Hydrofluoric Acid.

Manufacture of hydrofluoric acid.—An aqueous solution of hydrofluoric acid is manufactured in the following manner:

The best quality of powdered fluorspar, free from silica, is gently heated to about 130° with concentrated sulphuric acid in a cast-iron pot with a cast-iron cover dipping into an annular trough and sealed with concentrated sulphuric acid. The reaction is represented: $CaF_2+H_2SO_4=CaSO_4+2HF$. The cast-iron retorts are provided with a series of leaden boxes as condensers. These contain water or dilute hydrofluoric acid to absorb the gas from the retorts. The condensers are submerged in water to keep them cool, and the acid so obtained is collected in leaden bottles. Hydrofluoric acid is placed on the market in leaden, guttapercha, or wax (cerasine) bottles.

Hydrogen fluoride.—If potassium carbonate be neutralized with hydrofluoric acid, and then evaporated to dryness, potassium fluoride separates in cubic crystals, resembling potassium chloride, and readily soluble in water. If the potassium fluoride be dissolved in hydrofluoric acid and evaporated, crystals of the double salt **potassium hydrogen fluoride**—KF.HF—are obtained. This double salt is also called "acid potassium fluoride," "potassium bifluoride," and also **Fremy's salt.** If this salt be dried by fusion in a platinum retort and the platinum retort be then connected with a long platinum tube and platinum bottle immersed in a freezing mixture, the double fluoride decomposes when heated to redness: $KHF_2=KF+HF$, and the hydrogen fluoride is condensed to a liquid.

Properties.—Anhydrous hydrogen fluoride is a limpid liquid which fumes strongly in air. It is very poisonous and dangerous to manipulate. It forms ulcerated sores if a drop comes in contact with the skin. The metals potassium and sodium dissolve in the pure acid, forming the corresponding fluorides and hydrogen. The liquid acid boils at 19·5°, and the solid melts at −92·3. Hydrogen fluoride is very soluble in water, forming a corrosive liquid which readily dissolves many metals with evolution of hydrogen: $Fe+2HF=FeF_2+H_2$. Silver and copper also dissolve in the acid.

Etching glass.—Silicon burns in hydrogen fluoride, forming a mixture of gases—**silicon fluoride**, SiF_4, and hydrogen. Hydrogen fluoride attacks quartz and siliceous substances, glass, etc., also forming silicon fluoride: $SiO_2+4HF=SiF_4+2H_2O$.

Hydrofluoric acid is used in the analysis of silicates, because most silicates, when repeatedly evaporated with a mixture of hydrofluoric and sulphuric acids, decompose, all the silica is volatilized as silicon fluoride, etc., and the residue of sulphates examined by the standard methods. One of the most important properties of hydrofluoric acid is its etching action on glass. Glass may be etched with the gas or with an aqueous solution of the gas. In the former case, the etching appears opaque and dull ; in the latter case, shining and transparent. For etching, the glass is covered with a film of wax, and the design to be etched on the glass is drawn on the waxed surface with a stylus ; or else the parts of the glass not to be etched are coated with a resistant varnish. The surface is exposed to the action of the acid or gas, and very soon the glass is etched. The wax or varnish is then washed off with turpentine. The corrosive action of the hydrogen fluoride is due to the ready decomposition of the glass in contact with hydrogen fluoride. The silica forms silicon fluoride. The process is used for marking the scales on glass instruments.

Etching tests for fluorides.—In testing for fluorides, the substance under examination is warmed with sulphuric acid in a leaden vessel covered with a watch-glass. The watch-glass is coated with wax, and a design ✠ is scratched with a pin or knife, so as to expose the glass to the action of the acid. The wax is afterwards removed, and if the design is etched on the glass, fluorides are present.

§ 8. Fluorine.

Occurrence.—Fluorine does not occur free in nature, but its compounds are widely distributed, though not abundantly, in such minerals as cryolite, fluorspar, etc. Small quantities occur in some of the micas, topaz, tourmaline, etc. Traces occur in sea-water, some mineral springs, bones, teeth, blood, milk, plants, etc.

History.—The fact that glass is attacked when exposed to the fumes produced when fluorspar is warmed with sulphuric acid was known in the seventeenth century, and in 1771 K. W. Scheele stated that fluorspar is the calcium salt of "a peculiar acid"—fluoric acid. He prepared this acid by heating fluorspar

with sulphuric acid in a tin retort. From the analogy between potassium fluoride and potassium chloride, it might be expected that a mixture of manganese dioxide, concentrated sulphuric acid and potassium fluoride would furnish a gas—fluorine—analogous with chlorine. This is not the case. Indeed, the isolation of fluorine has proved extraordinarily difficult. The feat was accomplished in 1886, when H. Moissan isolated the gas by the electrolysis of a solution of potassium fluoride in liquid hydrogen fluoride, and thus solved what H. E. Roscoe called " one of the most difficult problems in modern chemistry." The student can readily verify the facts about chlorine, bromine, iodine, and hydrogen fluoride in the laboratory, but he will probably have to accept the testimony of others about this gas, since the apparatus is very expensive, and manipulation difficult.

Preparation.—When an electric current is passed through a concentrated solution of hydrogen chloride, chlorine is liberated at the anode, and hydrogen at the cathode. When aqueous hydrofluoric acid is treated in the same way, water alone is decomposed, for oxygen is liberated at the anode, and hydrogen at the cathode. The anhydrous acid does not conduct electricity, and it cannot therefore be electrolyzed. Moissan found that if potassium fluoride be dissolved in the liquid hydrogen fluoride, the solution conducts electricity, and when electrolyzed, hydrogen is evolved at the cathode, and fluorine at the anode. The primary products of the electrolysis are potassium at the anode, fluorine at the cathode: $2KHF_2 = 2HF + 2K + F_2$. The potassium reacts with the hydrogen fluoride, reforming potassium fluoride and liberating hydrogen: $2K + 2HF = 2KF + H_2$. The electrolysis was first conducted in a U-tube made from an alloy of platinum and iridium which is less attacked by fluorine than platinum alone. Later experiments showed that a tube of copper could be employed. The copper is attacked by the fluorine, forming a surface crust of copper fluoride which protects the tube from further action. Electrodes of the platinum iridium alloy are used. A tube is illustrated in Fig. 134. The open ends of the tube are closed with fluorspar stoppers ground to fit the tubes and bored with holes which grip the electrodes.

Properties.—Fluorine is a light canary-yellow gas which condenses to a clear yellow liquid boiling at −187° ; and freezes to a pale yellow solid melting at −233° ; at −252° the solid is colourless. Fluorine is probably the most active element known. It combines with hydrogen with explosion, even in the dark, and at low temperatures. It decomposes water, forming hydrogen fluoride, and liberating oxygen. Sulphur melts and takes fire in the gas. Iodine, bromine, phosphorus, arsenic, and antimony combine with the gas with incandescence ; so do crystalline silicon, amorphous boron, powdered charcoal. All metals are acted upon by the gas ; some take fire spontaneously, others when heated, to, say, 300°, *e.g.* gold and platinum. Fluorine also liberates chlorine from sodium chloride. Liquid fluorine has no action on silicon, phosphorus, sulphur, and glass.

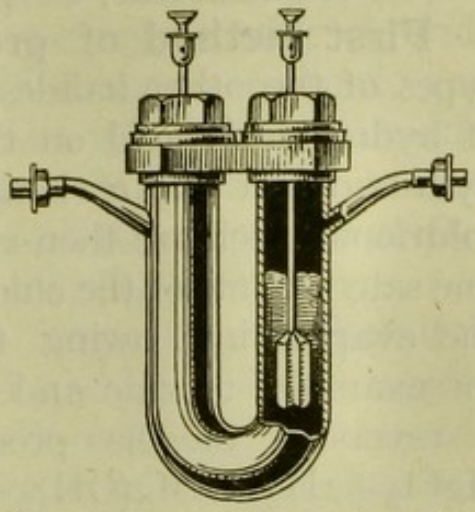


FIG. 134.—Tube for the Electrolysis of Hydrofluoric Acid.

§ 9. The Halides.

Fluorine, chlorine, bromine, and iodine together form a remarkable family of elements. The whole group is sometimes called the **halogens**—from the Greek ἅλς (hals), sea-salt ; γεννάω (gennao), I produce. This name was applied because these elements—principally chlorine, bromine, and iodine—are found in sea-water, and their sodium salts resemble sea-salt (sodium chloride). The fluorides, chlorides, bromides, and iodides are often called the **halides.**

The halides of the monad metals—sodium, potassium—have the general formula M′X, where M′ stands for an atom of the monad metal, and X for an atom of the halogen. Examples have already been considered—sodium and potassium chlorides. If M″ stands for an atom of a dyad metal, the general formula for the corresponding halides is $M''X_2$. Examples, calcium chloride, $CaCl_2$; calcium fluoride, CaF_2 (p. 272) ; zinc chloride (p. 278), etc. For the triad metals M‴ and the tetrad

element M'''', the corresponding chlorides are respectively $M''''Cl_3$ and $M''''Cl_4$. Examples of the former are aluminium chloride, $AlCl_3$; ferric chloride, $FeCl_3$, etc., and of the latter carbon tetrachloride, CCl_4; silicon chloride, $SiCl_4$, etc.

First method of preparation.—Taking the chlorides as types of the other halides, they are all prepared by the action of hydrochloric acid on the metal, on the metallic oxide, the hydroxide, or the carbonate. This process furnishes aqueous solutions which are then evaporated so as to obtain the crystalline salt. Some of the chlorides are partially decomposed during the evaporation, owing to hydrolysis (p. 54). This applies, for example, to zinc and magnesium chlorides. Hydrolysis is a reversion of the process of neutralization, symbolized: $MgCl_2+2H_2O \rightleftharpoons Mg(OH)_2+2HCl$. During the evaporation, the hydrogen chloride is volatile and escapes from the system, and instead of getting crystals of magnesium chloride at the end of the evaporation, a basic salt, Mg_2OCl_2, is obtained. The difficulty is overcome by evaporating the solution in a stream of hydrogen chloride which prevents the hydrolysis reaction proceeding very far.

Many of the chlorides crystallize from aqueous solutions combined with the elements of water in some curious manner. Thus we have calcium chloride, $CaCl_2.6H_2O$; barium chloride, $BaCl_2.2H_2O$; zinc chloride, $ZnCl_2.H_2O$, etc. Sometimes the water can be expelled and the anhydrous chloride obtained by merely heating the hydrated salt—*e.g.* calcium and barium chlorides; in other cases, it is necessary to calcine the hydrated salt in an atmosphere of hydrogen chloride to prevent hydrolysis, as indicated above.

Potassium iodide, KI, and **potassium bromide**, KBr, can be made by the general process just described, but they are usually made by mixing the proper halogen—iodine or bromine—with iron and water in a flask. A yellow solution of ferrous halide is formed. This is converted into the ferric halide by the addition of more halogen. The clear solution is then digested with an excess of a solution of potassium carbonate until the clear solution is free from iron. The clear liquid is then evaporated until cubic crystals of the required halide separate on cooling. Both

salts are used in medicine and in photography, and in many of their properties are very like the corresponding chloride.

Second method of preparation.—By adding an aqueous solution of hydrogen chloride or of some soluble chlorides to solutions of some of the metallic salts, a sparingly soluble chloride is precipitated. This is the case with silver, mercurous, and lead chlorides. Thus, with silver nitrate and sodium chloride, a white precipitate of **silver chloride** is obtained, and sodium nitrate remains in solution: $AgNO_3+NaCl=AgCl+NaNO_3$; with lead nitrate, $Pb(NO_3)_2+2NaCl=PbCl_2+2NaNO_3$.

Silver halides.—Silver chloride is interesting in that it is decomposed on exposure to light. The white chloride rapidly darkens, passing through various shades of violet, brown, and black. Silver bromide and iodide behave in a similar manner. Silver iodide is least soluble in water and in ammonia; the fluoride is most soluble, the chloride next, and the bromide next again. The undecomposed chloride is soluble in a solution of sodium thiosulphate, the decomposed chloride is not dissolved. These facts are utilized in photography.

Photography.—A celluloid film or glass plate is coated on one side with a film of gelatine containing, say, silver bromide in suspension, and dried. The plate is placed in the camera, and *exposed* by focusing the image of the object to be photographed on to the plate for a moment. The silver bromide is affected in some way as that the most intense change occurs where the light is brightest, while the change is less intense in the shadows. No visible change is apparent until the plate is *developed*. The plate is developed by treating it with a reducing agent—ferrous sulphate, pyrogallol, or some special developer. The developer continues the change started by the light, but is without action on the unexposed parts of the plate. As a result, finely divided silver is deposited on the parts of the plate illuminated by the light reflected from the object. The deposit is thickest where the light was most intense. Hence, the dark parts of the object appear lightest on the plate, and the light parts dark. The image is thus the reverse of the object, and the plate is accordingly called a *negative*. The silver salt which has not been affected by the light nor by the developer is now removed, and the image thus *fixed* on the plate by immersing the plate in a solution of sodium thiosulphate. The plate is then washed and dried. A *print* is made by laying the negative upon sensitized paper—that is, paper prepared in a similar way to the

negative—so that the light must pass through the negative before striking the paper. The negative absorbs the light in proportion to the thickness of the deposit of silver, so that the print has the same shading as the object. The paper is then treated with a solution of sodium thiosulphate to fix the image. The print may be *toned* by immersing it in a solution of gold chloride so that some of the silver is replaced by gold ; this gives the print a warm reddish tone ; if a platinum salt be used instead of gold, a steel-grey tone is produced. The image on the print will be the reverse of that on the negative, and will therefore correspond with the object. Hence the print may be called the *positive*.

Cuprous iodide, CuI, is precipitated when potassium iodide and a copper salt are mixed together. This reaction is utilized in analytical work—copper can be separated from solutions of the salts of many metals by the addition of a soluble iodide ; and iodides can be separated from solutions of chlorides or bromides by the addition of a copper salt. **Mercuric iodide** is formed when a soluble iodide is added to a solution of a mercuric salt. The precipitate is soluble in an excess of potassium iodide, and the resulting solution, made alkaline with potassium hydroxide, is called *Nessler's reagent*, and it gives a yellow coloration in the presence of ammonia.

Third method of preparation.—By exposing the metal, metallic oxide, or the metallic oxide mixed with carbon, to the action of chlorine or of hydrogen chloride gases at a raised temperature, it is often possible to prepare the anhydrous chloride. Thus if tin be exposed to the action of a stream of dry chlorine in the apparatus shown in Fig. 135, a fuming, colourless liquid collects in the receiver. This liquid, boiling nearly at 114°, is anhydrous **stannic chloride,** $SnCl_4$. Aqueous solutions of this salt hydrolyze very quickly with the separation of stannic hydroxide :

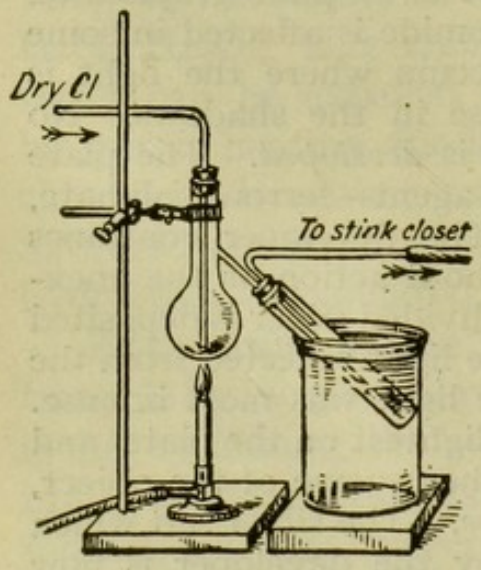


FIG. 135.—Preparation of Stannic Chloride.

$$SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl.$$

Stannic chloride forms crystalline compounds with water, and

curious complex compounds with some other chlorides. Thus with ammonium chloride it forms $SnCl_4.2NH_4Cl$. This is usually written $(NH_4)_2SnCl_6$ and called **ammonium chlorostannate.** It is the *pink salt* of the dyer. Ammonium chlorostannate is supposed to be the ammonium salt of an unknown acid—**chlorostannic acid,** H_2SnCl_6.

Ferric chloride, $FeCl_3$, and **aluminium chloride,** $AlCl_3$, are made by heating the proper metallic turnings in a stream of dry chlorine: the anhydrous chloride sublimes as deliquescent solids. Curiously enough, alumina, Al_2O_3, does not give aluminium chloride if it be heated in a current of chlorine, but it does give the chloride if it be first intimately mixed with carbon: $Al_2O_3 + 3C + 3Cl_2 = 3CO + 2AlCl_3$. If the iron be heated in a stream of hydrogen chloride, another compound, **ferrous chloride,** $FeCl_2$, is obtained.

Copper and mercury chlorides.—Several metals form more than one chloride—copper and mercury form chlorides of the type CuCl and $CuCl_2$, and HgCl and $HgCl_2$. The cuprous and mercurous chlorides—like silver chloride—are but sparingly soluble in water when compared with cupric and mercuric chlorides. **Mercuric chloride,** $HgCl_2$, is also called *corrosive sublimate.* It is very poisonous; a dilute solution—1 : 1000—is used as an antiseptic. **Mercurous chloride,** HgCl, also called *calomel*, is used as a medicine. Mercuric chloride sublimes as a white crystalline powder when a mixture of mercuric sulphate and sodium chloride is heated; if metallic mercury be also present, mercurous chloride is formed. **Cupric chloride,** $CuCl_2$, is made by the first method of preparation described above—action of and on carbonate or oxide. If an acid solution of this chloride be digested with metallic copper, it forms **cuprous chloride,** CuCl, which separates as a white powder when the solution is diluted with water. When cuprous or mercurous chlorides are heated in a stream of chlorine they form respectively cupric or mercuric chlorides; and if cupric or mercuric chlorides be heated in a stream of hydrogen they pass into cuprous or mercurous chlorides respectively. In the latter case the chlorides are said to be reduced, and in the former oxidized, although no oxygen is concerned in the

reaction. During reduction, the valency of the element is diminished, and during oxidation it is augmented.

Tin likewise forms **stannous chloride,** $SnCl_2$, as well as stannic chloride described above. The anhydrous chloride is made like ferrous chloride by heating metallic tin in a stream of hydrogen chloride. Stannous chloride is formed in aqueous solution by the solvent action of hydrochloric acid on tin. The crystals of the dihydrate, $SnCl_2.2H_2O$, pass into the anhydrous salt when dried *in vacuo*. Stannous chloride is a powerful reducing agent ; for instance, it converts ferric chloride, $FeCl_3$, into the lower chloride, $FeCl_2$. Thus

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

Mercuric chloride is reduced to the mercurous chloride, and this compound, in turn, is reduced to metallic mercury by the action of stannous chloride. Stannous chloride solutions, when exposed to the air, form a mixture of stannous oxychloride and stannic chloride.

§ 10. Dialysis.

Dialysis.—While studying the rate of diffusion of salts through membranes of parchment paper, Thomas Graham (1861) noticed that certain substances diffuse very slowly through the parchment. Gelatine and glue might be cited in illustration. The membrane is nearly impervious to these substances. Graham applied the term **colloids**—from the Greek κόλλα (kolla), glue—to those substances which diffuse but slowly through the parchment. On the other hand, substances like sodium chloride, magnesium sulphate pass through the membrane much more quickly. Crystalline salts are typical of those substances which diffuse rapidly, and hence Graham called them **crystalloids**. In illustration :

Crystalloids.	Colloids.
Potassium chloride.	Albumen.
Cane sugar.	Gums.
Magnesium sulphate.	Starch.
Hydrochloric acid.	Gelatinous aluminium hydroxide.
Sodium chloride.	Gelatinous ferric hydroxide.
Barium chloride.	Gelatinous silicic acids.

It must be added that a great many substances can exist in both the colloidal and crystalloid condition, so that it is better to distinguish between the colloidal and crystalline conditions of matter rather than between "crystalloids" and "colloids." In modern chemistry the term "colloid" comprises much of what was formerly called "amorphous." It must not be supposed that the colloids do not pass through the parchment at all. Graham found that when the time of diffusion of hydrochloric acid—HCl—was taken as unity, the rate of diffusion of an equal quantity of sodium chloride was 2·3, cane sugar 7, egg albumen 49, and caramel 98. On account of these great differences, Graham proposed a useful method of separating colloids from crystalloid substances in solution. The crystalloid is removed by diffusion through a membrane of parchment, bladder, or some similar substance. The process is called **dialysis**—from the Greek δια (dia), through ; λύω (lyo), I loosen. The operation will be understood from the following description :

A piece of parchment or bladder is bound across one end of a glass or guttapercha hoop so as to form a kind of shallow dish, Fig. 136, narrower at the base than the open top. A mixed solution of albumen (the white of an egg) and potassium chloride in water is poured into the "dish." This vessel is placed in another dish *B*, containing distilled water. The water in the outer vessel is renewed every few hours. The dish containing the mixed solution is covered by a clock glass to protect it from dust. In about three days, practically all the potassium chloride will have passed through the membrane into the outer vessel, while the egg albumen will remain in the inner compartment. The whole apparatus is called a **dialyzer**. See also Fig. 221.



FIG. 136.—Dialyzer.

If a few drops of ammonia be added to a solution of ferric chloride, a reddish-brown precipitate of ferric hydroxide will be formed. This redissolves in the unchanged ferric chloride. When the solution of ferric chloride is saturated with the ferric hydroxide, any further addition of ammonia will give a permanent precipitate of ferric hydroxide. Add a few drops of

hydrochloric acid to dissolve the precipitated ferric hydroxide, and dilute the solution with water so that it contains about 5 per cent. of solid in solution. Pour this solution into the dialyzer, the soluble ferric chloride and ammonium chloride pass into the outer vessel, and a dark red liquid, called "dialyzed iron," remains in the inner vessel. If dialyzed iron be allowed to stand for some weeks in a glass vessel, it gelatinizes. Here, then, we have two kinds of colloids: *fluid* colloids are said to be in the **sol** condition; and *gelatinous* or pectinous colloids are said to be in the **gel** condition. When the solvent is water, the colloids are either **hydrogels** (gelatinous) or **hydrosols** (fluid). The dialyzed iron is in the hydrosol condition.

Solutions are sometimes defined to be "mixtures which appear clear and homogeneous in ordinary daylight, and which cannot be separated into their constituent parts by filtration through paper, and by decantation." It is now possible to apply Graham's dialysis test, and subdivide solutions according as the substance in solution diffuses rapidly—**crystalloid solutions**; or slowly—**colloidal solutions**—through parchment paper. To summarize:

Solutions are clear and homogeneous in daylight.

1. *Crystalloid solutions* are optically inert, and the dissolved matter diffuses rapidly through parchment.
2. *Colloidal solutions* give an opalescence with Tyndall's test—by directing a beam of light through the solution they usually appear heterogeneous under the ultramicroscope, and the substance in solution diffuses very slowly through parchment.
   (*a*) *Sol.* The fluid colloidal condition.
   (*b*) *Gel.* The solid or gelatinous colloidal condition.

It must be clearly understood that no hard-and-fast line of demarcation can be made between mere suspensions, colloidal and crystalloid solutions. Perfect definitions are not yet possible.

Questions.

1. A white salt is known to be either chloride, bromide, or iodide of potassium. How would you ascertain with certainty which of these substances it is?—*London Univ.*

2. Specify the common sources of the elements chlorine, bromine,

and iodine ; explain with the aid of equations the methods adopted for their liberation, and state how you would distinguish between aqueous solutions of each of the free elements.—*London Univ.*

3. By what tests or chemical reactions could you distinguish carbonate of lime from fluorspar ?—*London Univ.*

4. How is bromine prepared ? In what forms does it commonly occur in nature ? Give some account of the chief properties of bromine, and of the tests by which it may be recognized.—*London Univ.*

5. Describe the experiments you have seen in illustration of the principal properties of iodine. How may this element be obtained from potassium iodide ?—*London Univ.*

6. Some strong hydrochloric acid is added to some manganese dioxide in a flask, and the mixture warmed. Name and describe the chief properties of the gas which is given off. What happens when the gas is bubbled through solutions of (*a*) litmus, (*b*) potassium iodide ?—*Adelaide Public Exam. Board.*

7. How could you convert bromine into hydrobromic acid, and this latter into silver bromide ? The density of bromine is 2·9 ; from 5 c.c. of it how much silver bromide could be obtained ? Of what importance is silver bromide ? (Ag = 108, Br = 80.)—*Adelaide Public Exam. Board.*

8. The gas obtained by the electrolysis of concentrated hydrochloric acid is collected in tubes. How would you show that it consists of equal volumes of hydrogen and chlorine ? One of the tubes is exploded by exposing it to a brilliant light. How would you show that it now contains neither free hydrogen nor free chlorine ?—*Cambridge Univ.*

9. A quantity of common salt was heated with an excess of sulphuric acid, and the whole of the gas which was liberated collected in water ; on adding silver nitrate to the solution a precipitate was formed, the weight of which was 2·54 grms. How much salt was taken, and what volume of gas at 0° and 760 mm. was evolved ? (Ag = 108.)—*London Univ.*

10. Describe how you would prepare iodine from potassium iodide, and explain your process by means of symbols. Describe properties of iodine by which you could distinguish this element from bromine.—*London Univ.*

11. Describe the properties of fluorine, bromine, and iodine, and state how these elements occur in nature.—*Univ. Tasmania.*

12. How could you convert bromine into hydrobromic acid, and this latter into silver bromide ? The density of bromine is 2·9, from 5 c.c. of it, how much silver bromide could be obtained ? Of what importance is silver bromide ? (Ag = 108, Br = 80.)—*Adelaide Public Exam. Board.*

13. Starting from sodium iodide, describe how you would

obtain from it a sample of pure dry iodine? Give the chief physical properties of iodine.—*Adelaide Public Exam. Board.*

14. How is hydrogen bromide prepared? What are the properties of that substance? What are the points of resemblance and of difference between chlorine and bromine? Given a solution of hydrogen bromide, how would you prepare bromine?—*Bombay Univ.*

15. Compare the elements bromine and iodine as to (*a*) physical properties, (*b*) affinity for hydrogen, and (*c*) affinity for oxygen.—*Cape Univ.*

16. Of a certain substance 0·732 grm. gives 0·861 grm. of silver chloride, AgCl. What is the percentage of chlorine in the substance? (Ag=108, Cl=35·5.)—*Staffs. Major County Schol.*

17. If separate solutions of chlorine, bromine, and iodine in water were presented for examination, state accurately how you would distinguish between them.—*Science and Art Dept.*

18. By what experiments would you show the principal properties of iodine? How would you distinguish a solution of potassium iodide from one of potassium bromide?—*Science and Art Dept.*

19. A solution of hydrobromic acid has a density of 1·055, 10 c.c. of this gave 1·878 grms. of silver bromide; calculate the amount of HBr in 100 c.c. and in 100 grms. of the solution. (H=1, Br=80, Ag=108.)—*London Univ.*

CHAPTER XVI

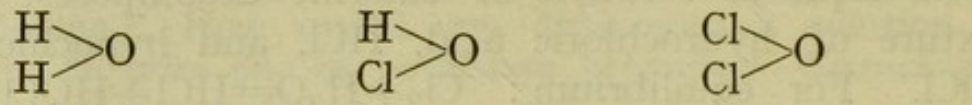
Oxygen Compounds of the Halogens

§ 1. Hypochlorous Acid and the Hypochlorites.

The action of chlorine on cold water.—It is probable that a *cold* aqueous solution of chlorine decomposes, forming a mixture of hydrochloric acid, HCl, and hypochlorous acid, HOCl. For equilibrium: $Cl_2+H_2O \rightleftharpoons HCl+HOCl$. This is evidenced by the fact that chlorine water reacts acid with litmus before it bleaches; and some acid can be separated by distillation. However, the amount of the two acids present when the system is in equilibrium is very small. If one of the products, say hydrochloric acid, be removed, the equilibrium is disturbed and the reaction proceeds in the direction needed to re-establish equilibrium, and more HOCl is formed. If freshly precipitated mercuric oxide, for example, be present, the hydrochloric acid reacts with the mercuric oxide; forming mercuric chloride, $HgCl_2$. The hypochlorous acid is such a weak acid that it has practically no action on the mercuric oxide. The action of chlorine on water containing mercuric oxide is therefore represented: $HgO+H_2O+2Cl_2 \rightleftharpoons HgCl_2+2HOCl$. Similarly, if calcium carbonate be suspended in the water: $CaCO_3+H_2O+2Cl_2 \rightleftharpoons CaCl_2+CO_2+2HOCl$. If the resulting liquid be distilled, a dilute solution of hypochlorous acid passes over.

Properties.—Pure hypochlorous acid free from water has not been obtained because the acid is so very unstable. It can be concentrated so as to form a golden-yellow liquid, but only the yellowish solutions containing about 5 per cent. of HOCl can be distilled without decomposition. More concentrated

solutions are decomposed. Hypochlorous acid is a monobasic acid and forms salts with bases. The radicle "ClO" is a monad, and its compounds with the bases are called **hypochlorites.** Hypochlorous acid is so feeble in strength that the carbon dioxide of the air is sufficient to displace the acid from hypochlorites. Hypochlorous corresponds with **hypochlorous anhydride** or **chlorine monoxide,** Cl_2O, prepared by the action of dry chlorine on mercuric acid. The greenish orange coloured gas can be condensed to a reddish-brown liquid by cooling with a mixture of ice and salt. The gas is explosive, with water it forms hypochlorous acid, thus: $Cl_2O+H_2O = 2HOCl$. The relation between water, chlorine monoxide, and hypochlorous acid may now be represented graphically:



Water—H_2O. Hypochlorous acid—HOCl. Chlorine monoxide—Cl_2O.

The action of chlorine on cold solutions of alkali hydroxides.—A similar action occurs if cold water containing a little potassium hydroxide be treated with chlorine, but both acids are neutralized:

$$H_2O + Cl_2 \rightleftharpoons \begin{cases} HOCl & HOCl + KOH = KOCl + H_2O \\ & \text{and} \\ HCl & HCl + KOH = KCl + H_2O \end{cases}$$

equilibrium is disturbed, and the reaction from left to right is almost complete. The net result of the reaction is represented: $Cl_2+2KOH \rightleftharpoons KCl+KOCl+H_2O$. The resulting solution is called *Javel water*, because it was prepared by C. L. Berthollet's process at Javel, a suburb of Paris, in 1792. In 1834, A. J. Balard proved that Javel water is a mixture of potassium chloride and hypochlorite. The solution is sometimes used for bleaching purposes. If sodium hydroxide be employed, as suggested by A. G. Labarraque, in 1820, the so-called *chlorinated soda*, or *Labarraque's solution*, is obtained. The electrolysis of cold solutions of sodium or potassium chloride furnishes sodium or potassium hydroxide and chlorine. If the products of

electrolysis are allowed to intermix, sodium or potassium hypochlorites are formed in a similar manner.

The oxidizing action of hypochlorous acid.—When warmed, hypochlorous acid furnishes chloric acid—$HClO_3$—thus : $3HOCl = 2HCl + HClO_3$; and it is also decomposed with the evolution of oxygen : $2HOCl = 2HCl + O_2$. This reaction is particularly active in sunlight, and in the presence of oxidizing agents. If a little nickel or cobalt nitrate solution be added to water containing hypochlorous acid and the mixture warmed in a flask, oxygen is evolved : $2HOCl = 2HCl + O_2$. The cobalt salt acts as an actalytic agent. The mechanism of the reaction is generally supposed to involve the concurrent reactions corresponding with the transformations of the cobalt oxide : $CoO \rightarrow Co_2O_3 \rightarrow CoO \rightarrow Co_2O_3 \rightarrow$ etc. When oxygen is prepared by this process, bleaching powder suspended in water is the usual source of the hypochlorous acid. In illustration of the oxidizing action of hypochlorous acid, calcium hypochlorite or bleaching powder may be boiled for some time with a solution of a manganous salt, and manganese dioxide, MnO_2, will be precipitated. More prolonged boiling may give a green solution of calcium manganate, $CaMnO_4$, or a pink coloured solution of calcium permanganate, $Ca(MnO_4)_2$.

The rapid decomposition of hypochlorous acid in sunlight renders it probable that the action of light on chlorine water results in the formation of the hypochlorous acid by hydrolysis : $Cl_2 + H_2O = HCl + HOCl$, and this acid is at once decomposed : $2HOCl = 2HCl + O_2$, so that the hydrolysis goes to completion, and leaves, as final products, hydrochloric acid, water, and oxygen.

Test.—When mercury is shaken up with an aqueous solution of hypochlorous acid, a brownish-yellow precipitate of mercuric oxychloride, $HgO.HgCl_2$, is formed ; this is decomposed by hydrochloric acid. Mercuric chloride passes into solution and mercurous chloride remains undissolved. With chlorine water mercury gives a white precipitate of mercurous chloride, HgCl ; hence, the reaction can be used to distinguish between hypochlorous acid and chlorine water.

§ 2. Bleaching Powder.

History.—The bleaching properties of Javel water were discovered by C. L. Berthollet in 1785. The facts were communicated to James Watt in Paris about the same time, and Watt soon afterwards brought the news to Glasgow. In 1798, Charles Tennant patented a process for the use of cheaper lime in place of potash. The patent was later declared void because lime had been used for the same purpose in Lancashire prior to Tennant's patent.

The action of chlorine on calcium hydroxide.—If chlorine be allowed to act upon an aqueous solution of a bivalent base, say calcium hydroxide, in place of potassium or sodium hydroxide, a molecule of each of the two monobasic acids, formed by the action of chlorine on water, is neutralized by one molecule of the base, and what seems to be a **mixed salt** is formed :

$$Ca\begin{matrix}OH\\OH\end{matrix} + \begin{matrix}HOCl\\HCl\end{matrix} = Ca\begin{matrix}OCl\\Cl\end{matrix} + 2H_2O$$

The salt Cl—Ca—OCl is called " bleaching powder " or " chloride of lime." The constitution of bleaching powder has been much discussed, and the subject is not yet definitely settled.

Preparation.—Bleaching powder is made on a large scale by the action of chlorine on slaked lime, $Ca(OH)_2$. The lime is spread in 3- or 4-inch layers on perforated shelves in a large chamber, and then raked into furrows. Chlorine is led through the chambers. At first the absorption of chlorine is rapid, but it afterwards slows down. The lime is then turned over from time to time so as to expose a fresh surface. After standing for 12 to 24 hours a shower of fine dust lime is blown into the chamber to absorb the excess of chlorine. The amount of chlorine absorbed is never so complete as is represented by the equation : $Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O$. The commercial value of the bleaching powder depends on the amount of available chlorine it contains. The amount of available chlorine depends upon the method of preparation, temperature, etc.

The action of water and acids.—If bleaching powder be treated with cold water, it forms a strongly alkaline solution,

and insoluble calcium hydroxide remains. It is probable that the action is due to the hydrolysis of the calcium hypochlorite : $2Ca(OCl)Cl = Ca(OCl)_2 + CaCl_2$; followed by $Ca(OCl)_2 + 2H_2O = Ca(OH)_2 + 2HOCl$. If the bleaching powder be treated with a very dilute acid, hypochlorous acid, HOCl, is formed : $Ca(OCl)Cl + HCl = CaCl_2 + HOCl$. If an excess of acid be present, the hypochlorous acid is decomposed, forming water and chlorine : $HOCl + HCl = H_2O + Cl_2$.

Bleaching powder decomposes when exposed to atmospheric moisture. The carbon dioxide of the air also reacts like a feeble acid as indicated above. Bleaching powder also decomposes slowly when kept in a well-stoppered bottle. When heated with ammonia, nitrogen is obtained : $2NH_3 + 3Ca(OCl)Cl = 3H_2O + 3CaCl_2 + N_2$; and when boiled with water and a little cobalt salt, oxygen is obtained as indicated above. Thus, hypochlorous acid, chlorine, and oxygen can be obtained from bleaching powder.

Bleaching.—In bleaching by Javel water or by bleaching powder, the fabric is steeped in a dilute aqueous solution of bleaching agent, and then in dilute acid. Hypochlorous acid is thus produced, and then free chlorine. The free chlorine does its work within the fibres of the wet fabric, as indicated on p. 143. The bleaching action of hypochlorous acid is generally stated to be twice as great as that of the chlorine it contains, supposing the latter were free : $2Cl_2 + 2H_2O = 4HCl + O_2$; $4HOCl = 4HCl + 2O_2$. But it must be remembered that two atoms of chlorine are needed to form one molecule of HOCl, since an equivalent amount of HCl is formed at the same time.

§ 3. Chloric Acid and the Chlorates.

The manufacture of potassium chlorate, $KClO_3$.—We have seen that when chlorine is passed into a cold solution of potassium hydroxide, a mixture of potassium chloride and hypochlorite is formed ; and when the solution of the hypochlorite is boiled, it decomposes, forming a mixture of potassium chlorate and chloride. A similar result is obtained when chlorine is passed into a *hot* (70°) aqueous solution of potassium hydroxide : $6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O$; and the

two salts—potassium chloride and potassium chlorate—can be separated by fractional crystallization. Potassium chlorate is far less soluble than the corresponding chloride. It will be observed that the amount of chlorate obtained by the action of chlorine on a given amount of potassium hydroxide is small, because one molecule of potassium chlorate is accompanied by five molecules of potassium chloride as by-product. This loss is serious because the potassium hydroxide is relatively expensive. This led J. von Liebig (1842) to modify the process. It is cheaper to substitute a hot solution of slaked lime in water for the potassium hydroxide solution. In that case: $6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O$. This clear solution of calcium chlorate and chloride is concentrated a little by evaporation, and a slight excess of potassium chloride is added. Potassium chlorate has but one-tenth the solubility of the corresponding calcium salt, and is far less soluble than the other two chlorides; hence, by a further concentration of the solution, the least soluble potassium chlorate separates: $Ca(ClO_3)_2+2KCl=2KClO_3+CaCl_2$. The potassium chlorate so obtained is purified by recrystallization. The salt is also made by the electrolysis of *hot* solutions of potassium chloride.

The chlorates.—The chlorates are powerful oxidizing agents. An explosion may occur if a chlorate be mixed with organic matter, charcoal, sulphur, etc., and the mixture struck with a hammer, or heated. Hence, mixtures of chlorates with such materials must not be ground together with a pestle and mortar. The materials should be ground separately, and then carefully mixed on paper with a feather. Phosphorus in contact with a chlorate may explode spontaneously. Thus if a drop of a solution of phosphorus in carbon disulphide be allowed to fall on a little potassium chlorate, a loud explosion occurs as soon as the carbon disulphide has evaporated, owing to a reaction between the residual phosphorus and the chlorate.

The chlorates are all soluble in water. Potassium chlorate is one of the least soluble of the chlorates. The salts are fairly stable, but decompose into chlorides and oxygen when heated. The chlorates are recognized by giving no precipitate with

silver nitrate; although, after ignition, the silver nitrate will give a precipitate of silver chloride with an aqueous solution of the residue. If a few drops of a solution of indigo sulphate be added to an aqueous solution of a chlorate, and the liquid be acidified with sulphuric acid, and sulphurous acid, or a sulphite be added, the chloric acid is reduced to a lower chlorine oxide which bleaches the blue colour of the indigo.

Potassium chlorate is used medicinally; in the manufacture of matches, fireworks, and explosives; as an oxidizing agent; for preparing small quantities of oxygen, etc.

Chloric acid, $HClO_3$, has been made by treating barium chlorate with the right amount of sulphuric acid to precipitate all the barium as sulphate. The acid is very unstable, and is only known in aqueous solution.

§ 4. Chlorine Peroxide.

Preparation of chlorine peroxide.—While studying the action of concentrated sulphuric acid upon potassium chlorate, H. Davy (1811) found that a highly explosive gas was produced. Finely powdered potassium chlorate is gradually added to concentrated sulphuric acid in a small flask or retort, *A*, Fig. 137. The salt dissolves, producing a reddish-brown liquid, but no gas is evolved if the liquid be kept cold. When the solution is gradually warmed, by placing the retort in a vessel, *B*, of warm water, taking care not to heat the glass above the level of the liquid in the retort, chlorine peroxide is evolved as a gas. The first action of the sulphuric acid probably forms chloric acid: $KClO_3 + H_2SO_4 = KHSO_4 + HClO_3$; and the chloric acid is then decomposed into perchloric acid, $HClO_4$, chlorine peroxide, and water: $3HClO_3 = HClO_4 + 2ClO_2 + H_2O$.

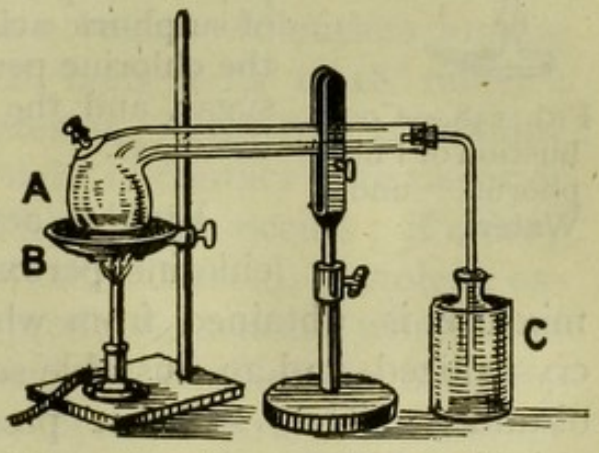


FIG. 137.—Preparation of Chlorine Peroxide (Dangerous !).

Properties.—Chlorine peroxide is a reddish-yellow gas with an unpleasant smell which produces headache. The gas

is much heavier than air, and is collected by the upward displacement of air, since it decomposes by contact with mercury, and is fairly soluble in water. The gas is very unstable, and decomposes with explosion if an electric spark or a hot wire be introduced into the gas. Chlorine peroxide also decomposes into its elements if it be exposed to the light. The gas is liable to suddenly explode, especially if in the liquid or solid condition, or if organic matter be present. Chlorine peroxide is a powerful oxidizing agent—a piece of phosphorus, sugar, or other combustible takes fire spontaneously in the gas.

Two well-known experiments may be cited to illustrate this. Place some crystals of potassium chlorate at the bottom of a test glass, and half fill the vessel with water. A few small pieces of phosphorus (the size of canary seeds) are dropped into the glass, and concentrated sulphuric acid is allowed to flow through a tube funnel on to the chlorate, Fig. 138. The bubbles of chlorine peroxide which are evolved produce bright flashes of light when they come in contact with the phosphorus under the water. Again, powdered sugar and powdered potassium chlorate are mixed with a feather on a sheet of paper and placed on a stone slab. When a drop of sulphuric acid is allowed to fall upon the mass, the chlorine peroxide which is formed ignites the sugar, and the flame rapidly spreads throughout the mass.



FIG. 138.—Combustion of Phosphorus under Water.

By the action of an aqueous solution of chlorine peroxide on potassium hydroxide, a mixture is obtained from which potassium chlorate can be crystallized, and an unstable solution with bleaching properties obtained. The solution presumably contains **potassium chlorite**, $KClO_2$, also the action of the peroxide on the alkali is usually represented by the equation :

$$2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O$$

When the potassium chlorite solution is acidified with hydrochloric acid, it is supposed to contain **chlorous acid**, $HClO_2$.

§ 5. Perchloric Acid and the Perchlorates.

Potassium perchlorate, $KClO_4$, is made when potassium chlorate is heated just above its melting-point until the fluid becomes very viscid or almost solid. The cold mass, when treated with water at 50°, gives a crop of crystals of potassium perchlorate, since this salt is much less soluble in water than either potassium chloride or chlorate.

Preparation of perchloric acid.—Perchloric acid is formed when chloric acid is heated or exposed to light: $3HClO_3 = Cl_2 + HClO_4 + 2O_2 + H_2O$; and by the action of sulphuric acid on, say, potassium perchlorate: $2KClO_4 + H_2SO_4 \rightleftharpoons K_2SO_4 + 2HClO_4$.

If 50 grams of pure dry potassium perchlorate be distilled under reduced pressure in a 300 c.c. distilling flask, Fig. 159, with 150 to 175 grams of concentrated (96 to 97½ per cent.) sulphuric acid, a white crystalline mass of $HClO_4.H_2O$ collects in the receiver. The water is formed by the decomposition of the acid during the distillation. By the redistillation of this product under reduced pressure, pure perchloric acid can be obtained.

Properties.—Perchloric acid is a volatile colourless fuming liquid; specific gravity 1·764 at 22°, boils at 14° to 18° under a pressure of 15 to 20 mm., and freezes at −112° to a crystalline solid. If a drop of the acid be brought in contact with paper or wood, instantaneous and violent inflammation occurs; if a drop of the acid be brought in contact with charcoal, a violent explosion occurs. Perchloric acid produces serious wounds in contact with the skin. If the acid be distilled at ordinary pressures, the liquid may gradually become darker and darker in colour, and finally explode violently. The pure acid is also said to be liable to explode after standing some days. Water can be removed from perchloric acid by means of phosphorus pentoxide, and an explosive oil-like substance separated by distillation at 82°. This appears to be **chlorine heptoxide,** Cl_2O_7, which forms perchloric acid with water, and is hence called **perchloric anhydride.**

Thermochemistry of the oxychlorine acids.—Perchloric

acid is not so powerful an oxidizing agent as chloric acid, and this in turn is less vigorous than hypochlorous acid. This corresponds with the greater amount of available energy per atom of available oxygen associated with hypochlorous acid than with either chloric or perchloric acid. For instance, the thermochemical equations are represented :

$HOClaq = HClaq + O + 9{\cdot}3$ Cals. ; or 9·3 Cals. per atom of oxygen.
$HClO_3aq = HClaq + 3O + 15{\cdot}3$ Cals. ; or 5·1 Cals. per atom of oxygen.
$HClO_4aq = HClaq + 4O + 0{\cdot}7$ Cals. ; or 0·2 Cals. per atom of oxygen.

Since the bleaching effect of these reagents is supposed to depend upon the action of nascent oxygen, it follows that in this case there is no particular need for the assumption that atomic oxygen is more active than molecular oxygen, because the " nascent oxygen " is associated with a larger amount of available energy, which can do chemical work. The available energy of each acid must be *added to* that which free oxygen could give if it alone were performing the same oxidation ; according to the principle of maximum work, the amount of energy degraded during a chemical reaction measures the " tendency of a reaction to take place." Hence, the greater oxidizing properties of these acids must, at least in part, be due to the greater amount of available energy associated with their " nascent oxygen " during decomposition.

Perchlorates.—An aqueous solution of perchloric acid reddens litmus, and forms salts—perchlorates—where the radicle " ClO_4 " is univalent. Hence, perchloric acid is monobasic. The potassium salt is one of the least soluble perchlorates. It is practically insoluble in absolute alcohol. When perchloric acid is added to an alcoholic solution of a soluble potassium salt, potassium perchlorate is quantitatively precipitated. The weight of potassium perchlorate so obtained enables the amount of potassium in the given solution to be computed. The acid is now much used for the separation of potassium from sodium chloride in analyses. Unlike the chlorates, the perchlorates are not decomposed by hydrochloric acid ; nor do they yield an explosive gas when warmed with concentrated sulphuric acid. They are not reduced to chlorides by sulphur dioxide ; and

they require a higher temperature for their decomposition than the corresponding chlorates. Sodium perchlorate as well as sodium chlorate occur with sodium nitrate in native Chili saltpetre.

§ 6. The Valency of Chlorine.

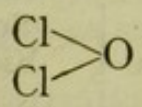
The known oxides and oxyacids of chlorine are :

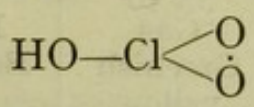
Oxides.		Acids.	
Chlorine monoxide . .	Cl_2O	Hypochlorous acid . .	$HClO$
[Chlorine trioxide . .	Cl_2O_3]	Chlorous acid . . .	$HClO_2$
Chlorine peroxide . .	ClO_2	... ...	
[Chlorine pentoxide .	Cl_2O_5]	Chloric acid	$HClO_3$
Chlorine heptoxide . .	Cl_2O_7	Perchloric acid . . .	$HClO_4$

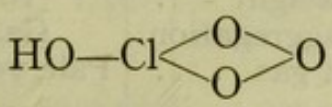
The anhydrides indicated in the brackets have not been prepared, while hypochlorous and chloric acids are only known in solution. The constitution of these compounds is by no means clear. Some base the graphic formulæ on bivalent oxygen and univalent chlorine :

HO—Cl HO—O—Cl HO—O—O—Cl HO—O—O—O—Cl
Hypochlorous acid. Chlorous acid. Chloric acid. Perchloric acid.

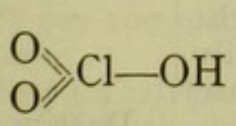
It is probable that with a series of compounds whose molecules have atoms, the longer the chain the less stable the compound. Here HOCl is the least stable, and HOOOOCl is the most stable of these acids. Some, therefore, suppose that the chain formulæ are improbable, and that chlorine monoxide, chlorine peroxide, and chloric acid are constituted thus :

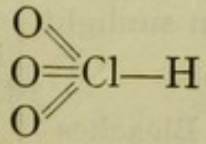

Chlorine monoxide.

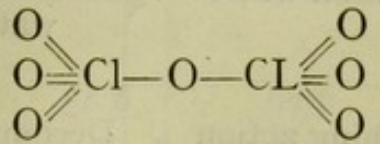

Chloric acid.


Perchloric acid.

where chlorine may be uni- and ter-valent. Others consider that in chloric acid the chlorine is quinquevalent ; and in perchloric acid, septavalent :


Chloric acid.


Perchloric acid.


Perchloric anhydride.

There is no uniform agreement among chemists about this, because insufficient facts are known to give a decisive verdict. The latter formulæ are generally preferred.

Several iodine oxides, even more stable than the chlorine oxides, are known, but bromine does not appear to form stable oxides. **Hypobromous acid, hypoiodous acid, bromic acid** and **iodic acid** compounds have been made. **Periodic acid** is fairly stable, **perbromic acid** is unknown. Fluorine is one of the few elements which does not form an oxygen compound.

§ 7. The Halogen Family of Elements.

The family relationship of the halogens is illustrated by—(1) The *similarity* in the chemical and physical properties of the elements and their corresponding compounds. (2) The *gradual transition* of chemical and physical properties such that if the elements be arranged in order: F, Cl, Br, I, the variation in any particular property in passing from fluorine to iodine nearly always proceeds in the same order, and that is the order of their atomic weights.

The relationship in the properties of the halogens can best be emphasized by a tabular scheme compiled from data in the dictionaries of chemistry:

TABLE XI.—THE PROPERTIES OF THE HALOGENS.

Property.	Fluorine.	Chlorine.	Bromine.	Iodine.
Atomic weight .	19	35·46	79·92	126·92
State of aggregation	Gas	Gas	Liquid	Solid
Colour of gas . .	Pale yellow	Greenish yellow	Brownish red	Violet
Melting-point . .	−233°	−102°	−7·3°	+114°
Boiling-point . .	−187°	−33·6°	58° to 63°	183°
Specific gravity .	1·14 (liq.)	1·55 (liq.)	3·19 (liq.)	5 (solid)
Atomic weight÷sp. gr.	16·7	22·9	25·1	25·6
Action on water .	Decomposes water	Decomposes in sunlight	Decomposes in sunlight less readily than Cl water	No action
Bleaching action .	Decomposes reagents	Bleaches readily	Bleaches feebly	Does not bleach

Property.	Fluorine.	Chlorine.	Bromine.	Iodine.
Affinity for hydrogen	Very vigorous	Combines in sunlight	Very slight combination in sunlight, but does when heated	Combines when heated less readily than with Br
Stability of hydrogen compound	Very stable	Less stable than the fluoride	Partially decomposes at red heat	Total decomposition at red heat
Stability of oxygen compounds	None known	Unstable oxides Cl_2O ClO_2 and Cl_2O_7	None known	Stable oxides are known, *e.g.* I_2O_5

All the halogens form compounds with hydrogen, and the readiness with which union occurs decreases as the atomic weight increases. The properties of the halogen acids and their salts show as striking a relationship as the elements themselves, and some of the properties compiled from a dictionary of chemistry are illustrated in Table XII.

TABLE XII.—THE PROPERTIES OF THE HALOID ACIDS.

Property.	Hydrogen fluoride.	Hydrogen chloride.	Hydrogen bromide.	Hydrogen iodide.
Molecular weight .	20	36·46	80·93	127·93
Boiling-point . .	19·4°	−83·7°	−64·9°	−34·1 (4 atm.)
Melting-point . .	−92·5°	−116°	−87°	−51°
Solubility in water	35·3 %	42 %	49 %	57 %
Specific gravity saturated aqueous solution	1·15	1·21	1·49	1·70
Heat of formation (Cals.)	+38·5 gas	+22·0 gas	+12·3 gas	−6·0 solid
Heat of formation of K salt (Cals.)	110·6	105·7	95·3	80·1
Potassium salt melts	885°	790°	750°	705°
Calcium salt melts	1330°	780°	760°	740°
Solubility Ag salt (20°) per 100 c.c. water	181·8	0·016	0·00084	0·000028
Solubility Ca salt per 100 c.c. solution	0·16	42·7	58·8	67·6

Again, while the affinity of the halogens for hydrogen decreases with increasing atomic weight, the reverse is the case with oxygen. But with oxygen the relationship is not so clearly defined. Thus, although fluorine forms no known compound with oxygen, numerous compounds of oxygen with chlorine have been obtained; and, judging by the known compounds with oxygen, the affinity of bromine for oxygen appears to be less, not greater, than is the case with chlorine. Chlorine, bromine, and iodine form an unstable series of compounds analogous with hypochlorites and chlorates, but the bromine analogue of perchlorates has not been prepared.

Questions.

1. Give an account of the group of elements termed "halogens." Point out the characters which distinguish them (*a*) as a class, and (*b*) individually, both in the free state and in their compounds.—*London Univ.*

2. What compounds does chlorine form with oxygen, and with oxygen and hydrogen? How are they respectively obtainable? In each case, enumerate any analogous compounds of other elements with which you are acquainted and compare their properties.—*London Univ.*

3. By what experiments would you prove that chlorine is a constituent of (*a*) common salt and (*b*) potassium chlorate?—*Science and Art Dept.*

4. How is bleaching lime manufactured? What is its composition? Explain the action of water upon it.—*London Univ.*

5. Describe the preparation and properties of the three oxy-acids of chlorine, viz. hypochlorous, chloric, and perchloric acid.—*Panjab Univ.*

6. Compare the substances hydrochloric, hydrobromic, and hydriodic acids as to their preparation and properties.—*Cambridge Univ.*

7. You wish to test an aqueous solution for hydrofluoric acid. Describe fully how you would do so.—*London Univ.*

8. Chlorine is passed into a dilute cold solution of potash, the liquid is boiled; it is then evaporated to a small volume and allowed to cool. Finally, the whole is evaporated to dryness and the residue is strongly heated. Describe what happens at each of these four stages, and represent by chemical equations the reactions involved.—*Science and Art Dept.*

9. What is the method in general use for the preparation of bleaching powder? What is the composition of this substance?

What is the action of water upon it ? Why is it alkaline ? What action has carbon dioxide on a solution of bleaching powder ?—*Science and Art Dept.*

10. How is perchloric acid prepared and how is it distinguished from hypochlorous and chloric acids ?—*Science and Art Dept.*

11. How can potassium chloride, hypochlorite, and chlorate be obtained by the action of chlorine upon caustic potash ? Give the composition and properties of these salts.—*Science and Art Dept.*

CHAPTER XVII

Sulphur and its Compounds

§ 1. Sulphur—Occurrence and Extraction.

The element sulphur—occurring, as it does, free in nature—has been known from the beginning of history. It is mentioned in the Bible and in Homer. It is commonly called *brimstone* (literally "fire-stone") in reference to its combustibility. It was placed

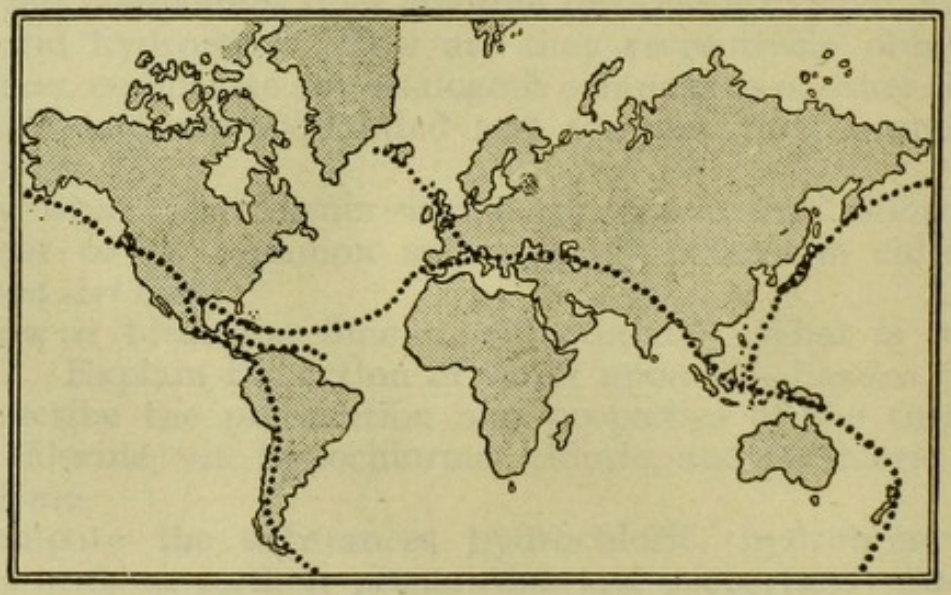


Fig. 139.—Imaginary Lines showing Chief Regions of Volcanic Phenomena and Occurrence of Sulphur Deposits.

among the elements by Lavoisier, but for some time previously it was regarded as "the principle of fire."

Occurrence.—Sulphur is widely distributed in nature both as free and as combined sulphur. Deposits of free or native sulphur occur in volcanic districts, Fig. 139. Sicily has long been famous for its sulphur, and most (perhaps 90 per cent.) of the sulphur in the world's markets comes from there. It is also

mined in Japan, Louisiana, and several other places. Sulphur is also an essential part of many minerals. In *sulphides*, the sulphur is united directly with one or more metals—chiefly iron, copper, lead ; sulphur is also combined in all *sulphates*—the commonest of which are calcium and barium sulphates. Sulphur also occurs in many organic compounds ; in animal and vegetable products—onions, garlic, mustard, horseradish, hair, many oils, eggs, proteids, etc. ; and dissolved in the water of many sulphur springs.

The extraction of crude sulphur.—The " sulphur earth " in Sicily occurs in lodes mixed with limestone and gypsum. The amount of sulphur in " workable " ore varies from 8 up to

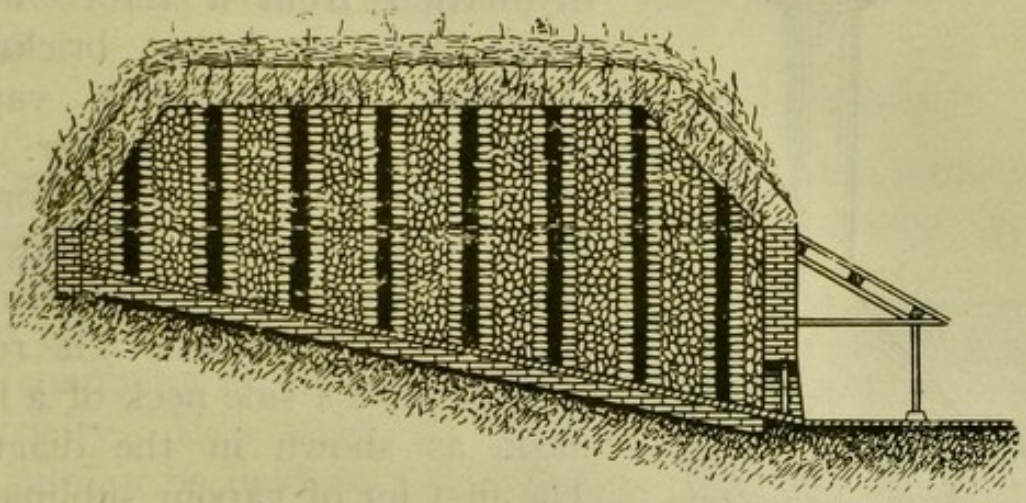


FIG. 140.—Calcarone or Sulphur Kiln (Diagrammatic Section).

about 25 per cent. The sulphur is separated by heating the ore, and allowing the molten sulphur to flow away from the mineral impurities. This is effected by stacking the ore on the sloping floor, Fig. 140, of a circular kiln without a permanent roof. The kilns are called *calcaroni*. In stacking the ore, air spaces are left at intervals to serve for ventilation. The stack is covered with powdered or burnt ore. The sulphur is ignited near the bottom. One portion of the sulphur acts as fuel, and melts the remainder, which collects at the lowest point of the inclined bottom of the kiln. After about five days, a plug at the lower end of the kiln is removed, and the sulphur is run into small wooden moulds. The opening is closed, to be reopened day by day until, in from three to five more days, the sulphur

ceases to flow. About one-third of the sulphur is lost in the calcarone system of extraction. It is, however, considered cheaper to use the sulphur as a fuel than to import coal, although in recent years the calcarone method is being displaced by more economical kilns. In H. Frasch's method (1891), used at Louisiana, the sulphur is melted *in situ*. Pipes are driven into the sand and superheated water is forced into the lode. The molten sulphur collects in a central well from which it is raised to the surface by compressed air.

The purification or refining of crude sulphur.—The crude sulphur from the kilns is graded and put on the market. It may be afterwards purified by distillation from a retort which opens into a large brickwork chamber. The sulphur vapour condenses in the chamber. An idea of the process can be formed from the experiment illustrated in Fig. 141, where the sulphur in the small retort is heated. The retort is filled into a side neck of a large flask as shown in the diagram. The first lot of vapour sublimes as a light powder on the walls. This powder is called *flowers of sulphur*. As the condensing chamber gets hot, the condensed sulphur melts and collects on the floor as a liquid which is drawn off from time to time and cast into large wooden moulds—*rock sulphur ;* or in cylindrical wooden moulds—*roll sulphur*.

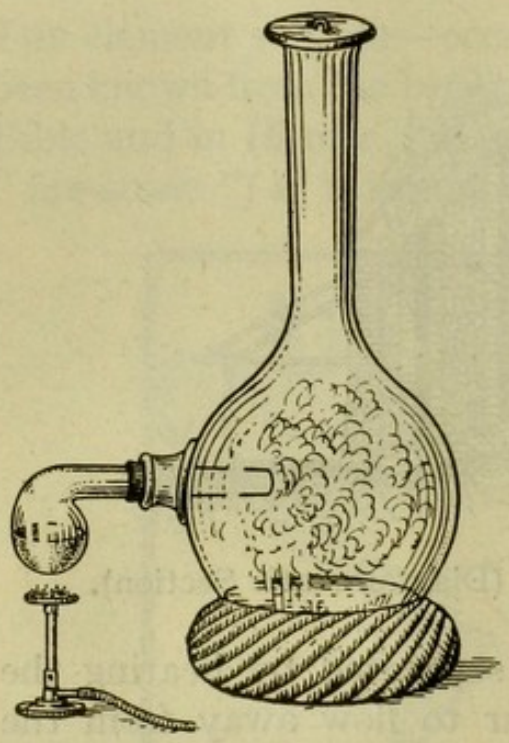


FIG. 141.—Distillation and Sublimation of Sulphur.

Uses.—Crude sulphur is used in making sulphur dioxide for bleaching straw, wool, etc. ; for the manufacture of sulphites for bleaching wood fibres, etc. ; and for the manufacture of sulphuric acid. It is also used in making carbon disulphide. Purified sulphur is used in making gunpowder, matches, colours, vulcanite, and medicinally. Flowers of sulphur is used as an insectide and fungicide.

Some chemical properties.—Sulphur unites with oxygen when it burns in air, forming a gaseous oxide (p. 93) called sulphur dioxide. Oxidation, even at ordinary temperatures, can be detected, but it is very slight. It ignites at about 360°, and at about 280° if heated in oxygen. Sulphur also unites directly with many metals, forming **sulphides.** Heat is usually required to start the reaction. The combination is often attended with incandescence. Examples with iron and zinc have been indicated on p. 70. A strip of copper introduced into the vapour of sulphur enters into combination with vivid combustion. Sulphur unites with carbon at a red heat, forming carbon disulphide—CS_2; with chlorine at the boiling-point of sulphur; and with hydrogen at the same temperature.

§ 2. Rhombic, Octahedral, or α-Sulphur

Ordinary sulphur is a pale-yellow brittle solid, without taste or smell. At −50° the sulphur is almost colourless. It has a specific gravity varying from 2·03 to 2·06. It is a bad conductor of heat and electricity. If a stick of roll sulphur be held in the hand it begins to crackle and breaks owing to expansion of the surface crust by the heat before the interior has warmed. Sulphur is practically insoluble in water; and readily soluble in carbon disulphide, CS_2. For instance, 100 grams of carbon disulphide at 0° dissolve 22 grams of sulphur; at 20°, 41·8 grams, and at 40°, 100 grams. If the solution in carbon disulphide be allowed to stand at ordinary temperatures, rhombic or octahedral crystals of sulphur are deposited as

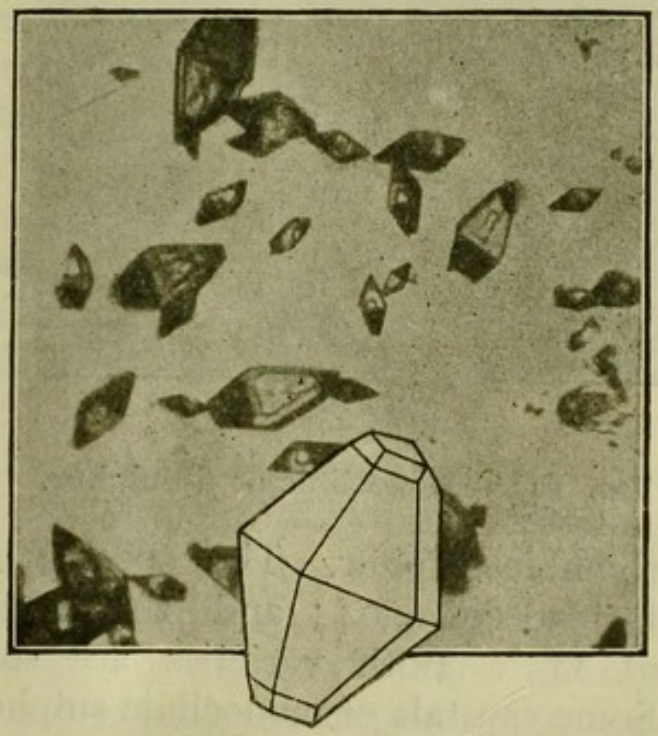


FIG. 142.—Rhombic or α-Sulphur.

the solvent evaporates. The appearance of the crystals is shown by the photograph, Fig. 142 : ideal crystal sketched in outline. About 60 or 70 per cent. of flowers of sulphur consists of more or less imperfect crystals of this kind. Native sulphur also occurs in this form. The crystals are quite stable at ordinary temperatures.

§ 3. Monoclinic, Prismatic, or β-Sulphur.

In 1823, E. Mitscherlich announced the fact that the element sulphur can be crystallized in two distinct forms ; up to that time it was considered that the crystalline form of a substance is fixed and invariable. If, say, 500 grams of sulphur be melted in a clay or porcelain crucible and the mass allowed to stand until a surface crust is formed, when the crust is pierced, and the still fluid sulphur is poured away, beautiful long prismatic needle-like crystals of waxy yellow sulphur will be found to have grown on the walls of the crucible, and on the under side of the surface crust. These crystals have many properties different from ordinary rhombic sulphur. The specific gravity, for instance, is 1·93 instead of 2·04 ; and the melting-point is 120° in place of 115°. Both varieties are soluble in carbon disulphide. Some crystals of monoclinic sulphur are illustrated in Fig. 143, along with an outline sketch of an ideally perfect crystal.

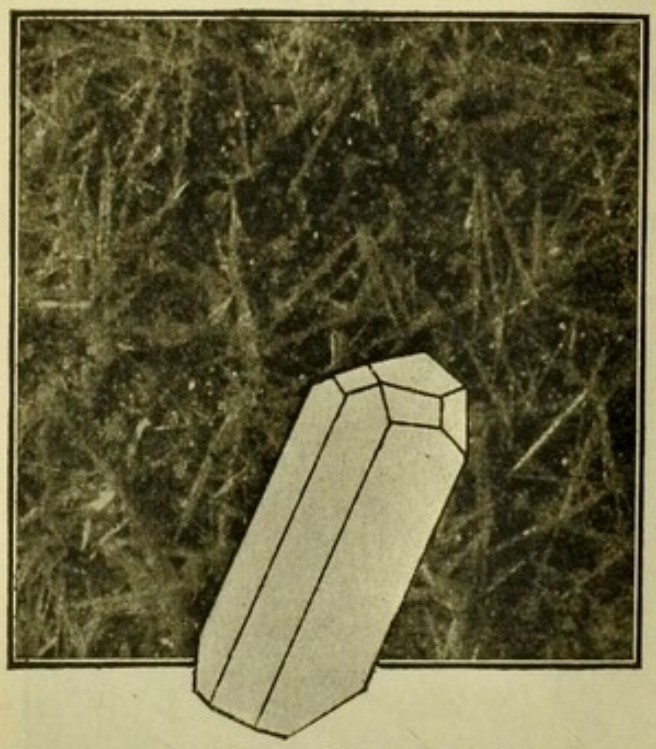


Fig. 143.—Monoclinic or β-Sulphur.

In about a day's time, the prismatic crystals become light yellow, opaque, brittle, and crumble into powder at the slightest touch. The grains of powder are small rhombic crystals of α-sulphur. If the rhombic crystals be kept a few hours between

108° and 112°, they also become opaque and change to a friable crumbling mass of prismatic crystals. The two reactions are thus reversible. Experiment shows that the prismatic crystals are unstable below 94·5°, and slowly pass into the rhombic variety. Conversely, the rhombic sulphur is unstable above 94·5°, and slowly passes into the prismatic variety. With the notation previously employed, the change is symbolized :

$$S_{rhombic} \overset{94\cdot5^\circ}{\rightleftharpoons} S_{prismatic} \text{ ; or } \alpha\text{-S} \overset{94\cdot5^\circ}{\rightleftharpoons} \beta\text{-S}$$

Hence, 94·5° is a transition temperature.

§ 4. The Action of Heat on Sulphur—Amorphous Sulphur.

Sulphur is pale yellow at ordinary temperatures, and almost colourless at −50°, and at 100° it is intense yellow. If a piece of ordinary rhombic sulphur be gradually heated in a test tube, the sulphur crackles and falls to pieces as indicated above. As the temperature rises, the sulphur melts to a clear, limpid, amber-coloured liquid between 113° and 115°. If this liquid be suddenly chilled, the yellow mass is nearly all soluble in carbon disulphide. If, however, the temperature of the molten liquid be raised, the colour darkens, and the liquid loses its mobility, until, at about 162°, the mass is almost black, and so viscid that the test tube can be turned upside down without pouring out the sulphur. If the dark brown mass be cooled it is nearly all insoluble in carbon disulphide. The viscosity of the molten sulphur reaches a maximum at about 180°, and the test tube can now be turned upside down without the sulphur running out. As the temperature rises still higher, the dark colour remains, but the mass becomes more and more mobile until, at 444·5°, the liquid begins to boil, forming a reddish orange vapour. If the liquid be allowed to cool, the sulphur undergoes the same changes, but in the reverse order and very slowly. If the vapour be heated still higher, it becomes deep red at 500°, and straw yellow at about 650°. The vapour of sulphur ignites just over 280° in air.

Molten sulphur.—If sulphur, heated to about 350°, be

poured into cold water, a tough elastic material resembling indiarubber—called **plastic sulphur**—is obtained. Plastic sulphur is also obtained by distilling ordinary sulphur from a glass retort and allowing the liquid sulphur which condenses in the neck of the retort to flow into cold water, Fig. 144. A long continuous thread of plastic sulphur is then obtained. The specific gravity of plastic sulphur is about 1·95, nearly the same as monoclinic sulphur; but unlike the crystalline varieties, this form of sulphur can be moulded between the fingers, and drawn into somewhat elastic threads. The plastic sulphur slowly crystallizes to rhombic sulphur on standing. It is sometimes called amorphous sulphur, because it has no crystalline form. The word **amorphous** is derived from the Greek words meaning "without definite shape."

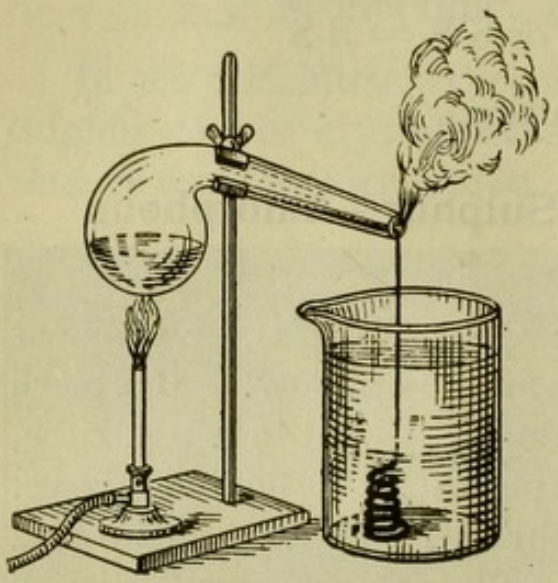


FIG. 144.—Formation of Plastic Sulphur.

The curious difference in the behaviour of the products obtained by cooling molten sulphur at 118° and 180° respectively is supposed to be due to the formation of two different varieties of sulphur—the pale yellow mobile fluid is called **λ-sulphur**; and the dark brown viscid liquid is called **μ-sulphur.** Plastic sulphur is the latter variety cooled down suddenly to ordinary temperatures at which it crystallizes somewhat slowly.

The vapour density of sulphur at about 1000° corresponds with a molecule S_2, and at low temperatures with S_8. At intermediate temperatures, say, 500°, sulphur vapour is a mixture of S_2 and S_8 molecules; or it may be a mixture of S_2, S_4, S_6, S_8 molecules—we do not know which, because the experimental vapour densities may be interpreted either way.

§ 5. Allotropy.

The relation between ozone and oxygen and between the different forms of sulphur must be interesting. Ozone and

oxygen contain but one elemental form of matter. This was proved on p. 260. The different modifications of sulphur likewise contain but one elemental form of matter. This can be proved by showing that a known weight of any of the different forms of sulphur furnish the same amount of sulphur dioxide when burnt in oxygen gas. The experiment can be made by an apparatus resembling that depicted in Fig. 145. About 0·1 gram of pure dry sulphur is introduced into a porcelain boat, and all is weighed. The boat is introduced into a hard glass tube, *C*, which is connected at one end with a gas-holder, *A*, containing oxygen, and wash-bottles, *B*, containing concentrated sulphuric acid to dry the oxygen gas. The other end of

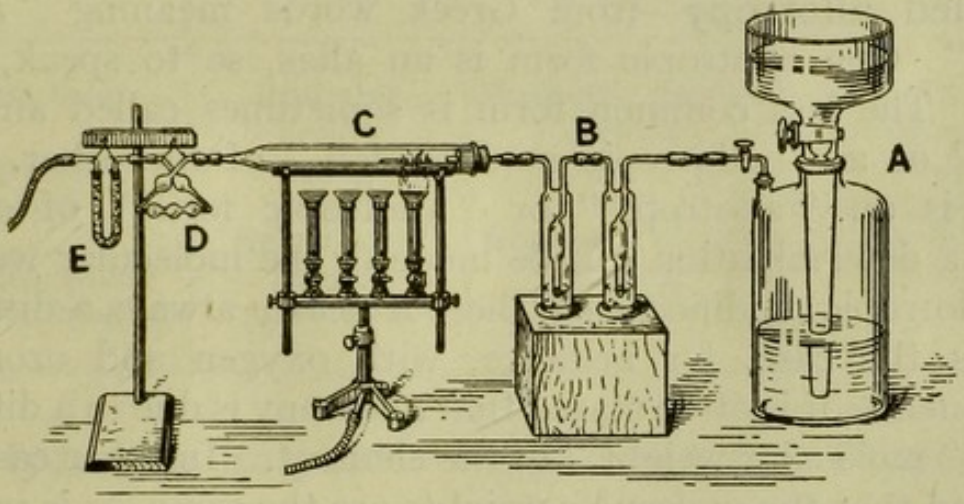


FIG. 145.—Synthesis of Sulphur Dioxide (by weight).

the combustion tube is connected with weighed glass bulbs, *D*, containing a concentrated solution of potassium hydroxide, and a tube, *E*, containing soda lime in one leg and calcium chloride in the other. The current of oxygen is passed through the tube, and the sulphur is very gently heated. The sulphur burns, forming sulphur dioxide, which is absorbed by the potash bulbs. Take care that the sulphur is all burnt, and that none is left sublimed in the cooler parts of the combustion tube. When all the sulphur has been oxidized, the apparatus is disconnected and reweighed. The increment in the weight of the potash bulbs represents the sulphur dioxide formed, and the loss in the weight of the porcelain boat, the amount of sulphur consumed. This is evidence that **each of the different forms of sulphur is but a modification of one element.**

En passant it may be noted that the same experiment gives a close approximation to the combining weight of sulphur.

Weight of sulphur burnt in boat	0·500 grms.
Increase in weight of absorption vessels	1·000 ,,
Oxygen with 0·5 grm. sulphur	1·500 ,,

Hence, the combining weights of oxygen and sulphur are as 0·5 : 1·0, or as 16 : 32 ; and since the latter number represents, very nearly, the atomic weight of sulphur, sulphur dioxide must have its two constituent elements in the ratio SO_2.

That property in virtue of which one element may exist in two or more forms with different properties is called allotropy—from Greek words meaning "another shape." One allotropic form is an alias, so to speak, of the other. The less common form is sometimes called an "allotrope" or an "allotropic modification" of the other. Thus, ozone is an "allotrope" or "allotropic form" of oxygen. When a determination can be made of the molecular weight of two allotropic modifications, there is nearly always a difference. This is the case, for instance, with oxygen and ozone. In consequence, it is often stated that allotropy is due to a difference in the "molecular weight" of the element. In other cases, it is assumed that the molecular weights are the same, as is probably the case with some of the different forms of sulphur, but the atoms of the molecule are arranged differently. The idea is sometimes expressed in this way: "Just as bricks of the same kind in the hands of the builder may be fashioned into various structures ; so nature, from the same kind of atoms, builds up molecular structures with widely different properties."

The heat evolved during the combustion of the two forms of sulphur is different. Thus :

$$\alpha\text{-S}+O_2=SO_2+71{\cdot}08 \text{ Cals.}; \quad \beta\text{-S}+O_2=SO_2+71{\cdot}72 \text{ Cals.}$$

This means that the conversion of 32 parts by weight of rhombic sulphur into the prismatic crystals is attended by an absorption of 0·64 Cals. There is a difference in the available energy of the two forms of sulphur, as is also the case with oxygen and ozone ; and with the different allotropic forms of the other

elements. Hence the definition: **two allotropic modifications of a substance are composed of one element associated with different proportions of available energy, and consequently they exhibit different physical and chemical properties.**

Summary.—We can now summarize the more salient differences in the properties of the three main allotropic forms of sulphur:

TABLE XIII.—DIFFERENCES IN THE PROPERTIES OF THREE VARIETIES OF SULPHUR.

	Rhombic or α-sulphur.	Prismatic or β-sulphur.	Amorphous.
Crystalline form .	Rhombic	Prismatic needles	Nil
Colour	Yellow	Yellow	Brown
Specific gravity .	2·04	1·93	1·95
Melting-point . .	145°	120°	Is a congealed fluid
Stable	Below 94·5°	from 94·5 to 115°	Unstable
Carbon disulphide	Soluble	Soluble	Insoluble
Heat of combustion	71·08 Cals.	71·72 Cals.	?

§ 6. Hydrogen Sulphide—Preparation and Properties.

Occurrence.—Hydrogen sulphide occurs in several mineral waters—sulphur springs; in the exhalations from volcanic vents, etc. It is also formed during the putrefaction of animal and vegetable matters containing sulphur.

Preparation.—Hydrogen and sulphur combine directly when sulphur vapour and hydrogen are passed through a red-hot tube, particularly if the tube be packed with pumice stone or some other similar porous material. The gas is best prepared by the action of dilute hydrochloric or sulphuric acid upon ferrous sulphide, FeS, which, in turn, is made by fusing iron and sulphur together (p. 70). The reactions are symbolized:

$$FeS+H_2SO_4=FeSO_4+H_2S\,;\quad FeS+2HCl=FeCl_2+H_2S$$

For small quantities, a similar apparatus to that employed for the preparation of hydrogen is used (Fig. 42); and when

comparatively large quantities of the gas are required intermittently in a testing laboratory, Kipp's apparatus may be used (Fig. 62). For this, hydrochloric acid is generally preferred to sulphuric acid, because the resulting ferrous chloride —$FeCl_2$—is not so liable to crystallize as ferrous sulphate—$FeSO_4$—and choke up the tubes. The gas is generally washed by passing it through a wash-bottle containing water, and it can be dried with alumina which has been calcined about 600°.

Ferrous sulphide often contains a little free iron, and hence some hydrogen will be mixed with the gas. For ordinary purposes this does not matter. A more pure gas is made by the action of water on calcium, barium, magnesium, or aluminium sulphide at the ordinary temperatures: $BaS + 2HCl = BaCl_2 + H_2S$.

Properties.—Hydrogen sulphide is a colourless gas with an offensive smell resembling " rotten " eggs. The gas is poisonous, and it produces headache and vomiting if breathed diluted with air, for a long time. Owing to its solubility, the gas should not be collected over cold water, but it is sometimes collected over hot water. It can be collected by the upward displacement of air, since it is nearly 1·2 times as heavy as air. The gas liquefies at —62°, and freezes at —85°.

Aqueous solutions.—Hydrogen sulphide is fairly soluble in water: one volume of water at 20° dissolves about three volumes of the gas, and at 100° no gas remains in solution. The solution is called " hydrogen sulphide water." The aqueous solution is not very stable, for it decomposes slowly with deposition of sulphur, particularly if exposed to the light—$2H_2S + O_2 = 2H_2O + 2S$. The aqueous solution has an acid reaction, and it reddens blue litmus. Hydrogen sulphide reacts with bases forming **sulphides.** When it is desired to emphasize the acid nature of the gas, the aqueous solution is sometimes called **hydrosulphuric acid,** and the sulphides are considered to be salts of this acid. Hydrosulphuric acid is oxidized so easily that it acts as a useful reducing agent, for instance, purple-coloured solutions of potassium permanganates can be decolorized; orange solutions of potassium dichromate converted

into a greenish solution ; ferric salts can be made to give no red coloration with potassium thiocyanate, etc.

Combustion.—Hydrogen sulphide is inflammable in air, and burns with a bluish flame, forming sulphur dioxide and water : $2H_2S+3O_2=2SO_2+2H_2O$. A mixture of two volumes of hydrogen sulphide with three volumes of oxygen explodes violently when ignited. If the supply of air is limited, free sulphur may separate : $2H_2S+O_2=2H_2O+2S$. A lighted taper dipped into a jar of the gas is extinguished, showing that the gas does not support combustion.

Action on metals.—Hydrogen sulphide reacts with the metals something like water ; thus when passed through a hot tube containing iron, hydrogen and an iron sulphide are formed :

$$3Fe+4H_2O=Fe_3O_4+4H_2$$
$$3Fe+4H_2S=Fe_3S_4+4H_2$$

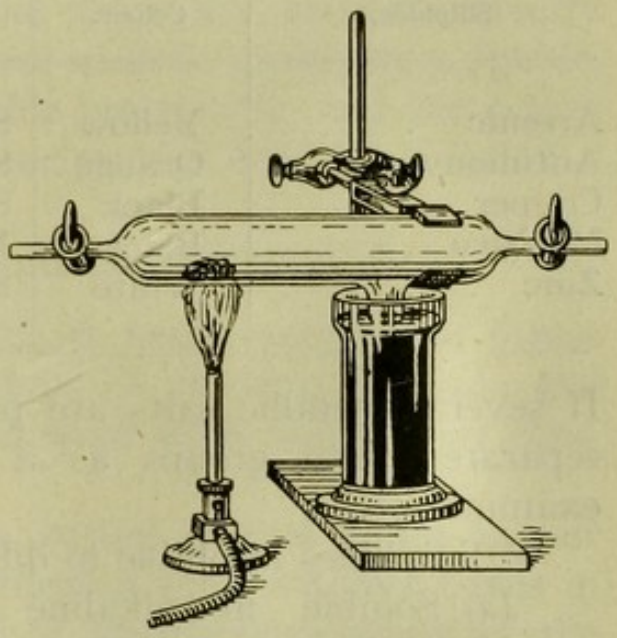


FIG. 146.—Combustion of Tin in Hydrogen Sulphide.

Let a piece of tin be placed in a tube resembling Fig. 146, and the tube filled with hydrogen sulphide, by passing a current of the gas from right to left. The long side arm dips in a jar of mercury. Raise the tube until the mercury is at the same level inside and outside, and heat the tin as indicated in the diagram. The tin forms tin sulphide and hydrogen, and, when all is cooled to the temperature of the room, *the gas, after the experiment, has the same volume as before.* This is what might be expected from Avogadro's hypothesis. The reaction is represented :

$$\underset{\text{2 vols.}}{H_2S} + \underset{\text{Solid}}{Sn} \rightarrow \underset{\text{Solid}}{SnS} + \underset{\text{2 vols.}}{H_2}$$

The difference in the volumes of tin and the tin sulphide is inappreciable.

§ 7. The Action of Hydrogen Sulphide on Metallic Salt Solutions.

Hydrogen sulphide is a valuable reagent in analytical work. Its reactions with solutions of the different metallic salts enable the metals to be identified, for, if the sulphides are alone, their colour is often characteristic and enables the element present to be recognized directly ; in other cases, the metal is identified from the effect of various reagents on the sulphide. For instance :

TABLE XIV.—EFFECT OF HYDROGEN SULPHIDE ON SOLUTIONS OF METALLIC SALTS.

Sulphide.	Colour.	Behaviour towards other reagents.
Arsenic . . .	Yellow	Soluble in sodium sulphide
Antimony. . .	Orange	Soluble in sodium sulphide
Copper . . .	Black	Soluble in concentrated nitric acid
Mercury . . .	Black	Not dissolved by nitric acid
Zinc	White	Soluble in hydrochloric acid

If several metallic salts are present in solution, they can be separated into groups as a preliminary to more detailed examination.

I. Sulphides insoluble in dilute acids.

(*a*) Soluble in alkaline sulphides—arsenic, antimony, stannic, gold, and platinum sulphides.

(*b*) Insoluble in alkaline sulphides—mercury, silver, lead, copper, bismuth, cadmium, and stannous sulphides.

II. Sulphides soluble in dilute mineral acids but insoluble in the presence of alkalies—iron, cobalt, nickel, manganese, and zinc sulphides.

III. Sulphides not precipitated by hydrogen sulphide—chromium, aluminium, magnesium, barium, strontium, calcium, potassium, and sodium. Chromium and aluminium are precipitated as hydroxides.

The elements can be arranged in two groups—those which form soluble and those which form insoluble sulphides in

hydrochloric acid. The action is an illustration of the principle of opposing reactions. Take the case of antimony chloride, where the precipitation of antimony sulphide is represented by the equation:

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 6HCl$$

Concentrated hydrochloric acid can dissolve antimony sulphide, and in such a solution no antimony sulphide would be precipitated; on the other hand, if the solution contains no more than 15 c.c. of hydrochloric acid per 100 c.c. of solution, all the antimony in the solution will be precipitated as sulphide. The reverse reactions are represented by the reversed arrows. Hydrochloric acid is usually considered much stronger than hydrosulphuric acid, but the latter is able to conquer in the struggle of the two acids for the antimony, because directly the hydrosulphuric acid forms ever so little antimony sulphide, the latter separates as an insoluble precipitate, and the action continues until all the metal is precipitated from the solution.

§ 8. Sulphur Dioxide and Sulphurous Acid.

Occurrence.—Sulphur dioxide is found among the fumes from volcanic vents, in the springs of volcanic districts, and in the air of towns where it is derived from the sulphur compounds in the coal.

Composition.—It has been stated several times in our studies that sulphur dioxide is formed when sulphur burns in air, and on page 93, the result of quantitative study of the reaction was indicated. We found the equivalent of one molecule of sulphur united with two molecules of oxygen. The density of the gas ($H_2=2$) is 64, corresponding with the formula SO_2. The formation of sulphur dioxide by the combustion of sulphur in air is represented by the equation:

$$\underset{\text{Solid.}}{S} + \underset{2\text{ vols.}}{O_2} = \underset{2\text{ vols.}}{SO_2}$$

Since the volume of the solid sulphur is negligibly small in comparison with the volume of the resulting gas, it follows that the sulphur dioxide has the same volume as the oxygen from which it was formed. The fact is most conveniently illustrated

by the apparatus, Fig. 94. The bulb contains oxygen. A small piece of sulphur is placed in the deflagrating spoon. The volume of the oxygen is noted with a strip of gummed paper when the level of the mercury in the two tubes is the same (raise or lower the levelling tube, if necessary). Pass a current of electricity through the wires so as to heat a thin bit of platinum wire touching the sulphur. After the sulphur has burned, and the apparatus has cooled to the temperature of the room, the adjustment of the mercury to the same level in the two tubes will prove that the volume remains changed.

Preparation.—The most convenient laboratory process, for small quantities, is to decompose commercial sodium bisulphite with concentrated sulphuric acid. A concentrated—40 per cent.—solution of sodium bisulphite, $NaHSO_3$, is placed in a flask, which is then fitted with a tap funnel containing concentrated sulphuric acid, as indicated in Fig. 52. The gas can be washed by passing it through concentrated sulphuric acid. The reaction is symbolized :

$$NaHSO_3+H_2SO_4=NaHSO_4+H_2O+SO_2$$

The same gas is made by reducing sulphuric acid with charcoal, sulphur, mercury or copper. Half fill a flask with copper turnings, and add sufficient sulphuric acid to not quite cover all the copper. The gas comes off when the flask is gently warmed. The apparatus is illustrated in Fig. 57, where two washing bottles containing concentrated sulphuric acid are shown attached to the delivery tube in order to dry the gas. The reaction is commonly represented by the equation :

$$Cu+2H_2SO_4=CuSO_4+2H_2O+SO_2$$

The changes are no doubt more complex than this. Some hydrogen is probably formed : $Cu+H_2SO_4\rightarrow CuSO_4+H_2$; and some of the sulphuric acid is probably reduced to hydrogen sulphide. At any rate, cuprous sulphide, Cu_2S, will be found associated with the copper sulphate in the flask, when the residue in the flask is examined.

Properties.—Sulphur dioxide is a colourless gas with a smell characteristic of burning sulphur. Sulphur dioxide is an acute

blood poison. Sulphur dioxide is also injurious to vegetation, and it is one of the "noxious vapours" complained about in manufacturing districts. The gas is easily liquefied. The liquid boils at −8°, and it solidifies at −70°. Syphons of liquid sulphur dioxide are on the market, and, where available, the "syphons" are convenient for supplying sulphur dioxide when it is wanted in the laboratory—*e.g.* one is shown on left of Fig. 147.

The gas is more than twice as heavy as air, and in consequence it can be collected by the upward displacement of air. Sulphur dioxide neither supports combustion nor does it burn in air. The gas cannot be collected satisfactorily over water, because it is easily soluble in that menstruum, but it can be collected over mercury. 100 volumes of water at 20° dissolve 38·4 volumes of sulphur dioxide. The aqueous solution is strongly acid, and it has the general properties characteristic of acids. It is hence called **sulphurous acid,** and it is represented by the formula H_2SO_3. The gas itself is accordingly called **sulphurous anhydride.** The dissolved gas is all expelled on boiling the aqueous solution.

Sulphur dioxide is rather active chemically. An aqueous solution of the gas is an excellent reducing agent, for it readily takes up oxygen from the air, and other substances whereby it is changed to sulphuric acid, H_2SO_4. Solutions of permanganates, dichromates, and ferric salts are reduced as they are when treated with hydrosulphuric acid. When an aqueous solution of iodine is treated with sulphur dioxide, hydriodic and sulphuric acids are formed: $I_2+2H_2O+SO_2=2HI+H_2SO_4$. Sulphur is deposited when hydrogen sulphide and sulphur dioxide are brought into contact, say, by placing a jar of sulphuric dioxide and of hydrogen sulphide mouth to mouth; or by leading sulphur dioxide and hydrogen sulphide separately into a large globe, Fig. 147, provided with a vent. It is conceivable that gaseous exhalations from volcanoes may contain these two gases which, on mingling together mutually decompose with the formation of sulphur: $2H_2S+SO_2=2H_2O+3S$. This reaction does not occur if the gases are thoroughly dried, although curiously enough water is a product of the reaction.

Moist sulphur dioxide bleaches colouring agents owing to its reducing qualities; chlorine, it will be remembered, bleaches by oxidation. Coloured carnations and roses bleached by sulphurous acid gradually return on exposure to the air—presumably by reoxidation. A coloured flower quickly drawn through the flame of burning hydrogen sulphide is bleached wherever the flame touches. This is not the case with the flame of burning sulphur—presumably owing to the paucity of water vapour. Dry sulphur dioxide, like dry chlorine, does not bleach.

Uses of sulphur dioxide.—Sulphur dioxide is used in manufactures when a milder bleaching agent than chlorine is desired.

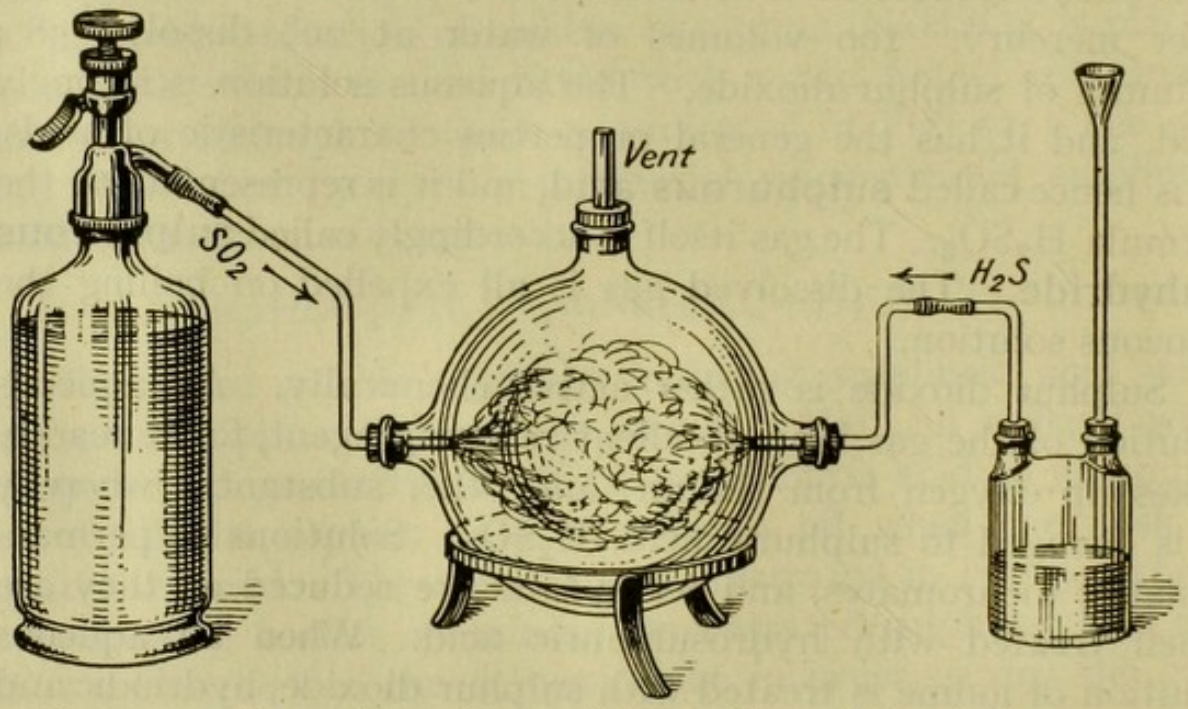


FIG. 147.—Formation of Free Sulphur from Volcanic Gases.

Sulphur dioxide has marked antiseptic properties. The use of sulphur for disinfecting purposes has been known from very early times. It is referred to in Homer, where Ulysses, after the slaughter of the suitors, and probably recognizing the need for a general cleansing, calls :

> "Quickly, O Nurse, bring fire that I may burn
> Sulphur, the cure of ills."

Sulphites.—Sulphurous acid forms two series of salts—the normal and the acid sulphites. For instance, when sulphur

dioxide is passed into an aqueous solution of sodium hydroxide, **normal sodium sulphite,** Na_2SO_3 is first formed: $2NaOH+SO_2=H_2O+Na_2SO_3$; and if still more gas is passed into the solution, **sodium acid sulphite,** $NaHSO_3$, is formed: $Na_2SO_3+H_2O+SO_2=2NaHSO_3$. Normal sodium sulphite is neutral and acid sodium sulphite is acid towards litmus. The last-named salt is used in the manufacture of iodine (p. 270). When sodium sulphite is boiled with sulphur, the two substances combine, forming what is called **sodium thiosulphate,** $Na_2S_2O_3$, thus:

$$O=S\begin{matrix}ONa\\ONa\end{matrix}+S=\begin{matrix}O\\S\end{matrix}\!\!\gg S\begin{matrix}ONa\\ONa\end{matrix}$$

This reaction recalls very forcibly the similar reaction—oxidation of sodium sulphite to sodium sulphate, Na_2SO_4:

$$O=S\begin{matrix}ONa\\ONa\end{matrix}+O=\begin{matrix}O\\O\end{matrix}\!\!\gg S\begin{matrix}ONa\\ONa\end{matrix}$$

Under the name *sodium hyposulphite*, this salt, sodium thiosulphate, is used in photography because of its solvent action on silver chloride. The term hyposulphite is otherwise obsolete.

§ 9. Sulphur Trioxide and Sulphuric Acid.

Sulphur dioxide is fairly active chemically. It can combine directly with the oxygen of the air to form a higher oxide. A small amount of sulphur trioxide is always formed when sulphur burns in air or in oxygen, and this substance is the cause of the cloudiness of the gas. If sulphur dioxide alone were formed, the gas would be clear. If a mixture of sulphur dioxide and oxygen be passed over platinized asbestos at about 400°, the oxidation of the sulphur dioxide is nearly complete. The platinized asbestos acts as a catalytic agent (p. 91). Instead of platinized asbestos, ferric oxide and other oxides can be employed, but none are so effective as platinized asbestos. The platinized asbestos is prepared by soaking asbestos in platinum chloride, and calcining the dried mass until nothing but asbestos and finely divided platinum remain. The action can

be illustrated by an apparatus similar to that depicted in Fig. 148. The mixture of sulphur dioxide and oxygen, from separate gas-holders is sent through a wash-bottle, *A*, containing concentrated sulphuric acid. The mixed gases travel through a tower, *B*, containing pumice stone saturated with concentrated sulphuric acid. The dried mixture of oxygen and sulphur dioxide then passes over platinized asbestos, *C*, warmed to about 400°, in a hard glass tube. Combination occurs, and the sulphur trioxide

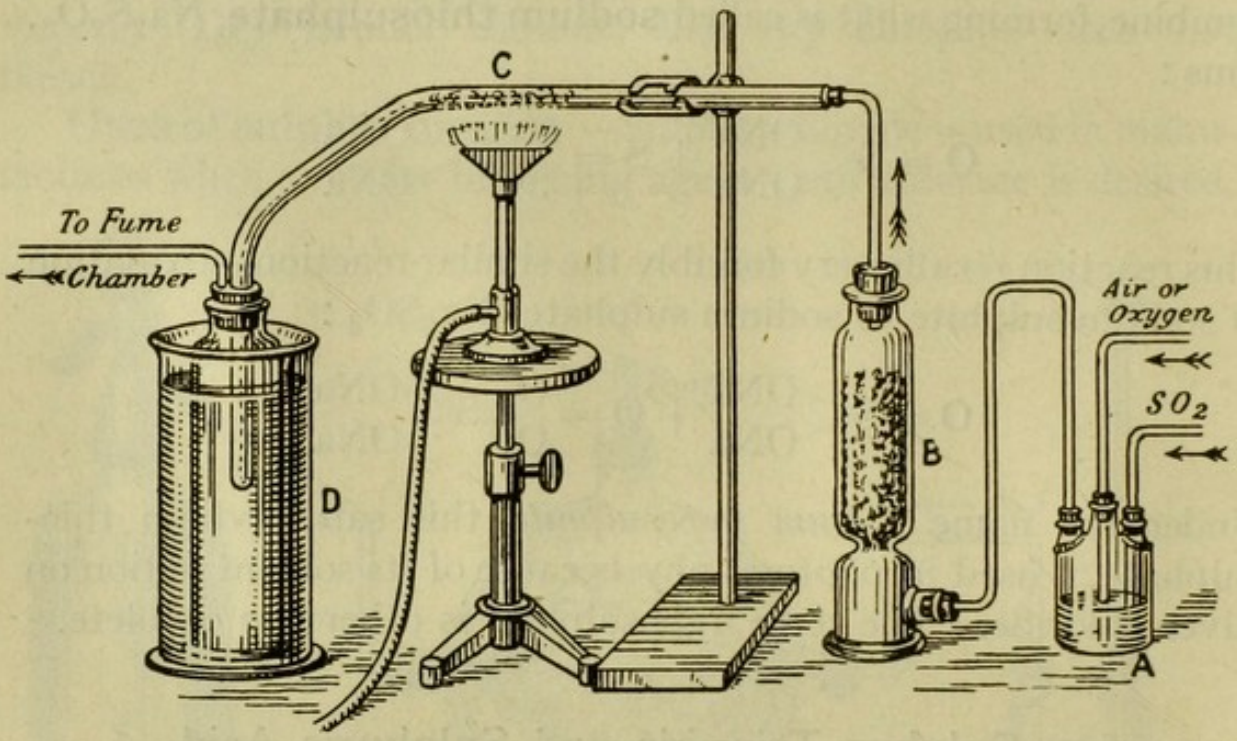


FIG. 148.—Preparation of Sulphur Trioxide (Contact Process).

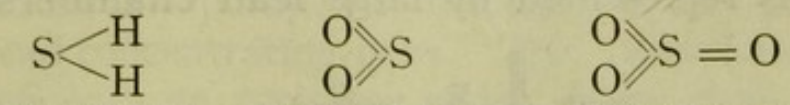
condenses in the tube and bottle, *D*, surrounded by a jar containing a freezing mixture. If the gases and the apparatus are not thoroughly dried, oily looking drops will collect in the receiver. If free from moisture, sulphur trioxide forms glistening needles like crystals. The crystals react with water with a hissing noise (like a red-hot iron plunged in water) forming sulphuric acid, H_2SO_4; thus, in symbols, $H_2O+SO_3=H_2SO_4$. If the catalytic platinum be much hotter than 350°, the trioxide will be decomposed into sulphur dioxide and oxygen again.

The vapour density of the trioxide corresponds with the formula SO_3, and if the trioxide vapour be sent through a red-hot tube, it furnishes a mixture of 2 volumes of

sulphur dioxide with one volume of oxygen. This reaction is interpreted :

$$2SO_3 = 2SO_2 + O_2$$
$$\text{2 vols.} \quad \text{1 vol.}$$

It may be of interest to here emphasize the variable valency of sulphur, for in hydrogen sulphide, sulphur dioxide, and sulphur trioxide, sulphur appears to be bi-, quadri-, and sexi- valent respectively. This is shown graphically :



Sulphur dyad. Sulphur tetrad. Sulphur hexad.

Contact process for sulphuric acid.—The above reaction is utilized in the so-called contact process for making sulphuric

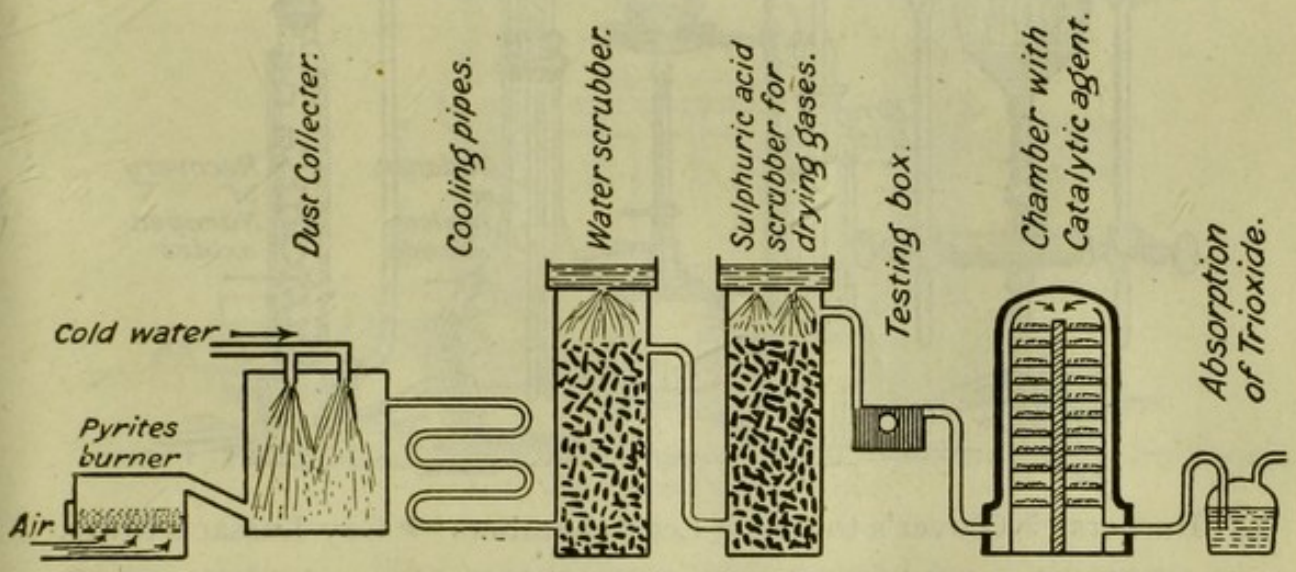
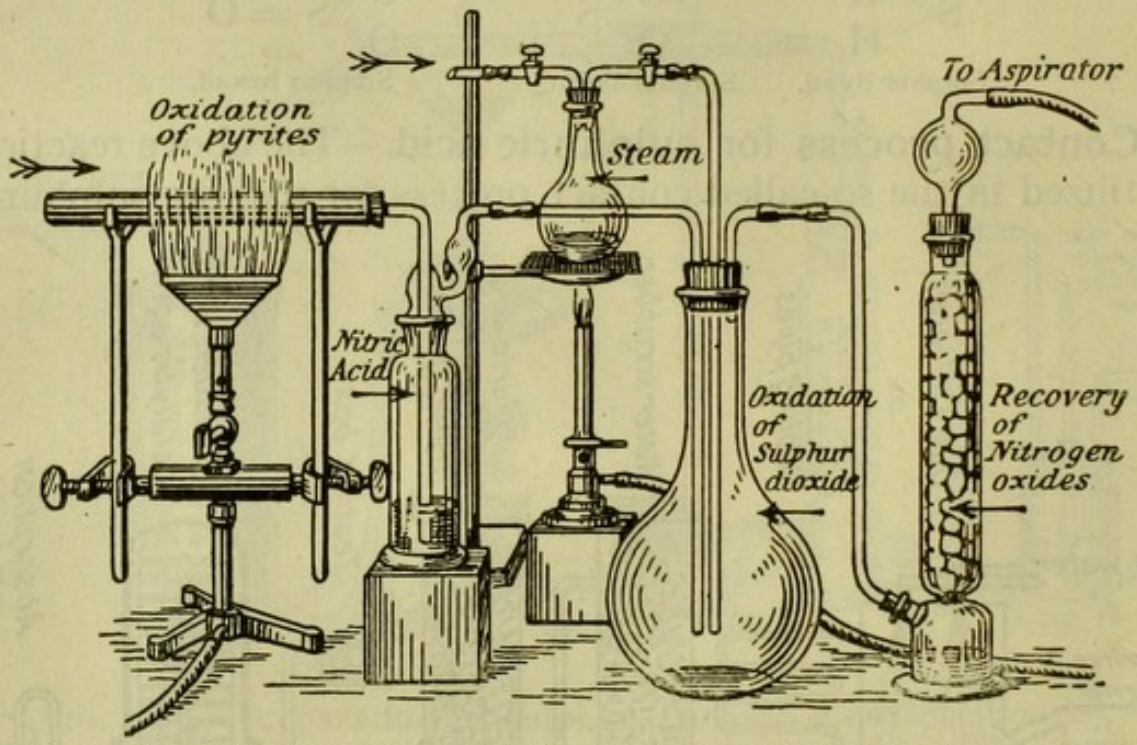


FIG. 149.—Diagrammatic Illustration of the Manufacture of Sulphuric Acid by the Contact Process.

acid. The sulphur dioxide and air mixture must be freed from impurities—dust, arsenic, etc.—or the platinum will not be effective for very long. The sulphur trioxide, as it issues from the chamber at about 350° containing the catalytic platinum, is sent through vessels containing fairly concentrated sulphuric acid, since this solution is a better absorbent for the trioxide than water alone. The solution of trioxide in concentrated sulphuric acid is afterwards diluted with water to the necessary strength. A rough diagrammatic sketch of plant is indicated in Fig. 149.

Chamber process for sulphuric acid.—Some of the principles involved in the manufacture of sulphuric acid by the lead chamber process are illustrated by the laboratory apparatus, Fig. 150. The sulphur or iron pyrites is heated in a porcelain boat placed in a quartz or porcelain tube, and a current of air is drawn through the tube. The sulphur or pyrites is oxidized. The mixture of air and sulphur dioxide is passed through a wash-bottle containing nitric acid, and thence into a large flask. The large flask is represented by large **lead chambers** on a real



Burners → Glover's tower → Lead chambers → Gay-Lussac's tower.

FIG. 150.—Illustrative Model of the Chamber Process.

factory. Steam is also generated in a flask connected with the same globe. The amount of air drawn in with the steam is regulated by means of the stopcocks. The sulphur dioxide is oxidized to the trioxide in the presence of the nitrogen oxides which were mixed with the gases as they bubbled through the nitric acid. The steam reacts at once with the trioxide, etc., forming sulphuric acid, which collects at the bottom of the flask. The nitrogen oxides pass along with the current of air, etc., to the base of the tower on the right of the diagram. The tower is filled with coke soaked in concentrated sulphuric acid. This is represented by the **Gay-Lussac's tower** on a large works.

The red fumes visible at the base of the tower are absorbed readily higher up, and the globe is placed at the top of the tower to enable this fact to be demonstrated. The nitrated acid which collects at the base of this tower is pumped to the top of a somewhat similar tower—called **Glover's tower**—placed between the burner and the lead chambers. The hot gases pass up this tower and the nitrated acid runs down. In this way the acid is "denitrated." Part of the acid which collects at the base of the tower is pumped to the top of Gay-Lussac's tower; or to the lead concentrating pans. The "Gay-Lussac's tower" is connected with an aspirator which draws gases through the

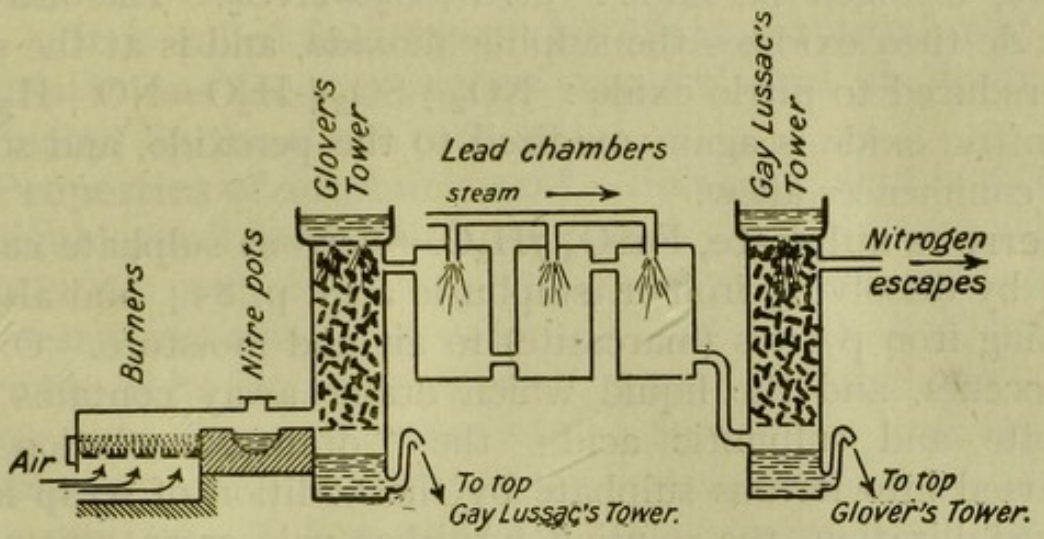


FIG. 151.—Diagrammatic Illustration of the Manufacture of Sulphuric Acid by Chamber Process.

whole system. The aspirator is represented by a chimney on a real works. Fig. 151 is a rough diagrammatic representation of a "chamber process" works.

The concentration of the acid.—The acid which collects in the lead chambers—called **chamber acid**—contains about 62–70 per cent. H_2SO_4. Part is concentrated in Glover's tower and part in leaden concentrating pans up to a strength of 79 per cent. sulphuric acid. A stronger acid than this attacks the lead rather seriously. This acid is the **brown oil of vitriol** of commerce. The brown colour is probably due to organic matter which is oxidized when the acid is further concentrated. The acid is further concentrated by distillation in glass, vitrefied quartz, or platinum stills. Acid stronger than 98·3 per cent.

H_2SO_4 cannot be obtained by this process, because an acid of that strength distils unchanged.

The catalytic agent.—It will be observed that in the chamber process the sulphur dioxide is oxidized by the air, and that the speed of the reaction is "stimulated" by the catalytic agent—nitrogen oxides; in the contact process the speed of oxidation was accelerated by the platinized asbestos. We do not know how the catalytic agent does its work in the chamber process. Several schemes have been suggested, one of the simplest, perhaps the best, is as follows: nitric oxide, NO, unites with the oxygen from the air, forming nitrogen peroxide: $2NO+O_2=2NO_2$. The nitrogen peroxide then oxidizes the sulphur dioxide, and is at the same time reduced to nitric oxide: $NO_2+SO_2+H_2O=NO+H_2SO_4$. The nitric oxide is again oxidized to the peroxide, and so the cycle commences anew.

Ferrous sulphate, $FeSO_4.7H_2O$.—Ferrous sulphate can be made by dissolving iron in sulphuric acid, p. 85; and also by exposing iron pyrites (marcasite) to air and moisture. Oxidation occurs, and the liquid which drains away contains iron sulphate and sulphuric acid; the "drainage solution" is converted into ferrous sulphate by the addition of scrap iron; on crystallization, the solution furnishes pale green crystals of the salt in question. Ferrous sulphate—$FeSO_4.7H_2O$—is also called *green vitriol* and *copperas*. The term "copperas" appears to be a corruption of the French "couperose," which, in turn, is a corruption of the Latin "cuprirosa"—literally "rose of Cyprus." Cyprus was once renowned for its copper mines. The German word for copperas is "vitriol," a term used by Pliny, about 50 A.D. Pliny described this substance as "vitriolus quasi vitrum," meaning "vitriol, a kind of glass," since the crystals resembled green glass, but differed from glass in being easily soluble in water. Sulphuric acid was obtained from "vitriol," and Geber accordingly gave it an Arabic name, which, translated into English, means **oil of vitriol**. The term "oil" was applied because the acid flows sluggishly, like olive oil, and it has an oily feel when rubbed between the fingers (this latter experiment is dangerous).

If crystals of ferrous sulphate be heated in a hard glass tube, Fig. 24, a deposit of moisture will be formed in the cooler part of the tube, and the green crystals become white and opaque. When heated still higher, some sulphur dioxide is given off, and the powder begins to turn red, owing to the formation of ferric oxide. If ferrous sulphate which has been dehydrated by heating it in an open dish be placed in a porcelain or fireclay retort, Fig. 31, and heated by a blast burner, dense white fumes issue from the mouth of the retort and condense in the receiver as a brown viscid liquid. White needle-like crystals—sulphur trioxide—collect on the walls of the receiver above the distillate. The distillate is a fuming solution of sulphur trioxide in sulphuric acid. It is called **fuming or Nordhausen sulphuric acid,** because it was for many years manufactured at Nordhausen (Germany) by the above process.

Properties of sulphuric acid.—Sulphuric acid is a colourless liquid which looks as if it were an oil. The ordinary acid has about 2 per cent. of water ; its specific gravity is 1·84, so that it is nearly twice as heavy as water ; and it boils at about 338°. In virtue of its high boiling-point, when sulphuric acid is competing with other more volatile acids for a given base, the more volatile acid leaves the field of the reaction until sulphuric acid alone remains. This is the case, for instance, when sulphuric acid is heated with sodium chloride and with sodium nitrate.

Sulphuric acid contains a relatively large proportion of oxygen, and in consequence it is a fairly good oxidizing agent. This is evidenced by the action of the boiling acid on carbon, sulphur, and many other substances. Thus, with carbon, carbon dioxide is a product of the oxidation, and the acid is reduced to sulphur dioxide : $H_2SO_4=H_2SO_3+O$; hence, $C+2H_2SO_4=2H_2O+2SO_2+CO_2$. With metals, the dilute acid furnishes hydrogen gas and a sulphate of the metal : $Zn+H_2SO_4=ZnSO_4+H_2$; but with the concentrated acid, the hydrogen reduces the acid, forming sulphur dioxide. Thus with copper : $Cu+H_2SO_4=CuSO_4+H_2$; $H_2SO_4+H_2=2H_2O+SO_2$.

Sulphuric acid mixes with water in all proportions, and during the mixing a considerable amount of heat is evolved. When sulphuric acid is to be diluted with water, the acid should

be added to the water, with constant stirring to prevent the heavier acid collecting at the bottom of the vessel, when a sudden generation of steam may cause spurting. If a piece of glass tubing with a bulb blown at one end, and a little benzene be poured into the bulb, be used as stirring rod, the heat developed suffices to boil the benzene, and the vapour may be ignited as shown in Fig. 152. Sulphuric acid readily absorbs moisture from the atmosphere and it is much used for drying gases which do not act upon it chemically. Organic substances containing hydrogen and oxygen may be so acted upon by sulphuric acid that the hydrogen and oxygen in the proportions they form water are removed and carbon remains behind. This action is illustrated by pouring 12 grms. of concentrated sulphuric acid upon 10 grms. of sugar in a beaker, Fig. 153. Clouds of steam arise, the sugar turns black, and a spongy mass of carbon swells up considerably, Fig. 153. The black mass when boiled in water and washed on a filter, gives a residue of fairly pure carbon. Flesh also is charred and burnt by the acid. Hence, painful wounds may be produced by contact of the acid with the skin.

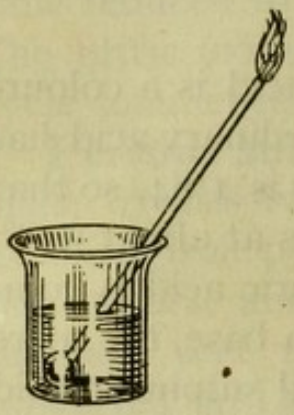


FIG. 152.—Heat developed on mixing Sulphuric Acid and Water.

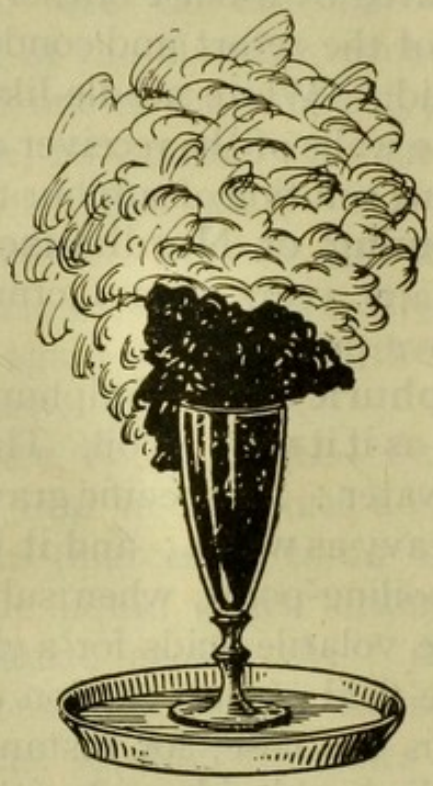
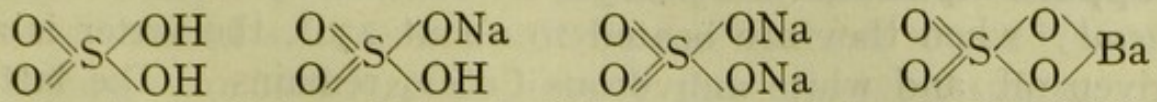


FIG. 153.—Action of Sulphuric Acid on Sugar.

§ 10. Salts of Sulphuric Acid—Sulphates.

Sulphuric acid produces salts—sulphates—when it acts upon certain metals, metallic oxides, hydroxides, and carbonates. The sulphates are also prepared by heating salts of the more

volatile acids—chlorides, nitrates, etc.—with sulphuric acid. Sulphuric acid is dibasic, forming two series of salts—normal and acid sulphates :



Sulphuric acid. Sodium acid sulphate. Sodium normal sulphate. Barium sulphate.

The sulphates are usually fairly soluble in water, and crystallize readily. The sulphates of lead, calcium, strontium, and barium are but sparingly soluble in water ; and they are best prepared by adding a soluble sulphate or dilute sulphuric acid to one of their soluble salts, say, the nitrate or chloride, *e.g.* $BaCl_2+H_2SO_4=BaSO_4+2HCl$. The sulphates of the metals of the alkalies and alkaline earths decompose only when heated to very high temperatures, the other sulphates decompose when heated in the apparatus shown in Fig. 31, giving off sulphur trioxide which latter decomposes into sulphur dioxide and oxygen ; the metallic oxide remains behind : $2CuSO_4 \rightarrow 2CuO+2SO_2+O_2$.

The recognition of sulphates and sulphuric acid.—The insolubility of **barium sulphate** is utilized in identifying sulphuric acid or soluble sulphates, for if a soluble barium salt—nitrate or chloride—be added to a soluble sulphate or dilute sulphuric acid, a white precipitate of barium sulphate is obtained. This precipitate is insoluble in water, dilute acids, and alkalies. A similar precipitate of **barium sulphite** may or may not be formed with soluble sulphites, or sulphurous acid, but the precipitate is not formed in dilute solutions, and it is decomposed by hydrochloric acid.

If insoluble barium sulphate be intimately mixed with sodium carbonate, and heated, soluble sodium sulphate can be leached from the mass by treating it with water ; insoluble barium carbonate remains behind. The reaction thus appears to be $BaSO_4+Na_2CO_3=BaCO_3+Na_2SO_4$. If the mass had been treated with a dilute hydrochloric acid, the barium carbonate and the sodium sulphate would have dissolved, and barium sulphate would have been precipitated at once. The first action of the acid on the carbonate is represented : $BaCO_3+2HCl=BaCl_2+CO_2+H_2O$; and this would here be followed by : $BaCl_2+Na_2SO_4=BaSO_4+2NaCl$.

Sodium sulphate crystallizes with ten molecules of water —$Na_2SO_4.10H_2O$—the crystals are called "Glauber's salt." **Copper sulphate,** $CuSO_4.5H_2O$, forms blue crystals called *blue vitriol;* when they are heated to about 230°, the water is all driven off and white anhydrous $CuSO_4$ remains. The latter is a fairly sensitive test for water, since a trace of water gives a blue coloration with the anhydrous sulphate. **Magnesium sulphate,** $MgSO_4.7H_2O$, is also called *Epsom salts*, because it occurs in the water of the Epsom springs. The salt is a well-known purgative. The crystals of magnesium sulphate are isomorphous with those of **zinc sulphate,** $ZnSO_4.7H_2O$, also called *white vitriol;* and, ferrous sulphate described above, as well as the sulphates of cadmium nickel, cobalt, chromium, and manganese.

Calcium sulphate.—It occurs in nature in white masses as *gypsum*—$CaSO_4.2H_2O$. It is used as a fertilizer under the name "land plaster," and also in the manufacture of plaster of Paris. If the gypsum occurs in clean fine-grained masses, it is called *alabaster:* and if in colourless translucent crystals, *selenite.* An anhydrous form of calcium sulphate also occurs native in rhombic crystals, it is called *anhydrite*—$CaSO_4$. There is also a variety of soluble anhydrous calcium sulphate which is made artificially, and which is more soluble than native anhydrite. Artificial anhydrite is an unstable variety. When gypsum is heated to about 120° it loses the equivalent of $1\frac{1}{2}$ molecules of water, and forms a hemihydrate, $(CaSO_4)_2H_2O$, as a white powder called **plaster of Paris**—because of the large deposits of gypsum employed for the manufacture of plaster at Montemartre (Paris). The transformation or inversion temperature:

$$2CaSO_4.2H_2O \overset{107°}{\rightleftharpoons} (CaSO_4)_2H_2O + 3H_2O$$

If plaster of Paris be wetted with, say, one-third of its weight of water, it forms a plastic mass which "sets" in from 5 to 15 minutes to a white, porous, hard mass. **The setting of plaster of Paris is largely due to the rehydration of the hemihydrate and the interlacing of the resulting needle-like crystals of the dehydrate, $CaSO_4.2H_2O$.** Plaster of Paris is a valuable material for making exact reproductions of statues,

ornaments, moulds, decorative work, etc. The slight expansion which occurs during the setting of plaster of Paris enables it to make a sharp reproduction of the details of a mould. Different grades—mixed with certain salts to accelerate or retard the rate of setting—are used for wall plasters, cements, paper sizings, etc.

If gypsum be overheated—"deadburned"—the water is all expelled, and water is subsequently taken up so slowly that the product cannot be used like ordinary plaster.

Alums.—When sulphuric acid acts upon aluminium hydroxide, aluminium sulphate is formed, and when a hot solution of aluminium sulphate is mixed with potassium sulphate, and the solution is cooled, octahedral crystals of potash alum, that is, a double sulphate of aluminium and potassium, separate. The growth of the crystals can be well shown by suspending a small fragment of a crystal in a saturated solution of alum. The crystal fragment will probably grow into a large nearly perfect crystal. Potash alum has the empirical formula, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, or else $KAl(SO_4)_2.12H_2O$. This salt is a typical member of a large number of isomorphous compounds which are called "alums." Their general formula is :

$$R_2SO_4.R^{III}_2(SO_4)_3.24H_2O \text{ ; or, } R^IR^{III}(SO_4)_2.12H_2O$$

where R^I represents an atom of a univalent metal or radicle—potassium, sodium, ammonium, etc. ; and R^{III} represents an atom of a tervalent metal—aluminium, iron, chromium, manganese. Consequently, an alum is a compound which crystallizes with 12 molecules of water, and is derived from two molecules of sulphuric acid by replacing one hydrogen atom by a univalent atom or radicle ; and the remaining three hydrogen atoms by a tervalent metal ; *e.g.* :

Potash alum	$KAl(SO_4)_2.12H_2O$
Ammonia alum	$NH_4Al(SO_4)_2.12H_2O$
Iron alum	$KFe(SO_4)_2.12H_2O$
Chromium potash alum	$KCr(SO_4)_2.12H_2O$

§ 11. The Oxygen-Sulphur Family of Elements.

Oxygen, sulphur, selenium, and tellurium form an interesting group of elements. The relationship is not so clearly defined as

with the halogens. If we compare oxygen with tellurium, it would require some imagination to make the relationship significant, but on comparing any one element with its neighbour in the series—O, S, Se, Te—the relationship becomes more emphatic. They are all bi- and multi- valent. The physical characteristics are best compared in the form of a table which brings out the gradation in properties very clearly. For instance, the specific gravities, melting-points, boiling-points, etc., increase with increasing atomic weight. Oxygen is at one end, tellurium at the other :

TABLE XV.—PROPERTIES OF THE OXYGEN-SULPHUR FAMILY.

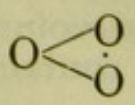
	Oxygen.	Sulphur.	Selenium.	Tellurium.
Atomic weight . .	16	32·07	79·2	127·5
Melting-point . . .	−227°	114°–115°	170°–217°	452°–454°
Boiling-point . . .	−183°	448°	688°	1390°
Specific gravity (solid)	1·43	1·96–2·06	4·28–4·80	5·93–6·4
Atomic weight÷sp. gr.	11	16	18	21
Colour of solid . .	Pale blue	Yellow	Reddish brown	Black

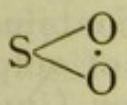
Selenium, and tellurium particularly, lie very close to that ill-defined border line between the metals and non-metals. All four elements exhibit allotropism. Oxygen occurs most abundantly, sulphur next, and tellurium least. They all produce hydrogen compounds of the same type, but while the hydrogen compounds of sulphur, selenium, and tellurium are fœtid-smelling gases at ordinary temperatures, hydrogen oxide, H_2O, is a colourless, odourless liquid. By consulting a dictionary of chemistry, we can tabulate the properties of the hydrides analogous with water. The result is given in Table XVI.

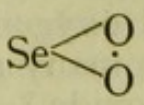
TABLE XVI.—PROPERTIES OF THE HYDRIDES OF THE SULPHUR-OXYGEN FAMILY.

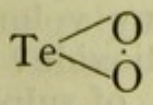
Symbol.	Molecular weight.	Boiling-point.	Melting-point.	Specific gravity.	Dissociation temperature.	Reaction (litmus).
H_2O	18·02	100°	0	1	1800°	Neutral
H_2S	34·09	−61·8°	−85·5°	1·17	400°	Acid
H_2Se	81·22	−42°	−64°	2·81	150°	Acid
H_2Te	129·52	0°	−48°	4·48	0°	Acid

Sulphur, selenium, and tellurium unite with oxygen to form trioxides. The dioxides, however, form an interesting set if we regard ozone as an oxygen dioxide, thus :


Oxygen dioxide.


Sulphur dioxide.


Selenium dioxide.


Tellurium dioxide.

The remarkable number of compounds of the metals with oxygen and sulphur, and the similarity in the construction of the compounds of sulphur and of oxygen, has already been emphasized. Tellurium and selenium have not been so closely studied as sulphur .and oxygen, but they undoubtedly show similar characteristics.

Questions.

1. What weight of barium sulphate can be obtained from 10 c.c. of a solution of decinormal sulphuric acid containing 4·9 grms. per litre ? (Ba=137, S=32.)—*London Univ.*

2. What experiments would you make with sugar to prove that it contains carbon, and with water to prove that it contains oxygen ?—*London Univ.*

3. How would you prove that sulphur was a constituent of sulphuretted hydrogen ? What weight of sulphur is contained in 100 grms. of sulphuretted hydrogen ?—*Science and Art Dept.*

4. Calculate the weight of sulphur required to afford 100 tons of sulphuric acid. Briefly explain the method by which sulphuric acid is made. (S=32.)—*London Univ.*

5. How would you conduct an experiment to show that 9·8 grms. of sulphuric acid are chemically equivalent to 7·3 grms. of hydrochloric acid ?—*Oxford Senr. Locals.*

6. What volume of sulphuretted hydrogen measured at 0° and 760 mm. pressure would in theory be required to precipitate the copper in 2 grms. of copper sulphate dissolved in water ? (Ca=63, S=32, O=16, one litre of hydrogen weighs 0·089 grm.)—*Cambridge Junr. Locals.*

7. Give reasons for the application of the formula H_2S to sulphuretted hydrogen.—*London Univ.*

8. Why is ordinary sulphuric acid often called " oil of vitriol " ? What is fuming sulphuric acid, and how is it manufactured ?—*London Univ.*

9. What is the composition, mode of preparation, and uses of Nordhausen oil of vitriol ? How is sulphuric anhydride obtained from a mixture of sulphur dioxide and oxygen ?—*London Univ.*

10. How would you prepare pure hydrogen sulphide? How would you prove that hydrogen sulphide contains its own volume of hydrogen?—*London Univ.*

11. What product is formed when sulphur is burned in oxygen? How many volumes of oxygen are contained in 100 volumes of sulphur dioxide? How many grams of sulphur are contained in 100 grms. of sulphur dioxide?—*London Univ.*

12. Describe each of the principal allotropic modifications of sulphur, and explain how one modification can be converted into the other.—*London Univ.*

13. Describe the manufacture of sulphuric acid, and state how you would distinguish this acid from sulphurous acid.—*Univ. Tasmania.*

14. What different substances could you prepare from a supply of sulphuric acid, manganese dioxide, and sodium chloride?—*Univ. Tasmania.*

15. Some pieces of roll sulphur are placed in a retort and gradually heated up to about 500°. Describe what goes on. Give the chief chemical properties of sulphur. A sample of sulphuric acid has a density of 1·8, and contains 87 per cent. of sulphuric acid by weight. How many grams of sulphur are contained in 5 c.c. of it? (S = 32.)—*Adelaide Public Exam. Board.*

16. How is sulphur dioxide prepared from (*a*) sulphur, (*b*) sulphuric acid, (*c*) a sulphite? How is sulphur dioxide liquefied, and what are the properties of the liquid? Describe a method of proving that sulphur dioxide contains its own volume of oxygen.—*Adelaide Public Exam. Board.*

17. Describe the preparation of crystals of Epsom salts, green vitriol, Glauber's salts, and give the formulæ of each of these substances.—*Madras Univ.*

18. Give an account of the different forms in which sulphur may be obtained, their preparation, and properties. What are the uses of sulphur in the industries? Discuss the valency of sulphur.—*Bombay Univ.*

19. What volume of hydrogen sulphide will be evolved when 4·25 grms. of ferrous sulphide are treated with hydrochloric acid? What weight of sulphur dioxide will be obtained by burning the hydrogen sulphide formed?—*Bombay Univ.*

20. Explain fully the use of sulphuretted hydrogen as a chemical reagent.—*Calcutta Univ.*

21. Describe an experimental proof for the molecular formula of sulphur dioxide.—*Cape Univ.*

22. Give an account of the preparation of sulphuric acid. What precaution must be observed when mixing concentrated sulphuric acid and water? Describe as fully as you can the action of sulphuric acid on (*a*) zinc, and (*b*) copper.—*Cape Univ.*

23. What are the properties common to acids? In what respects does sulphurous acid differ from sulphuric acid?—*Science and Art Dept.*

24. Distinguish by chemical formula between a sulphide, a sulphite, and a sulphate. What is the action of sulphuric acid upon ferrous sulphide and on sodium sulphite?—*Science and Art Dept.*

25. How much nitric acid can be obtained from 1000 grms. of each of the following nitrates: ammonium nitrate, potassium nitrate, and sodium nitrate?—*Science and Art Dept.*

26. How is sulphuretted hydrogen gas prepared? What are the products of its complete combustion in air? How would you separate the element sulphur from the gas?—*Science and Art Dept.*

27. Give illustrations which show that oxygen and sulphur resemble each other in chemical characters.—*London Univ.*

28. Describe the modes of origin and properties of sulphur dioxide. How could you demonstrate the volumetric composition of the gas?—*London Univ.*

29. How is sulphuretted hydrogen prepared? Write equations expressing the changes which take place when the gas is (*a*) mixed with chlorine; (*b*) heated with tin; and (*c*) led through an aqueous solution of sulphurous acid.—*London Univ.*

30. What volume of atmospheric air (measured at 15° and 750 mm.) is required for the complete combustion of one gram of sulphur? (S=32.)—*London Univ.*

31. Describe and explain with equations the methods of preparing sulphur dioxide from (*a*) sulphur, (*b*) sulphuric acid, (*c*) a sulphite.—*London Univ.*

32. Some milk of sulphur is suspected to be adulterated with plaster of Paris (calcium sulphate). How would you test it, and by a simple process ascertain the amount of impurity?—*London Univ.*

33. What is gypsum? Describe the preparation of plaster of Paris. Explain the change which causes the setting of the plaster.—*Science and Art Dept.*

34. What volume of sulphur dioxide (measured at normal temperature and pressure) is theoretically obtainable by burning 1000 grms. of iron pyrites containing 48 per cent. of sulphur?—*Science and Art Dept.*

35. An unknown volume of hydrogen sulphide required 157 c.c. of chlorine for complete decomposition. What was the volume of the hydrogen chloride?—*Science and Art Dept.*

36. A solution of hydrogen sulphide is added to equivalent solutions of chlorine, bromine, and iodine, the halogen in each case being in excess. Describe the reactions which you would expect to happen.—*Inst. Chem.*

CHAPTER XVIII

Nitric Acid and the Nitrates

1. Sodium and Potassium Nitrates

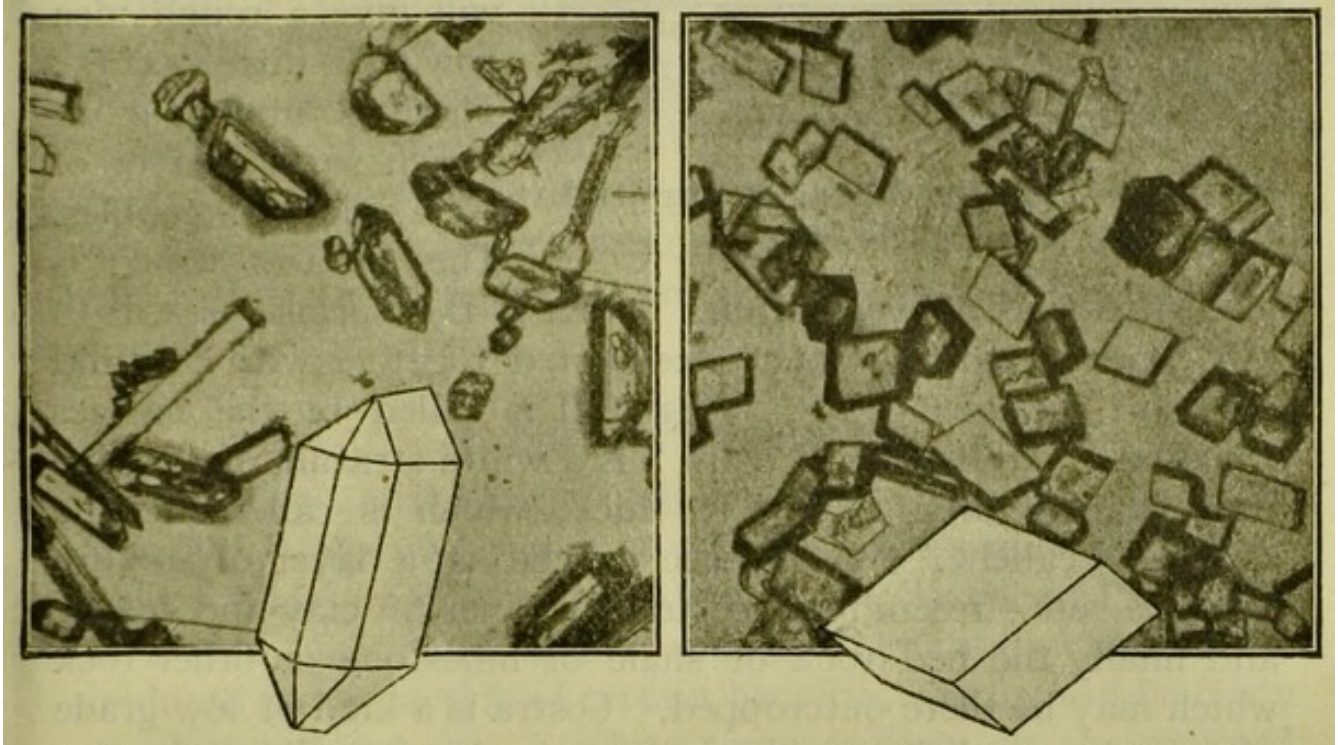
Potassium and sodium nitrates are two important salts. The former is also called "nitre" and "saltpetre." The word "nitre" is derived from Arabic and thence Greek words meaning "soda"; while "saltpetre" is a corruption of the Latin *sal petræ* —"salt of the rock." The salt designated by these two terms is very different from rock salt and from soda. Sodium nitrate is often called "soda nitre" or "Chili saltpetre," to distinguish it from "potash nitre" or "saltpetre" proper.

Crystallization of the two nitrates.—Potassium nitrate forms hexagonal prisms, and sodium nitrate rhombohedral crystals. The crystals are illustrated in Figs. 154, 155, where the salts have been crystallized on a slip of glass and photographed under the microscope. Ideal crystals are illustrated by the outline drawings. It is really interesting to watch the crystallization of a drop of warm, slightly supersaturated solution of potassium nitrate on a glass slip under the microscope. Crystallization starts at the edges. Here, rhombic crystalline plates (Fig. 154) are first formed; these are quickly followed by needle-like rhombohedra crystals, which are in reality isomorphous with the crystals of sodium nitrate (Fig. 155). As a matter of fact, both forms of crystals appear in the photograph (Fig. 155). Immediately the rhombohedral crystals touch the rhombic crystals, the latter lose their sharp outlines, and needle-like rhombohedra sprout forth on all sides. Hence, *potassium nitrate is dimorphous.* The rhombic crystals are stable above and unstable below 129°; and conversely, the rhombohedral crystals

are unstable above and stable below 129°. Hence, 129° is a transition temperature :

$$\text{Potas. nitrate}_{\text{rhombic}} \overset{129^\circ}{\rightleftharpoons} \text{Potas. nitrate}_{\text{rhombohedral}}$$

Both potassium and sodium nitrates are soluble in water ;



FIGS. 154 and 155.—Potassium Nitrate and Sodium Nitrate Crystals.

and, although sodium nitrate is more soluble than potassium nitrate at ordinary temperatures, the reverse is true at 100°. This is illustrated by the solubility curves, Fig. 156 (amount of salt per 100 grams of solvent) from 0° to 100°. Sodium nitrate is somewhat deliquescent, that is, it becomes damp on exposure to the air, and it cannot, therefore, be used for some purposes for which potassium nitrate is applicable. Potassium nitrate does not deliquesce under the same conditions. Sodium nitrate is much cheaper and more plentiful than the potassium salt.

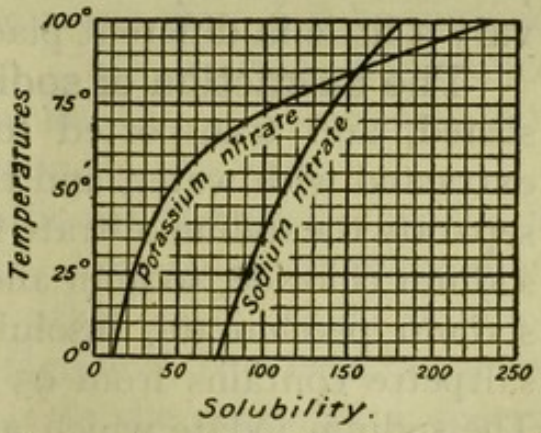


FIG. 156.—Solubility Curves of Sodium and Potassium Nitrates.

The occurrence of sodium nitrate.—Large quantities of sodium nitrate occur in the rainless zone on the West Coast of South America—Peru, Bolivia, Chili. The salt occurs in large flat basins between the ridges on the Tarapacca plateau. Fig. 157 represents a diagrammatic cross-section through a "nitre basin," which will give a rough idea how soda nitre occurs: There is first a 2- or 3-inch surface layer of grey sand and pebbles. The surface itself is almost devoid of vegetation. Below the surface is a 1 to 5-ft. layer of similar material cemented together with clay and salt and sodium nitrate. This stuff is called by the natives "costra." Below the "costra" is a white stratum of massive nitre-bearing rock, 1 to 5 ft. thick, which is called by the natives "caliche." Below the caliche is a layer of sodium chloride, etc., resembling costra; a layer of clay and loam; and finally the bed rock of shale or limestone or other rock which may be there outcropped. Costra is a kind of low-grade nitre rock or caliche running 5 to 12 per cent. sodium nitrate; the caliche runs 18 to 25 per cent., and in exceptional cases 50 or 60 per cent. sodium nitrate—the average runs 20 to 30 per cent. The deposits are close to the surface, and naturally vary a little in different places.

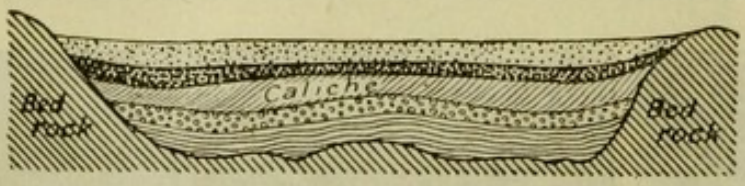


FIG. 157.—Geological Section of Nitre Bed (Diagrammatic).

The extraction of sodium nitrate.—The caliche is mined, sorted, and transported to the leaching works. It is then extracted with water, and the solution is recrystallized so as to separate the sodium nitrate from the accompanying impurities—sodium chloride, sodium and calcium sulphates, sodium iodate, sodium perchlorate, insoluble matter, etc. Commercial Chili saltpetre contains from 95 to 98 per cent. of sodium nitrate. The sodium iodate which accumulates in the mother liquid is used for the manufacture of iodine.

The conversion of sodium nitrate into potassium nitrate.—The Chili saltpetre is dissolved in about 1½ times its weight of boiling water, and a solution of sylvine—potassium

chloride, from the Stassfurt deposits—is poured into the sodium nitrate solution. Sodium chloride at once separates as a fine granular precipitate: $KCl+NaNO_3 \rightleftharpoons NaCl+KNO_3$. The crystals are removed, and the mother liquid is further concentrated by evaporation, and sodium chloride crystals are removed as they form ; when the concentration has progressed for enough, crude nitre crystallizes from the solution. This is purified by recrystallization from boiling water, which is stirred while cooling so that the nitre crystals may be small and granular—"nitre meal." The crystals are dried and packed in sacks for transport. The nitre still holds about half per cent. of sodium chloride. The by-product, sodium chloride, is preferred to ordinary salt for pickling meat, probably because of the quantity of nitre it still contains.

2. Nitre Plantations.

The origin of the nitre beds is not known. It is generally agreed that the nitrogen is of organic origin—animal or vegetable. When organic matter decays, say, in the soil of cattle yards and stables, ammonia and ammonium compounds are produced by the action of certain bacteria. If the soil be fairly dry, but not too dry, a white scum appears on the exposed surface. The scum is made up of small crystals of potassium nitrate ; and, after a time, if the soil be extracted with water, and strained, the liquid, on evaporation, furnishes yellowish-brown crystals of crude nitre. The crude nitre can be purified by re-solution and crystallization. The white efflorescence sometimes seen on the walls of stables, etc., is sometimes, not always, due to the formation of nitrates in this way.

The first stage in the decomposition of the organic matter is due to the action of certain bacteria. Ammonia and ammonium compounds are formed along with other gases which produce the characteristic odour of putrefaction. The next stage in the process of decomposition is due to the action of a special bacterium—**the nitrous ferment**—which converts the ammonia into nitrous acid: $2NH_3+3O_2=2H_2O+2HNO_2$. Another bacterium—**the nitric ferment**—transforms the nitrous into nitric acid: $2HNO_2+O_2=2HNO_3$. By the agency of these

three types of bacteria, the soil is constantly receiving fresh supplies of nitrates necessary for the growth of plants derived from the decomposition of the organic matter present in the soil.[1] The free acids are not really present in the soil, because the alkalies or alkaline earths present interact with the acids producing the nitrates and nitrites. It is owing to these reactions that water, contaminated by drainage from surface soil, contains nitrates.

In the hot dry countries of the East, India, Persia, Arabia, etc., particularly in the neighbourhood of villages where urine and other organic matters find their way into the soil owing to imperfect systems of " sewage disposal," the process of nitrification goes on rapidly. The soil is extracted with water every few years, and the nitrates, chiefly calcium and potassium nitrate, are extracted as indicated above. The product from the soil in the Valley of the Ganges (Bengal) is called *Bengal saltpetre*; it is principally potassium nitrate. If calcium nitrate be present, potassium carbonate is added to the aqueous extract from the soil, so that calcium carbonate may be precipitated, and potassium nitrate remain in solution: $Ca(NO_3)_2+K_2CO_3 = 2KNO_3+CaCO_3$. The nitre is then purified by recrystallization.

During the Napoleonic wars, France had great difficulty in procuring sufficient nitre for the manufacture of gunpowder. This led to the construction of nitre beds in various parts of the country. But when the French ports were thrown open, after these wars, the manufacture of nitre, in France, was abandoned, because it could be imported more cheaply from India. The process is still used in a few localities—*e.g.* Sweden. Soil rich in humus, dung, or animal offal is piled into heaps with the *débris* from buildings, or with lime, or wood ashes. The heaps are protected from rain by sheds. A system of gutters or pipes may also distribute the liquid excretions of animals over the top of the heap. The piled mass is called a nitre plantation. Before long a white film of nitre " grows " on the windward face of the pile. This is scraped off regularly, and leached as indicated

[1] Of course, as indicated shortly, nitrates occur in rain-water derived from the direct oxidation of nitrogen by electric discharges—lightning, etc.

above. If lime be present, the resulting calcium nitrate is converted into potassium nitrate by the addition of wood ashes —potassium carbonate.

3. The Nitrogen Cycle.

All living matter and the waste products of animals contain considerable quantities of combined nitrogen. It is a necessary constituent for the growth of living organisms. During the decay of organic matter through the agency of bacteria, part of the nitrogen finds its way back to the atmosphere, and part passes directly into the soil, to be absorbed by plants. Animals cannot assimilate free nitrogen, and they are accordingly dependent upon the plants for their supply. Nor can plants usually obtain their nitrogen direct from the atmosphere. Most plants get their nitrogen from the soil, where it is present in the form of nitrates, ammonium, or other complex compounds. The organic matter in the soil is attacked by bacteria of various kinds, and part is converted into nitrates and part into free nitrogen. A certain amount is brought back from the atmosphere during a rainstorm, where it has been oxidized into ammonium nitrate by electric discharges. But these supplies of available nitrogen do not suffice to maintain the fertility of cultivated soils. It is therefore necessary to make good the constant draining of the available nitrogen by the cultivated plants. This is done by allowing nitrogenous organic matter—manures—to decay on the soil, or to add a mixture—fertilizer—containing available nitrogen.

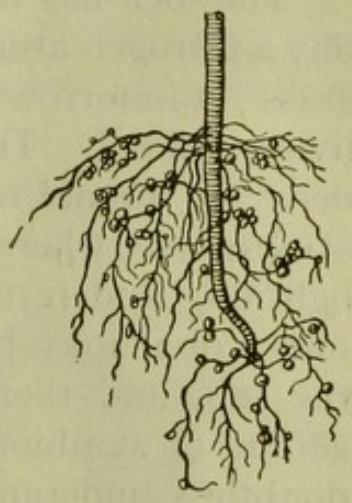
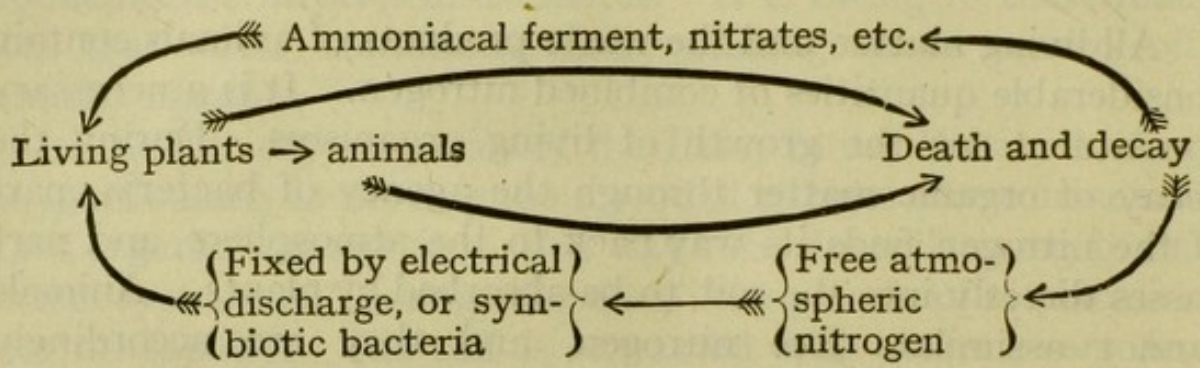


FIG. 157A.—Nodules on Root of Bean Plant.

Some plants, principally the leguminosæ—peas, beans, clover, lupins, etc.—appear to live in a kind of partnership with certain bacteria. The bacteria appear to live as guests in nodules on the rootlets of their host, and probably also in the neighbouring soil. The nodules on the rootlets of a *Phaseolus* (bean) are

illustrated in Fig. 157A. The symbiotic bacteria convert the nitrogen of the atmosphere into a form available as food for the plant on which they live.

The processes involved in the circulation of nitrogen in nature may be summarized in the scheme :



The idea has been expressed in a more romantic way. To-day a nitrogen atom may be throbbing in the cells of the meadow grass ; to-morrow it may be pulsating through the tissues of a living animal. The nitrogen atom afterwards may rise from decaying animal refuse and stream to the upper regions of the atmosphere, where it may be yoked with oxygen in a flash of lightning and return as plant food to the soil in a torrent of rain ; or it may be directly absorbed from the atmosphere by the soil, and there rendered available for plant food by the action of symbiotic bacteria. Thus each nitrogen atom has doubtless undergone a never-ceasing cycle of changes through countless æons of time.

§ 4. The Fixation of Atmospheric Nitrogen.

The fertility of cultivated fields and gardens, as we have just seen, is dependent upon the amount of combined nitrogen added as manure or fertilizer. Of course, cultivated plants require fertilizers containing other elements, particularly phosphorus and potassium—but nitrogen is the most expensive. The development of agriculture is largely dependent upon the cheap production of available nitrogen. The consumption of sodium nitrate is so great that it has been predicted that the nitre beds of Chili and Peru will be exhausted in less than a

century. Most of the sodium nitrate is employed as a fertilizer for wheat, etc. Since the comparatively small store available promises soon to be deplenished, it is obviously necessary to exploit other means of supplying farmers with the fertilizers they require. The nitre plantations do not give a large enough yield. F. Noble and L. Hiltner, in 1896, sold cultures of the "nitrogen-fixing" bacteria under the name *nitragen* for inoculating the soil. The results have not been altogether satisfactory.

There are at present three promising methods for the conversion, or "fixation" of atmospheric nitrogen in a form available for plant food. (1) By heating calcium carbide in dry nitrogen, whereby it is converted into calcium cyanamide (*q.v.*); (2) the direct synthesis of ammonia from its elements (*q.v.*); and (3) the direct oxidation of atmospheric nitrogen and absorption of the resulting oxides in water or alkaline solutions.

J. Priestley (1779) first noticed that an acid is formed when electric sparks are sent through the air, but he seems to have thought that the acidity was due to carbonic acid. H. Cavendish (1785) proved that the product of the action is nitric acid. In Cavendish's experiment, the air was confined over mercury in the bend of a ∧-shaped tube. The open ends of the tube dipped under mercury contained in separate glasses (Fig. 158). A series of sparks was sent from an electrical machine through the air confined in the tube. After the action, the gas turned blue litmus red, gave a turbidity with lime-water, was absorbed by potassium hydroxide, etc. In fine, the product of the action of potassium hydroxide upon the air after sparking, was nitre. W. Crookes (1892) showed that air burns to nitric and nitrous acids when heated in a powerful electric arc: and several very promising methods of burning nitrogen have been devised, in which air is passed through a chamber containing an electric arc

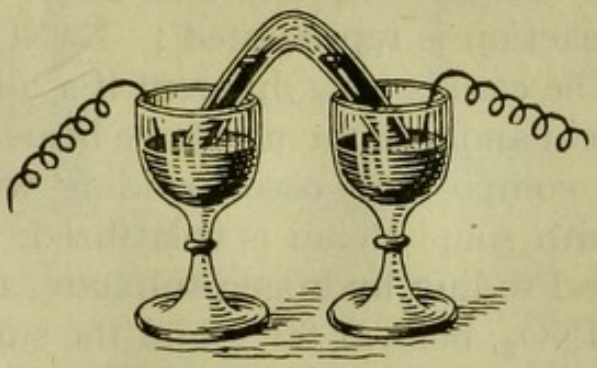


FIG. 158.—Cavendish's Experiment.

spread over as great a surface as possible by means of an electro-magnet. The products of the oxidation are then passed through a series of absorption towers, where they meet water and milk of lime. The absorbed nitrogen oxides form calcium nitrate ; the solution is evaporated, and sold as a fertilizer. This *Norwegian saltpetre* is almost anhydrous calcium nitrate. It contains nearly 13 per cent. of available nitrogen. In illustration of the growth of this industry, 115 tons were produced in Norway in 1905, and 9422 tons, valued at £72,590, were produced in 1909.

§ 5. Nitric Acid—Preparation and Properties.

When potassium or sodium nitrate is mixed with dilute sulphuric acid, no obtrusive sign of chemical action occurs, although it can be proved that a reversible change has taken place so that the sodium is distributed between the sulphuric and nitric acids. The same final mixture is obtained whether equivalent amounts of sodium nitrate and dilute sulphuric acid, or sodium sulphate and dilute nitric acid, are employed. The reaction is represented : $NaNO_3+H_2SO_4 \rightleftharpoons NaHSO_4+HNO_3$. The case is very different if a mixture of concentrated sulphuric acid and sodium nitrate be heated to about 130°, nitric acid with a composition corresponding with a compound, HNO_3, along with some steam is volatilized. The two salts, sodium nitrate and sodiun hydrogen sulphate, are not volatile ; the nitric acid, HNO_3, boils at 86° ; and the sulphuric acid at 330°. Hence on warming to about 100°, the nitric acid is volatilized and the state of equilibrium of the solution is disturbed ; in consequence the sodium nitrate is all decomposed. If the temperature be higher, normal sodium sulphate is formed, and less sulphuric acid is needed for a given yield of nitric acid: $2NaNO_3+H_2SO_4 = Na_2SO_4+2HNO_3$. But appreciable quantities of the nitric acid are decomposed at the higher temperature.

Preparation of nitric acid.—The acid can be prepared in the laboratory by means of the apparatus illustrated in Fig. 159. This explains itself. All rubber and cork stoppers and connections must be avoided, because the acid rapidly attacks organic

matter. The retort is charged with the sodium nitrate and sulphuric acid, and heated. Brownish-red fumes appear and the distillate is more or less coloured brown because of the solution of the red-coloured gas in the distillate. The brownish-red gas is a product of the decomposition of the nitric acid by heat. On a manufacturing scale, the sodium nitrate and sulphuric acid are heated in cast-iron retorts; the vapour is condensed in earthenware pipes cooled by water, and collected in earthenware jars. The last jar is connected with a tower filled with coke down which a stream of water trickles. The object is to recover the nitrogen peroxide produced by the decomposition of the nitric acid. The retort has an exit pipe from which the sodium disulphate can be run when the action is over. To reduce the amount of nitrogen oxides formed during the decomposition of the nitric acid by heat, the stills are often worked under a reduced pressure, so that the acid may come off at as low a temperature as possible. The acid is purified by redistillation, rejecting the first portion (fraction) of the distillate which comes over. The best commercial acid runs about 65 per cent. HNO_3.

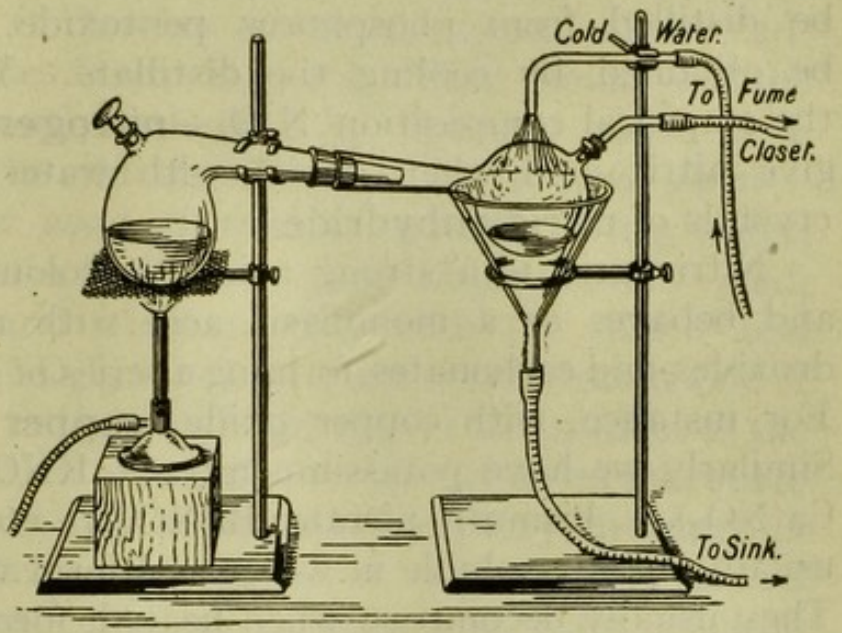


FIG. 159.—The Preparation of Nitric Acid.

Uses.—Nitric acid is one of the common acids. It is used as a solvent for metals, for etching designs upon copper; for the manufacture of silver nitrate used in photography; barium and strontium nitrates used in pyrotechny; lead nitrate used in calico printing; etc. It is also used in the manufacture of dyestuffs, explosives, sulphuric acid, etc., and in metallurgy, etc.

Properties.—Nitric acid is a colourless mobile liquid which fumes strongly in air. It has a peculiar smell. The pure acid is hygroscopic and rapidly absorbs moisture from the air. It mixes in all proportions with water. The pure anhydrous acid is made by working at a low temperature, then mixing the product with concentrated sulphuric acid and distilling in a current of an inert gas. When heated alone a certain fraction of the acid is decomposed, furnishing oxygen and red fumes of nitrogen peroxide, NO_2. The reaction is symbolized: $4HNO_3 = 4NO_2 + 2H_2O + O_2$. A similar decomposition occurs when the acid is exposed to light. The dissolved nitrogen peroxide gives the acid a yellow colour. If the acid be distilled from phosphorus pentoxide, white crystals can be obtained by cooling the distillate. These crystals have the empirical composition N_2O_5—**nitrogen pentoxide.** They give nitric acid when mixed with water, and are therefore crystals of **nitric anhydride.**

Nitric acid is a strong acid; it colours blue litmus red; and behaves as a monobasic acid with metallic oxides, hydroxides, and carbonates, forming a series of salts called **nitrates.** For instance, with copper oxide, **copper nitrate** is formed. Similarly we have potassium nitrate, KNO_3; calcium nitrate, $Ca(NO_3)_2$; bismuth nitrate, $Bi(NO_3)_3$; etc. The nitrates are usually readily soluble in water and form well-defined crystals. They usually decompose when heated, forming an oxide of the metal and a mixture of nitrogen oxides.

Action on organic compounds.—Nitric acid is extremely corrosive, and when brought in contact with the skin causes painful sores. The dilute acid stains the skin yellow or brown, probably owing to the formation of xanthoproteic acid. If strong nitric acid be poured on sawdust, the mass often bursts into flame. If a dish of fuming nitric acid be placed in a basin in the bottom of a glass cylinder, and a little turpentine be added from a pipette, the turpentine will burst into flame. Glowing charcoal continues to burn when plunged into the acid. With organic compounds, one or more hydrogen atoms are replaced by an equivalent NO_2 radicle, and water is formed. For instance, cellulose or cotton becomes *nitrocellulose* or

gun-cotton; glycerol becomes *nitroglycerol*, which is the active agent in *dynamite*; and phenol becomes *picric acid*, which is the active agent in the explosive *melinite*.

Oxidizing action of nitric acid.—In consequence of the great proportion of oxygen in nitric acid, and in consequence of the ease with which it is decomposed, we should expect nitric acid to be a strong oxidizing agent. It is so. Sulphur is oxidized to sulphuric acid; *e.g.* $S+2HNO_3=H_2SO_4+2NO$; iodine is oxidized to iodic acid, HIO_3; ferrous to ferric salts; etc. Many metallic sulphides—iron, lead, etc., are oxidized by nitric acid to sulphates.

Action on the metals.—The purest acid does not attack carbonates, nor does it dissolve mercury, copper, silver, cadmium, but sodium takes fire in the acid. Most metals and the carbonates are vigorously attacked by ordinary nitric acid, and for this reason the old alchemists called it *aqua fortis*—the strong water; or *aqua dissolutiva*—the dissolving water. The acid does not attack the so-called noble metals—gold, platinum, rhodium, and iridium. Tin with the dilute acid gives **tin nitrate,** $Sn(NO_3)_2$; but with the concentrated acid it forms **stannic oxide,** SnO_2, which appears as the product of the action. With mercury, an excess of the acid produces **mercuric nitrate**, $Hg(NO_3)_2$; and with an excess of mercury, **mercurous nitrate**, $HgNO_3$. The action of nitric acid on the metals generally is somewhat complex, because the main reaction is complicated by side reactions. These again depend not only upon the particular metal under consideration, but also on the concentration of the acid, the temperature, and the concentration of the products of the reaction accumulating in the solution. For instance, when dilute nitric acid acts upon copper, copper nitrate and a colourless gas, nitric oxide, symbolized NO, are formed: $3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$; but several other oxides of nitrogen, and even nitrogen itself, have been found in appreciable quantities among the products of the reaction of copper with acids of different concentration, etc. Colourless nitric oxide is peculiar in forming a red-coloured gas in contact with the air, so that when nitric acid acts upon copper, red fumes seem to be evolved.

Aqua regia.—A mixture of hydrochloric and nitric acids—say, in the proportions 3 or 4 volumes of the former per one volume of the latter—will dissolve the metals gold and platinum. Hence the alchemists' term for this mixture, *aqua regia*—the kingly water—because it dissolves the very king of metals, gold. The mixture becomes coloured at about 10°, and it evolves gas at about 30°; the action is quite vigorous about 90°, and at 109° a mixture of nitric and hydrochloric acids distils over. The action of *aqua regia* on gold is supposed to be due to the oxidation of the hydrochloric acid by the nitric acid, whereby chlorine is formed, and this latter agent attacks the gold or platinum. Goldschmidt's equation for the reaction is: $HNO_3+3HCl=2H_2O+NOCl+Cl_2$, corresponding with the fact that some nitrosyl chloride—NOCl—is formed at the same time. The greater oxidizing properties of *aqua regia* over nitric acid are generally attributed to the presence of the free chlorine. The action of *aqua regia* on metallic sulphides furnishes sulphur and a chloride of the metal.

§ 6. Nitrous Acid and the Nitrites.

Sodium or potassium nitrate decomposes when heated, forming the corresponding nitrite, but, when specially preparing these nitrites, in practice, it is best to mix the nitrate with a mild reducing agent like metallic lead or iron filings. Thus by heating a mixture of lead filings with an equal weight of sodium nitrate in a crucible: $Pb+NaNO_3=PbO+NaNO_2$. Digest the cold mass with water, filter, and evaporate the solution to a small bulk, crystals of sodium nitrite will separate on cooling. Most of the nitrites are very soluble in water, but silver nitrite is not very soluble in cold water. It is precipitated in crystalline needles when a solution of silver nitrate is added to a solution of sodium nitrite.

Nitrous acid can be made by adding hydrochloric or sulphuric acid to a solution of the nitrite: $NaNO_2+HCl=KCl+HNO_2$. The aqueous solution of the acid gradually decomposes at ordinary temperatures: $3HNO_2=HNO_3+2NO+H_2O$. The decomposition is much quicker when the solution is warmed.

Nitrous acid is only known in dilute solutions. The acid acts both as an oxidizing agent and as a reducing agent. Thus, it *oxidizes* hydriodic acid or potassium iodide, liberating iodine. A solution of potassium permanganate, however, is rapidly decolorized by a nitrite in the presence of sulphuric acid with the formation of manganous sulphate. The permanganate is thus *reduced* by the nitrite solution.

§ 7. Identification of Nitrites and Nitrates.

(1) Dilute sulphuric acid decomposes all the nitrites in the cold. A gas, nitric oxide, NO, is formed which gives brownish-red fumes in the air: $3HNO_2 = HNO_3 + 2NO + H_2O$. Nitrates do not give the brown fumes, unless they be heated with concentrated sulphuric acid.

(2) Potassium iodide is not decomposed by pure dilute nitric acid, whereas a solution of a nitrite, when acidified with dilute sulphuric or acetic acid, becomes yellow or brown, owing to the separation of iodine. If a little starch paste be present, the solution will be coloured blue. Many other oxidizing agents give the same coloration—ozone, hydrogen peroxide, chlorine, and ferric salts. Nitrates give the same coloration if a little zinc be added to the acidified solution, owing to the reduction of the nitrates to nitrites.

(3) A sensitive test for the nitrates is based upon the oxidation of ferrous salts by nitric acid gas: (nitric oxide) is produced, and this gives a dark brown compound with the excess of ferrous salt. To apply the test, dissolve the nitrate in as little water as possible, pour in a cold saturated solution of ferrous sulphate slightly acidified with sulphuric acid. Shake concentrated sulphuric acid down the side of the tube. If nitric acid be present, the zone of contact will be coloured dark brown. With nitrites, the concentrated sulphuric acid need not be added.

(4) When a hot concentrated solution of sodium hyposulphite is added to a solution of a nitrate, no action occurs; with a solution of a nitrite, nitrogen gas is evolved.

Questions.

1. Explain the meanings of the syllables *-ous* and *-ic* in such names as nitr*ous* acid, nitr*ic* acid, sulphur*ous* acid, and sulphur*ic* acid.—*Science and Art Dept.*

2. Express by equations the reactions which occur when sulphuric acid is heated together with common salt, with sal-ammoniac, with nitre, and with copper respectively.—*London Univ.*

3. How is nitric acid usually prepared? What are its properties, and by what reactions can it be distinguished from hydrochloric acid and sulphuric acid?—*Science and Art Dept.*

4. Calculate the percentage composition of nitric acid. (N=14, O=16, H=1.)—*London Univ.*

5. How would you proceed to make a specimen of nitric acid? What do you understand by the statement that nitric acid is an oxidizing agent? Give an instance of its action as such.—*Oxford Junr. Locals.*

6. Explain by means of symbols the decomposition which takes place when sulphuric acid is mixed with saltpetre. What happens when nitric acid is added to a solution of potassium hydrate? What is the difference between a nitrate and a nitrite?—*London Univ.*

7. Describe any experiments you have seen in illustration of the oxidizing action of nitric acid.—*London Univ.*

8. What would be formed if nitric acid were (*a*) mixed with a solution of caustic soda and the liquid evaporated to dryness, (*b*) diluted with water and poured on to copper turnings, (*c*) mixed with fuming hydrochloric acid and warmed?—*London Univ.*

9. How would you prepare a specimen of nitric acid in the laboratory, and how would you prove it to be nitric acid? Give a short description of how nitrates found in the soil are formed.—*Oxford Junr. Locals.*

10. Given Chili saltpetre and oil of vitriol, how would you prepare pure nitric acid? Carefully discuss the properties of nitric acid, and contrast its behaviour, when distilled, with that of sulphuric acid. How is nitric anhydride obtained?—*London Univ.*

11. What is the difference between ordinary concentrated nitric acid and real or absolute nitric acid, and how may the latter be obtained from the former? Why does nitric acid become yellow when exposed to light?—*London Univ.*

12. Give some account of the various methods of obtaining nitre from the waste nitrogenous matters and from sodium nitrate.—*London Univ.*

13. You are requested to prepare pure saltpetre from a mixture of saltpetre and common salt. Describe how you would do so.—*London Univ.*

14. How would you prepare nitric acid from air ? Having prepared the nitric acid, state how you would obtain from it oxygen gas.—*Adelaide Public Exam. Board.*

15. How is sulphur dioxide most easily obtained pure ? Enumerate its properties and say what its action is upon (*a*) caustic soda solution, (*b*) chlorine water, (*c*) sulphuretted hydrogen. Give equation.—*Staffs. Major County School.*

16. Write formulæ for nitrous and nitric acids, sulphurous and sulphuric acids, carbon monoxide and carbon dioxide. What do the terminations *-ous* and *-ic*, and the prefixes *mon-* and *di-* in such names signify ?—*Science and Art Dept.*

CHAPTER XIX

The Alkaline Earths

§ 1. Calcium Carbonate.

Several different minerals occur in nature which have been called different names, although analysis shows that they are all more or less impure forms of one chemical substance—calcium carbonate. These different forms of calcium carbonate may be classed under three heads :

(1) Chalk and limestone usually occur in large masses, sometimes extending over large tracts of country. Chalk is a soft variety of limestone. Both forms of calcium carbonate are more or less impure, for they contain more or less magnesium carbonate, clay, and silica. Marl is a mixture of limestone with a relatively large proportion of clay. Egg-shells, sea-shells, pearls, corals, contain a large percentage of calcium carbonate.

Rub a little soft chalk to powder by the aid of a hard brush; stir up the powder with water; and when the mixture has stood for a few minutes, pour off the white "milky"-looking liquid, and examine the residue under a low power microscope. It will be at once apparent that chalk consists largely of the shells of minute organisms. The same thing can be observed by cutting a thin slice of some of the harder varieties of chalk and grinding the slice so thin that it is transparent enough to see under the microscope, *e.g.* Fig. 160. It is inferred that these shells are the remains of organisms which once lived in the sea, because similar-looking shells, Fig. 161, are found in the mud dredged from the bottoms of oceans to-day.

In the manufacture of whiting, chalk is ground, stirred up with water, and the mixture allowed to stand for a definite time.

The matter still remaining in suspension is decanted off, and dried.

(2) Another form of calcium carbonate occurs in more or less well-defined crystals modelled after a rhombohedron, but exhibiting a great variety of derived shapes, which have received special names—"dog's tooth spar," "nail-headed spar," etc. When transparent and colourless, it is called *Iceland spar*; and

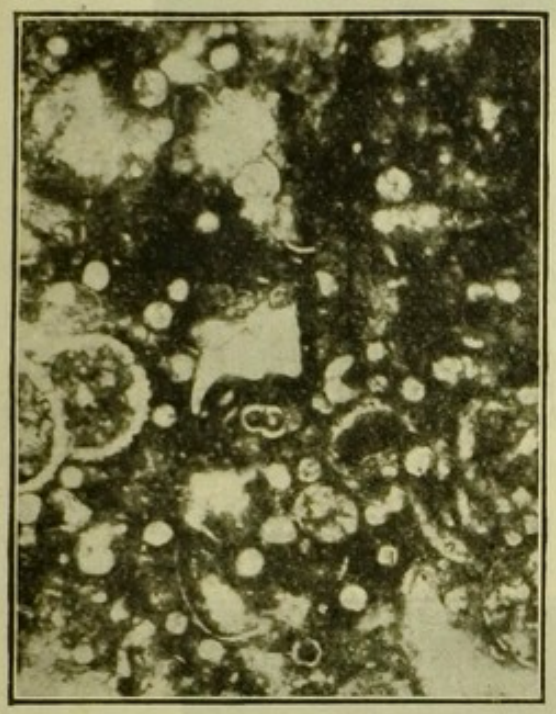


FIG. 160.—Thin Slice of Chalk from Erith (Kent): Magnified.

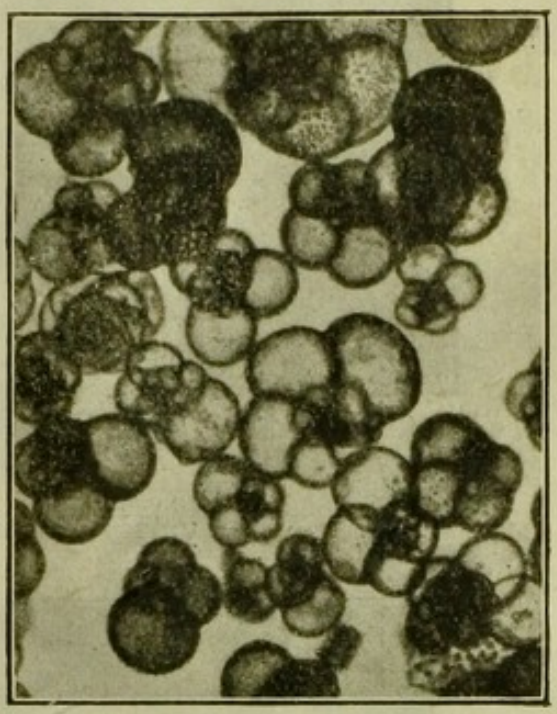


FIG. 161.—Shells in Mud dredged from the Bottom of the Atlantic Ocean (*Challenger* Expedition).

if more or less opaque and clouded, *calcite* or calcspar. Fig. 162 shows some crystals of calcite with an outline of an ideally perfect crystal below. A compact fibrous variety with a satin-like lustre is called *satin spar*. *Marble* is made up of minute crystals of calcite. *Onyx* is a variety which is streaked and coloured by associated impurities.

(3) One variety generally occurs in needle-like crystals, and is named *aragonite* after Aragon in Spain. If calcium carbonate be prepared in solutions at temperatures exceeding 30°, crystals corresponding with aragonite are formed, and if at temperatures below 30°, crystals of calcite are formed. Fig. 163 shows some crystals of aragonite with an outline of an ideally perfect crystal

below. Aragonite has a specific gravity about 2·9, calcite 2·72 ; the former is less rapidly attacked by acids than the latter.

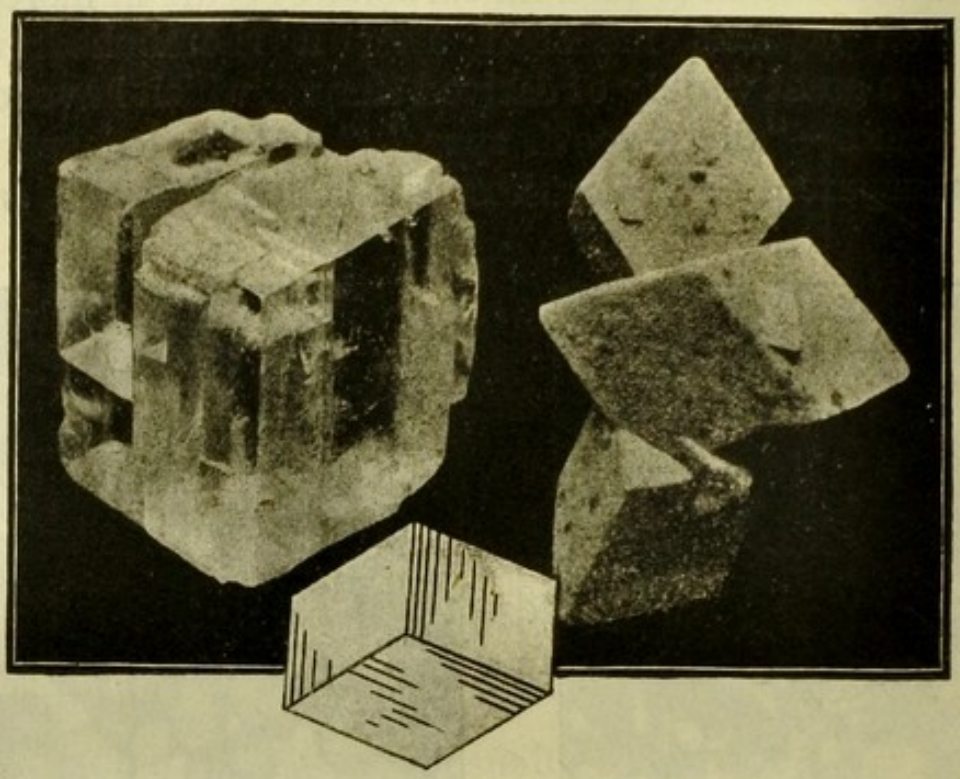


FIG. 162.—Crystals of Calcite (from Fontainebleau).

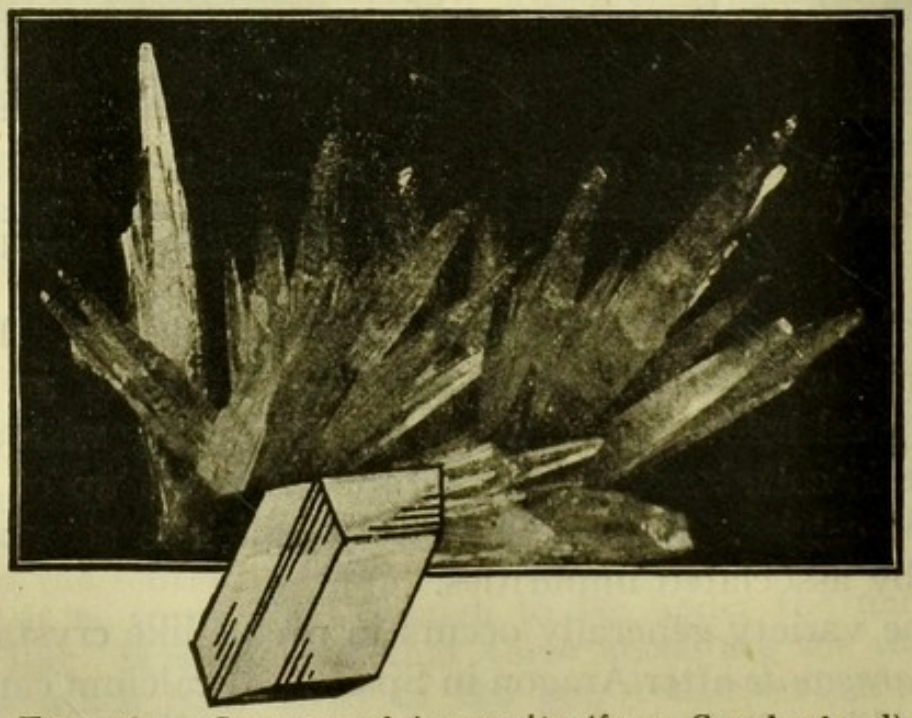


FIG. 163.—Crystals of Aragonite (from Cumberland).

§ 2. Limestone.

This substance has already been discussed in connection with our study of chalk.

Uses of lime.—Lime is used in preparing mortars and cements, as a flux in metallurgy, in the manufacture of glass, bleaching powder, calcium carbide, in purifying illuminating gas, in removing hair from hides before tanning, in drying gases, as a disinfectant, etc. Peaty soils containing too much organic acid are "sour." Lime, or chalk, or meal ploughed in with the soil helps to remove the sourness. The "lime-light" is produced by heating a pencil of lime in an oxy-hydrogen or oxy-coal gas flame. At this high temperature, the hot lime glows with a vivid incandescence.

Manufacture of quicklime.—Limestone is frequently "burned" in a cavity cut in a hill-side, as illustrated in Fig. 164, or in a kiln made from bricks or blocks of limestone. The kiln is loosely filled with limestone, or alternate layers of limestone and fuel. A fire is built at the base of the stack, and when the burning is complete, the fire is allowed to die out, and the lime is removed. In the more recent "shaft kilns," producer gas is led into the shaft near the base, and the hot products of combustion pass up the stack and decompose the limestone. The kiln is charged at the top, and the burned lime is raked out through openings at the bottom of the stack. The process is continuous—lime is charged in at the top as fast as it is removed at the bottom.

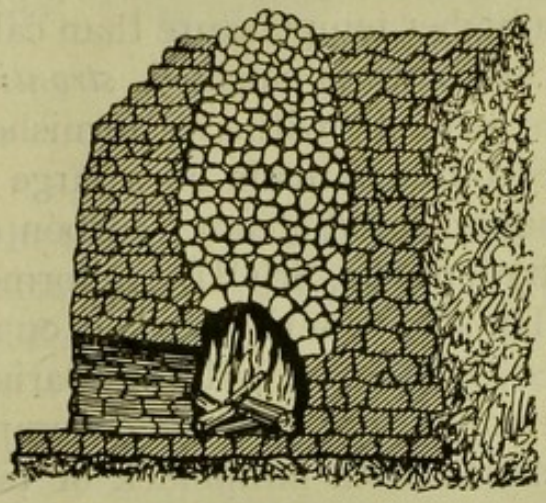


FIG. 164.—Primitive Limekiln (Diagrammatic Section).

Hydraulic cements.—Calcareous marls or mixtures of limestone, clay, and sand in the right proportions are heated until the mixture begins to sinter. The "clinker" so obtained is ground to powder, and the product called "cement," because if it be mixed with water it sets to a hard stone-like mass, even if exposed to the continued action of water. The cement is consequently used for work under water—bridge piers, etc.—under conditions where mortar would disintegrate and soften.

Several varieties are on the market under various names—Portland cement, hydraulic cement, etc. The ground clinker appears to consist mainly of a solid solution of lime, silica, and alumina. The setting of the wetted cement appears to be the joint effect of several different actions not yet clearly understood.

§ 3. Strontium and Barium Oxides and Hydroxides.

Oxides.—There are two carbonates found in nature, viz. the mineral *strontianite*, $SrCO_3$; and barium carbonate in the mineral *witherite*, $BaCO_3$, which closely resemble calcium carbonate in many of their properties. Carbonates decompose at a higher temperature than calcium carbonate. When strontium carbonate is calcined, *strontia*, that is, **strontium oxide**, SrO, is formed; witherite furnishes *baryta*, *i.e.* **barium oxide**, BaO. Strontia is made on a large scale by heating the carbonate in superheated steam; carbon dioxide is evolved, and **strontium hydroxide**, $Sr(OH)_2$, is formed: $SrCO_3+H_2O=Sr(OH)_2+CO_2$. The strontium hydroxide, on ignition, furnishes strontium oxide: $Sr(OH)_2=SrO+H_2O$. Barium carbonate requires so high a temperature for its decomposition that the raw material is mixed with lampblack or tar before calcination. The carbon burns off and the carbonate, at the same time, is decomposed at a much lower temperature: $BaCO_3+C=BaO+2CO$.

Hydroxides.—Like calcium oxide, both strontia and baryta slake in contact with water, with the evolution of much heat. In the case of baryta, the heat is so great that if but little water be used, the mass may become visibly red hot. Barium hydroxide is usually made by heating a mixture of *barytes*—barium sulphate, $BaSO_4$—with powdered coke, or coal. Crude barium sulphide is formed owing to the reduction of the sulphate: $BaSO_4+4C=4CO+BaS$. The barium sulphide is then heated in a stream of carbon dioxide, and is thus converted into barium carbonate: $BaS+CO_2+H_2O=BaCO_3+H_2S$. Barium carbonate is converted into the hydroxide by heating it in superheated steam as indicated above. Strontium hydroxide is formed in a similar manner from the mineral *celestine*—strontium

sulphate, $SrSO_4$. Strontium hydroxide is used in the manufacture of sugar. Strontium hydroxide is more soluble in water than calcium hydroxide, and barium hydroxide is more soluble than strontium hydroxide.

§ 4. Hydrogen Peroxide.

Barium peroxide.—When barium oxide is heated to about 500° in a stream of dry air, it is rapidly oxidized to another higher oxide called barium peroxide, and the latter is reconverted back into barium oxide when heated to 800°. Analysis of the two oxides furnishes—

	Barium monoxide.	Barium peroxide.	
Barium	89·1	81·1	per cent.
Oxygen	10·4	18·9	per cent.
Corresponding formula	BaO	BaO_2	

This agrees with the prediction from the atomic theory made on page 111: "when one element unites with another element in more than one proportion, these different proportions will bear a simple relation to one another by weight": these relations are respectively, Barium : Oxygen = 1 : 1, and 1 : 2.

Brin's process for preparing oxygen on a large scale was based upon the reactions just indicated, but it could not compete successfully against the liquid air process.

The preparation of hydrogen peroxide.—Barium peroxide suspended in a little water is gradually added to a mixture of equal volumes of water and sulphuric acid (cooled by a freezing mixture of ice and salt) until the solution is just barely acid. If too much barium peroxide has been added, a little more sulphuric acid is needed. Keep the solution in a freezing mixture for about a day. Filter off the insoluble barium sulphate, and evaporate the liquid on a water bath, at about 70°, in a smooth platinum or porcelain basin until signs of effervescence appear. This will occur when the solution contains about 45 per cent. of hydrogen peroxide. Cool the solution quickly. Concentrated solutions soon decompose if they are not kept cold. This solution

can also be further concentrated by evaporation over concentrated sulphuric acid *in vacuô*. This operation—**evaporation under reduced pressure**—is conducted as follows: The dish containing the mixture rests on the perforated shelf of a desiccator, Fig. 165. The desiccator has a layer of concentrated sulphuric acid below the perforated shelf. The lid of the desiccator, well greased, is placed in position. The desiccator is then exhausted by connecting the stoppered tube with the air pump. Any water vapour given off by the solution in the dish is gradually absorbed by the concentrated acid.

The properties of hydrogen peroxide.—The colourless syrupy liquid so obtained has peculiar properties, quite different from water. The most characteristic property is the ease with which the liquid gives off oxygen gas, and in this respect it resembles ozone. It liberates iodine from potassium iodide, it bleaches indigo and litmus, but it does not affect mercury like ozone. It reduces silver oxide, Ag_2O, as represented by the equation: $Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$. Finely divided solids—charcoal, platinum, silver, gold—facilitate the decomposition of the peroxide: $2H_2O_2 = 2H_2O + O_2$—sometimes with explosive violence. Dark brown lead sulphide, PbS, is bleached, as in the case of ozone, owing to the formation of white lead sulphate, $PbSO_4$. With baryta water, hydrogen peroxide forms barium peroxide, BaO_2. With titanium salts, hydrogen peroxide gives an orange-yellow coloration; and with potassium chromates in dilute sulphuric acid solutions, a perchromic acid is formed. When the solution is shaken up with ether, the supernatent ethereal liquid is coloured blue by the dissolved perchromic acid. Dilute solutions of the peroxide are fairly stable—particularly if acidified.

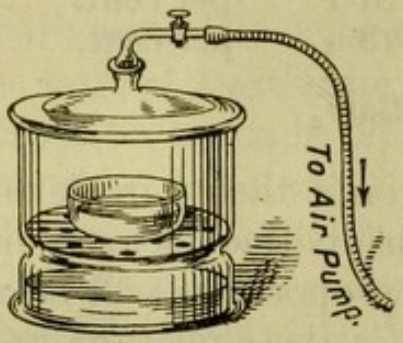


FIG. 165.—Evaporation under Reduced Pressure.

Distillation under reduced pressure.—A solution of hydrogen peroxide decomposes rapidly when heated to 100°—even if the solution be dilute. R. Wolffenstein (1902) discovered

that the hydrogen peroxide can be heated under reduced pressure; it boils just over 80° without undue decomposition. The apparatus is indicated in Fig. 166. The flask *A* contains the solution to be distilled, and this is heated by immersion in an oil bath, *F*. The temperature inside the flask is indicated by the thermometer *T*. The distilling flask *A* has a side neck fitting tightly into the neck of a similar flask, *B*, as shown in the diagram. The flask *B* serves as a condenser and it is cooled by a stream of water. The water is collected in a funnel placed below the condenser and run to the sink. A side neck of the receiver is connected with a vacuum pump.

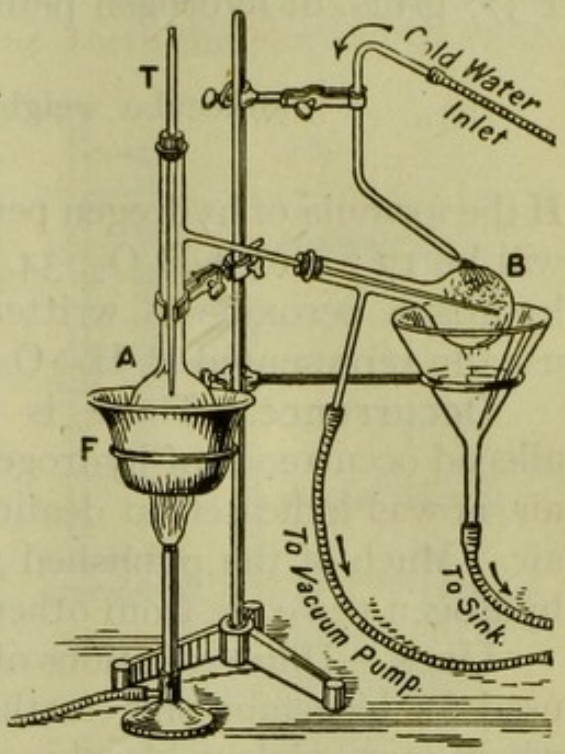


FIG. 166.—Distillation of Hydrogen Peroxide under Reduced Pressure.

The constitution of hydrogen peroxide.—Like water, pure hydrogen peroxide contains nothing but hydrogen and oxygen. Analyses of the two furnish—

	Water.	Hydrogen peroxide.	
Hydrogen	11·2	5·9	per cent.
Oxygen	88·8	94·1	per cent.
Corresponding formula	H_2O	HO	

This result also agrees with the prediction on page 111, which is called the law of multiple proportions. While studying the effect of different substances on the freezing-point of solutions, F. Raoult discovered that the freezing-point of the solvent is depressed to an extent proportional to the weight of the substance dissolved in a given weight of solvent, and also to an extent inversely proportional to the molecular weight of the dissolved substance. For water—

$$\text{Molecular weight} = \frac{18{\cdot}5 \times \text{grms. of substance per 100 c.c. of water}}{\text{Depression of freezing-point}}$$

A solution of 0·2735 grm. of hydrogen peroxide in 19·86 grms. of water lowered the freezing-point of water from 0° to —0·746°. These numbers mean that 100 c.c. of water would contain 1·377 grms. of hydrogen peroxide, and accordingly

$$\text{Molecular weight} = \frac{18{\cdot}5 \times 1{\cdot}377}{0{\cdot}746} = 34{\cdot}2$$

If the formula of hydrogen peroxide be HO, the molecular weight will be 17 ; and if H_2O_2, 34. Hence, the molecular formula of hydrogen peroxide is written H_2O_2. The graphic formula is usually represented as H—O—O—H.

Occurrence.—There is a similar uncertainty about the alleged occurrence of hydrogen peroxide in rain, snow, dew, and air as was indicated in dealing with the occurrence of ozone in air. Much of the published work does not clearly discriminate hydrogen peroxide from other oxidizing substances.

Uses.—Dilute solutions of hydrogen peroxide are accordingly used for bleaching silk, feathers, straw, hair, ivory, teeth, etc., where more violent bleaching agents would injure the material. Instead of hydrogen peroxide an acidified solution of sodium peroxide is sometimes employed. The actions are similar. Since the products of the decomposition of hydrogen peroxide—water and oxygen—are harmless, it is also used medicinally as an antiseptic. Hydrogen peroxide is also used in analytical work as an oxidizing agent.

§ 5. Metallic Calcium.

In 1808, H. Davy passed a current of electricity through fused calcium chloride, and found some small globules of a metallic-looking substance collected about the cathode. This he called calcium. Similar results are obtained with barium and strontium chlorides. For nearly a century the three metals, calcium, barium, and strontium, were little more than chemical curiosities. The metal calcium is now made on a large scale by the electrolysis of fused calcium chloride, $CaCl_2$.

In one process the anode is a graphite crucible, and the cathode a rod of iron which dips in the fused chloride, Fig. 167. When

the current passes, metallic calcium collects at the lower end of the cathode. Calcium chloride fuses at a lower temperature than metallic calcium, and the temperature is so regulated that the calcium solidifies at the base of the cathode. The resistance of the current keeps the calcium chloride fluid, and a current of cold water at the base of the crucible keeps the electrolyte solid. An irregular rod of metallic calcium is made by slowly raising the cathode by means of the screw shown on the left of the diagram. The end of the calcium rod, dipping in the fused chloride, then forms the lower end of the cathode. The rod of metallic calcium dipping in the bath is also cooled by an annular tube through which cold water flows—not shown in the diagram.

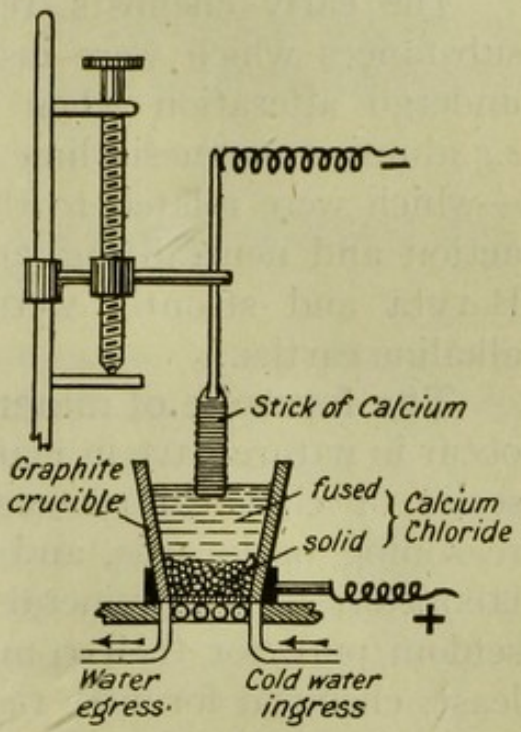


FIG. 167.—The Electrolytic Process for Calcium (Diagrammatic).

Properties. — Calcium is a silver white lustrous metal. It tarnishes slowly in air, and when heated in an atmosphere of hydrogen, it forms calcium hydride, CaH_2; and in an atmosphere of nitrogen, calcium nitride, Ca_3N_2; in air, calcium oxide, CaO; with chlorine, calcium chloride, $CaCl_2$; with phosphorus vapour, calcium phosphide, Ca_3P_2; with carbon, calcium carbide, CaC_2; with sulphur, calcium sulphide, etc. The reaction of these substances with water is interesting. The hydride gives hydrogen ($CaH_2+2H_2O=Ca(OH)_2+2H_2$); the nitride, ammonia; the phosphide, hydrogen phosphide; the carbide, acetylene; etc.

Occurrence of barium, strontium, and calcium in nature. —The free elements do not occur in nature. Calcium compounds are rather abundant. The occurrence of calcium as carbonate has already been discussed. Calcium also occurs as sulphate, in the mineral *gypsum or selenite*, $CaSO_4.2H_2O$; as calcium fluoride, CaF_2, in *fluorspar;* as calcium phosphate, in *phosphorite;* etc. The carbonate and sulphur are common in spring and river water. Calcium compounds occur in all animal and

vegetable organisms. Bones contain a large proportion of combined calcium. The chief natural compounds of barium and strontium have already been indicated—*strontianite*, $SrCO_3$; *celestine*, $SrSO_4$; *heavy spar* or *barytes*, $BaSO_4$; and *witherite* $BaCO_3$.

The early chemists reserved the term **earth** for those substances which were insoluble in water and which did not undergo alteration when calcined at a high temperature—*e.g.* alumina, magnesia, lime, etc. The earths—lime and magnesia—which were related to the alkalies by giving an alkaline reaction and neutralizing acids, were termed **alkaline earths.** Baryta and strontia were afterwards included among the alkaline earths.

The formulæ of minerals.—The minerals and rocks which occur in nature have in many cases been produced by a complex series of chemical processes which can often be traced by reasoning backwards, and imitated on a small scale in our laboratories. The minerals formed in Nature's laboratory are seldom pure, for their composition is exceedingly complex—at least, chemical formulæ rigorously based on their analyses are somewhat elaborate. Ideally pure minerals very seldom occur in nature, and accordingly, the formulæ usually employed represent ideal or imaginary minerals, to which real minerals approximate more or less closely. **The formulæ for minerals are commonly represented as if pure minerals really occurred in nature.** The secondary constituents are thus ignored when computing the formula of a mineral, or a specially pure sample is selected for analysis, and the less pure minerals are referred to it as a standard or type. Thus, many samples of calcite can be obtained which furnish :

Calcium oxide (CaO) 55·9 ; Carbon dioxide (CO_2) 44·0.

Dividing 55·9 by the molecular weight of calcium oxide (56), and 44·0 by the molecular weight of carbon dioxide (44), it follows that the ratio $CaO : CO_2$ is nearly 1 : 1. The formulæ is accordingly written $CaO.CO_2$ or $CaCO_3$. Other minerals whose external physical and chemical properties approximate more or

less closely to calcite are also called by the same name. Thus a mineral containing :

SiO_2	Al_2O_3 and Fe_2O_3	CaO	MgO	CO_2
2·3	0·8	52·4	1·3	42·1 . . .

is also called calcite by a mineralogist. The silica, alumina, iron oxide, etc., were supposed to be accidental impurities. The shape of the crystals, of course, were those characteristic of calcite, not aragonite.

§ 6. The Specific Heats of the Elements—Dulong and Petit's Rule.

The **thermal capacity** of a substance is the amount of heat required to raise its temperature 1°, and the **specific heat** of a substance is the amount of heat required to raise the temperature of *one gram* of the substance 1°. Each element has its own characteristic specific heat, but the thermal capacities of quantities of the different elements proportional to their atomic weights are all nearly the same, so that

Atomic weight × Specific heat = 6 (approximately)

This relation was discovered by P. L. Dulong and A. T. Petit in 1819, and it is hence termed **Dulong and Petit's rule.** In illustration :

TABLE XVII.—PRODUCTS OF SPECIFIC HEATS AND ATOMIC WEIGHTS OF THE ELEMENTS.

Element.	Specific heat.	Atomic weight.	Product.
Silver	0·0559	108	6·0
Gold	0·0304	197	6·2
Copper	0·0923	63·5	5·9
Bismuth	0·0305	208	6·3
Lead	0·0315	207	6·5
Aluminium	0·2143	27	5·8
Iron	0·1098	56	6·1
Sulphur	0·1774	32	5·7

The deviations from 6 are so small that they have been attributed (1) to experimental errors and (2) to variations of the specific heats with temperature. At what temperature ought the specific heats to be determined, since it is known that the specific heat increases as the temperature is augmented? The amount of heat required to raise the temperature of, say, iron from 999° to 1000° is greater than that needed to raise its temperature from 0° to 1°. Again, iron at 100° is in a very different condition with respect to its melting-point from, say, calcium at 100°. The former melts at 1530°, the latter at 780°. There are four exceptions. The elements beryllium, carbon, silicon, boron give other values, but even these elements fall in line if their specific heats be determined at higher temperatures. Taking these things into consideration, the long list of elements, from which a selection is made in Table XVII., which agree with Dulong and Petit's rule, is something more than a coincidence, and it undoubtedly hints at some hidden property of the atoms. Dulong and Petit inferred that the inner meaning of their empirical rule is that **the atoms of all elements have the same capacity for heat,** and the product, Atomic weight × Specific heat, is accordingly called the **atomic heat** of an element.

Note the important application of Dulong and Petit's observation. If atomic weight × specific heat is approximately 6, then

$$\text{Atomic weight} = \frac{6}{\text{Specific heat}}$$

and a determination of the specific heat of an element furnishes sufficient data to compute an approximation to the numerical value of the atomic weight of that element, and if the equivalent weight of the element has been exactly determined, Dulong and Petit's rule indicates how many times the equivalent weight must be taken to get the atomic weight of the element.

EXAMPLE.—An element has a specific heat of 0·94, what is the approximate atomic weight? From Dulong and Petit's rule, it follows that $6 \div 0{\cdot}94 = 7$ nearly.

§ 7. The Relations between Calcium, Strontium, and Barium.

The elements of the alkaline earths—calcium, barium, and strontium—exhibit a close kinship and display a gradation in their properties from member to member as the atomic weight increases in passing from calcium to barium. A few properties of the elements, compiled for comparison purposes from a dictionary of chemistry, are indicated in Table XVIII.

TABLE XVIII.—PROPERTIES OF THE ALKALINE EARTH METALS.

——	Calcium.	Strontium.	Barium.
Atomic weight	40·09	87·63	137·37
Specific gravity	1·52	2·55	3·75
Atomic volume	26·4	38·7	36·6
Melting-point	780°	800°	850°
Specific heat	0·152	—	0·068
Flame coloration	Brick-red	Crimson	Green
Heat of formation of monoxide	131·3 Cals.	131 Cals.	130·4 Cals.
,, ,, hydroxide	16·3 ,,	17·7 ,,	22·3 ,,
Carbonate decomposes	825°	1150°	1842°
100 c.c. water at 50° dissolve hydroxides	0·13 grm.	2·5 grms.	13·1 grms.
,, ,, 10° ,, sulphates	0·19 ,,	0·10 grm.	0·0002 grm.
,, ,, 50° ,, chlorides	126 grms.	72 grms.	44 grms.

The metals are fairly stable in dry air and tarnish quickly in ordinary air. When heated they burn to the monoxide; they are all bivalent; they combine with water with the evolution of hydrogen at ordinary temperatures; and form oxides of the type BaO, hydroxides of the type $Ba(OH)_2$, and peroxides of the type BaO_2. The normal carbonates are but sparingly soluble in water. The low solubility of the sulphates and carbonates is utilized in analytical work. All three carbonates are precipitated when ammonium carbonate is added to solutions of their salts. The low solubility of barium sulphate is utilized (1) for estimating barium in solution, and (2) for estimating sulphates in solution.

Questions.

1. How can limestone be distinguished from and converted into quicklime? How much hydrochloric acid would be required

to decompose 15 grms. of limestone, and how much calcium chloride would be formed ? What volume of gas at N.P.T. will be produced ? (Ca=40, Cl=35·5, O=16, C=12.)—*Victoria Univ.*

2. What different substances could be added to milk of lime, which would cause it to form a clear solution ? Explain the action of each one added.—*London Univ.*

3. How is peroxide of hydrogen prepared ? Describe its behaviour with charcoal, lead sulphide, and silver oxide.—*London Univ.*

4. Describe the family of alkaline earths with special reference to gradation of properties noticed in the same.—*Bombay Univ.*

5. How is hydrogen peroxide prepared ? Mention a few of its properties. How can the presence of this body be ascertained ?—*Cape Univ.*

6. Give the names and composition of the two chief minerals containing barium, and describe how the salts of barium are obtained from them both.—*Madras Univ.*

7. State the general characters of the metals of the alkaline earths. What is the relation of magnesium to this group ?—*Science and Art Dept.*

8. Hydrochloric acid of specific gravity 1·1964 contains nearly 40 per cent. of HCl. How much of this acid would be required to neutralize a ton of chalk weighing 2240 lbs. ?—*College Preceptors.*

9. How would you prepare a specimen of crystallized barium nitrate from heavy spar (barium sulphate) ?—*London Univ.*

10. What are the chief characteristics of the elements calcium, strontium, and barium, and the properties of their chlorides, oxides, and sulphates which lead to their classification in one family or subgroup ?—*Science and Art Dept.*

11. What are the insoluble sulphates ? How can the metals they contain be converted into chlorides ?—*London Univ.*

12. " Calcium, strontium, and barium constitute a group of closely related elements." Give reasons for this statement.—*Cape Univ.*

13. State the law of Dulong and Petit relating to specific heats. A certain element has an equivalent 40, and forms a volatile chloride the vapour density of which is about 226 (O=32). What should the specific heat of this element be, approximately ?—*Science and Art Dept.*

14. The specific heat of copper is 0·0952 ; calculate from this datum the atomic weight of the metal, stating the general principle involved. Refer to any exceptions to this general principle.—*Science and Art Dept.*

15. What is the value of a knowledge of the specific heat of an element in determining its atomic weight ?—*Science and Art Dept.*

16. The specific heat of an element is 0·031 ; what is approximately its atomic weight ? What other facts would be required in order to establish its atomic weight with accuracy ?—*Science and Art Dept.*

17. Define the terms "equivalent weight" and "atomic weight." Given that 0·1 grm. of an element on solution in HCl displaced 124·4 c.c. of hydrogen at 0° and 760 mm. ; further, that the specific heat of the metal is 0·214, calculate its atomic weight, and write down the formula for its oxide and chloride.—*Cambridge Senr. Locals.* [Ansr. 27 ; X_2O_3 ; XCl_3.]

CHAPTER XX

Magnesium, Zinc, Cadmium, and Mercury

§ 1. Magnesium.

History of magnesium.—In 1695, N. Grew published a pamphlet describing a peculiar salt obtained by evaporating the water of the mineral springs at Epsom. The medicinal properties of this salt attracted some attention ; in England it was called *Epsom salt ;* and on the Continent, *sal anglicum.* If a solution of sodium carbonate be added to a solution of Epsom salt, a white precipitate is obtained, as is also the case if the same salt be added to a solution of a calcium salt. If the two precipitates be washed and dried, and then treated with dilute sulphuric acid, sulphates are formed in both cases, but that derived from the calcium salt is but sparingly soluble in water, while the other is very soluble. In fact, the two solubilities are nearly as 1 : 120. This distinction between magnesium and calcium salts was pointed out in 1755 by J. Black. Before that time lime and magnesia were sometimes confused with one another.

The salts of magnesium.—When the washed and dried carbonates of lime and magnesium, prepared as just described, are treated as described on page 187, the magnesium carbonate is peculiar, for the loss on ignition (Fig. 82) is much more than the amount of carbon dioxide obtained by the method indicated in Fig. 87. Indeed, by heating the magnesium carbonate in a current of dry air, in an apparatus, Fig. 64, arranged to arrest any water given off, it will be found that magnesium carbonate, unlike calcium carbonate, contains both water and carbon dioxide. It is indeed a **basic magnesium carbonate**—presumably a compound of both the carbonate and hydroxide—

$MgCO_3.xMg(OH)_2$. The different salts of magnesium can be obtained by the action of the corresponding acids on magnesium carbonate or oxide. Thus with hydrochloride acid, **magnesium chloride,** $MgCl_2$, is obtained.

Preparation of the magnesium.—Magnesium can be prepared by the electrolysis of the magnesium chlorides ; or of a mixture of magnesium chloride with potassium chloride ; or of fused carnallite.

An artificial carnallite is first made by evaporating a solution of 20 grms. crystalline magnesium chloride, 7·5 grms. of potassium chloride, and 3 grms. of ammonium chloride to dryness in a platinum dish on a water bath, and fuse the residue over a blast gas burner (Fig. 31). Pour the molten liquid into the bowl of a clay pipe (Fig. 168) heated over a gas burner. Put a knitting needle down the stem of the pipe, and sink a carbon rod into the bowl as shown in the diagram. Connect the steel needle and the carbon rod with a source of electricity so that the former can act as cathode, the latter as anode. Cover the molten mass with a layer of charcoal dust. Pass a current of electricity (about 10 volts and 8 amps.) through the molten mass for about half an hour, and let everything cool. When the mass is broken up in a mortar, the small globules of magnesium metal, scattered here and there throughout the mass, can be picked out, and washed clean by means of alcohol. The object of the charcoal powder is to protect the metal from oxidation should any globules rise to the surface.

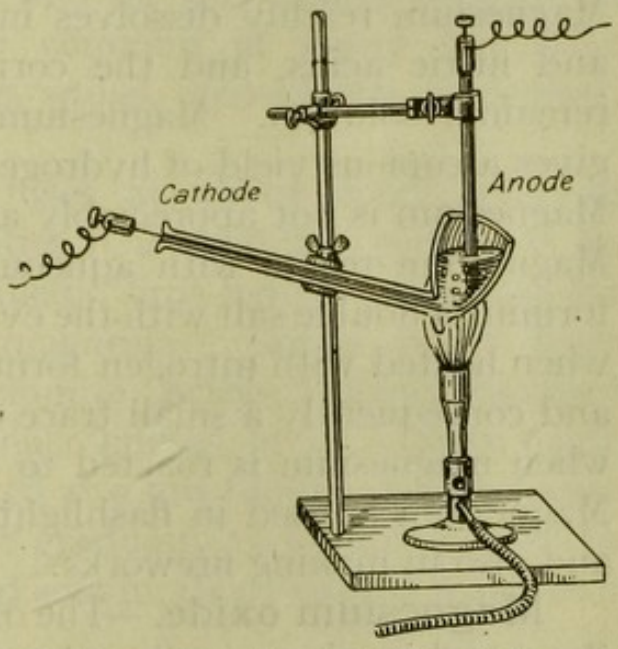


FIG. 168.—Electrolysis of Fused Carnallite.

The metal can also be obtained by heating magnesium chloride with metallic sodium in an iron crucible. Metallic magnesium and sodium chloride are formed : $MgCl_2+2Na=2NaCl+Mg$.

When H. Davy isolated the impure metal in 1808 he called it " magnium." At that time, the terms " magnesium " and

" manganesium " were applied synonymously to the element (manganese) derived from the mineral pyrolusite (manganese dioxide). To avoid confusion, the term " magnesium " was soon afterwards restricted to the element derived from magnesia alba ; and " manganese " to the element derived from pyrolusite.

Properties of magnesium.—The metal has a silvery-white lustre, and low specific gravity. When ignited magnesium burns in air giving a brilliant white light. Magnesium is slowly oxidised by moist air ; and it very slowly decomposes boiling water. When heated in a current of steam, magnesium takes fire, and continues burning : $Mg+2H_2O=Mg(OH)_2+H_2$. Magnesium readily dissolves in dilute hydrochloric, sulphuric, and nitric acids, and the corresponding salts of magnesium remain in solution. Magnesium is perhaps the only metal which gives a copious yield of hydrogen when treated with nitric acid. Magnesium is not appreciably attacked by alkaline hydroxides. Magnesium reacts with aqueous solutions of ammonium salt, forming a double salt with the evolution of hydrogen. Magnesium when heated with nitrogen forms **magnesium nitride,** Mg_3N_2, and consequently a small trace of the nitride is possibly formed when magnesium is roasted to the oxide while exposed to air. Magnesium is used in flashlight preparations for photography, and also in making fireworks.

Magnesium oxide.—The oxide can be prepared by igniting the metal in air, as well as by calcining the nitrate, carbonate, and sulphate in the presence of water vapour. Magnesium oxide is made from magnesium chloride of the Stassfurt deposits by converting the latter into the carbonate and calcining the resulting carbonate. The " magnesia usta " of commerce is made by the prolonged calcination of the carbonate at a low temperature.

Magnesia is slightly soluble in water, to which it gives a slight alkaline reaction : 100 c.c. of water dissolve about 0·001 gram of magnesia. The oxide is not completely converted into the hydroxide by the action of water. The hydroxide is precipitated from solutions of magnesium salts by the addition of alkali hydroxides. **Magnesium hydroxide,** $Mg(OH)_2$, is soluble in ammonium salts, and hence the precipitation with ammonia

is incomplete: $Mg(OH)_2+2NH_4Cl \rightleftharpoons MgCl_2+2NH_4OH$. If enough ammonium salt be present in the solution, magnesium hydroxide will not be precipitated at all; at the same time, a soluble salt—probably $(NH_4)_2MgCl_4$, that is, $MgCl_2.2NH_4Cl$—is formed in the solution.

Occurrence of magnesium.—Magnesium does not occur free in nature, but it occurs combined with other substances forming definite minerals; *e.g.* it occurs as magnesium carbonate in *magnesite*, $MgCO_3$; as double carbonate of calcium and magnesium in *dolomite*, $MgCO_3.CaCO_3$; as magnesium sulphate in *Epsom salts*, $MgSO_4.7H_2O$; and as magnesium chloride in *carnallite*. Magnesium is also common in many minerals: *olivine, enstatite, asbestos, steatite, spinel, meerschaum, serpentine, talc*, etc.

Uses.—Magnesium oxide fuses at about 2000°, and on account of its refractory qualities it is used for pencils as an alternative to lime, in the so-called "lime-light"; and also for making refractory bricks ("magnesia" bricks made from calcined magnesite, and "dolomite bricks" from calcined dolomite), crucibles, cupels, furnace linings, etc. A paste made with water and magnesia calcined at a low temperature behaves similarly to lime in mortar. It gradually re-hydrates, absorbs carbon dioxide from the air, and sets in about twelve hours to a hard mass.

§ 2. Zinc and Cadmium—Occurrence and Extraction.

History of zinc and cadmium.—Brass, an alloy of zinc and copper, was known to the ancients, and several references to "brass" occur in the sacred writings. R. Jagnaux says that bracelets made of zinc have been found in the ruins of Cameros, which was destroyed about 500 B.C. Such knowledge of zinc as was possessed by the ancients appears to have been lost for a time. The term "zinken" occurs in several books written about the sixteenth and seventeenth centuries, but its meaning does not appear to us now to have been clearly defined, and it was not till 1697 that G. E. von Löhneyes applied the term definitely to what we now call zinc. Zinc is a volatile metal,

easily oxidized, and an impure zinc oxide collects as flue dust in brass founders' furnaces. This is called " tutty " ; it was once called *cadmia fornacum* (flowers of zinc). The term " cadmia " was also applied by the old historians to a zinciferous earth found near the Black Sea. Hence, when F. Stromeyer (1817) discovered that flowers of zinc contains not only zinc but also a new element, volatile like zinc, but with several different properties, what more natural than to call the new element cadmium ? In 1695, W. Homberg discovered that zinc could be obtained from calamine. A works for the manufacture of zinc was erected at Bristol about 1740 by J. Champion. Champion's process was patented 1739 ; in this process the ore was distilled in large crucibles arranged with a pipe extending downwards through the bottom of the crucible. It is called the English process of " distillation per descensum." The process is obsolete.

Occurrence of zinc and cadmium.—Metallic zinc has been reported in the basaltic rocks of Victoria (Australia) ; but it usually occurs combined : as carbonate, *zinc spar, calamine*, $ZnCO_3$; sulphide, *zinc blende* or *black jack*, ZnS ; oxide, *zincite* or *red zinc ore*, ZnO ; silicate, *willemite*, $2ZnO.SiO_2$; *franklinite*, $(ZnFe)O.Fe_2O_3$; *zinc spinel* or *gahnite*, $ZnO.Al_2O_3$. Zinc and cadmium usually occur together. Less than 0·5 per cent. of cadmium is commonly found associated with zinc ores. The mineral *greenockite*—cadmium sulphide—is too scarce to be of commercial importance.

The extraction of zinc and cadmium.—The ores employed for the extraction of zinc are the carbonate, oxide, and sulphide. The process involves two operations :

(1) *Roasting.*—The object is to convert the sulphide into the oxide by calcination. The oxidation of the carbonate presents no difficulty : $ZnCO_3=ZnO+CO_2$. In the case of the sulphide, the sulphur is oxidized by calcination in air : $2ZnS+3O_2=2ZnO+2SO_2$.

(2) *Reduction of the oxide.*—The oxide can be reduced by heating it in a tube in a very rapid current of hydrogen. A slow current is not effective, probably owing to the back reaction between zinc and steam : $Zn+H_2O\rightleftharpoons ZnO+H_2$. On a large

scale the oxide is reduced by heating it with carbon. The crushed oxide is mixed with crushed coke and heated to bright redness in fireclay retorts. The oxide is reduced with the formation of carbon monoxide: $ZnO+C=Zn+CO$. The metal distils over and collects in fireclay or iron receivers. At first a fine grey powder—" zinc dust "—collects in the receiver. This is a mixture of zinc oxide and powdered metal. When the receiver is warm, the metal condenses to a liquid which is drawn off at intervals and cast into plates or bars. If zinc sulphate had been produced during the roasting of the sulphide: $ZnS+2O_2=ZnSO_4$, it would be reduced by the carbon back to the sulphide, and thus reduce the yield of metal by the ore. The zinc so obtained—called *spelter*—contains carbon, iron, lead, arsenic, and cadmium as impurities. It may be refined by careful distillation.

The retorts.—The fireclay retorts have different shapes, and different types of condensers are used in different smelting works. The so-called Belgian retort is an oval or cylindrical tube—6″ to 10″ diameter, and about 3′ or 4′ long. The retort is fitted with a conical tube—about 16″ long—as condenser, Fig. 169. The wide end fits the retort, and the narrow end is fitted with a sheet iron nozzle to catch any zinc dust. The retorts are built into the furnace in rows and tiers.

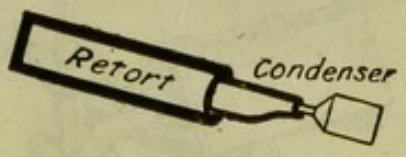


FIG. 169.—Belgian Zinc Retort.

Cadmium is obtained from the zinc dust of zinc smelting furnaces. The dust is redistilled a number of times, when the more volatile cadmium can be separated from the less volatile zinc. Electrolytic processes for separating zinc and cadmium are used.

§ 3. Mercury—Occurrence and Extraction.

History of mercury.—Theophrastus, a writer on natural history, 320 B.C., mentions the manufacture of *chutos argyros* (quicksilver) from cinnabar; and he states that it can be made by rubbing vinegar with cinnabar in a copper vessel. Dioscorides called it *hydor argyros*, *i.e.* liquid silver; hence the Latin

hydrargyrum, and the present-day symbol Hg. The metal had a certain fascination for the alchemists, and for a time they believed that it, or something similar, was a constituent of all metals; and they called it various names—*argentum vivum* (quicksilver), *mercurius*, etc. "Nimble volatile mercury" was named after the mythological Mercury, the messenger of the gods, and accordingly the ancient chemists symbolized the metal by the caduceus or herald's wand ☿, also used for the planet Mercury.

Occurrence of mercury.—Free mercury in small quantities occurs disseminated in the ores of mercury. *Cinnabar*, HgS, is the chief ore of mercury, and it is mined in Almaden (Spain), Idria (Carniola), Bavarian Palatinate, Peru, California, Japan, China, etc.

Extraction of mercury.—Mercury is obtained almost exclusively from cinnabar, HgS. The cinnabar is roasted to oxidize the sulphur, and the metal is liberated: $HgS + O_2 = SO_2 + Hg$; or else the ore is distilled with lime in closed retorts, whereby calcium sulphide and mercury are formed: $HgS + CaO = CaS + Hg + O_2$. The latter process can easily be imitated in the laboratory in an apparatus resembling Fig. 170, where the mixture of cinnabar and lime is heated in a hard glass tube fitted with a U-tube for collecting the condensed mercury. The calcium sulphide remains in the tube.

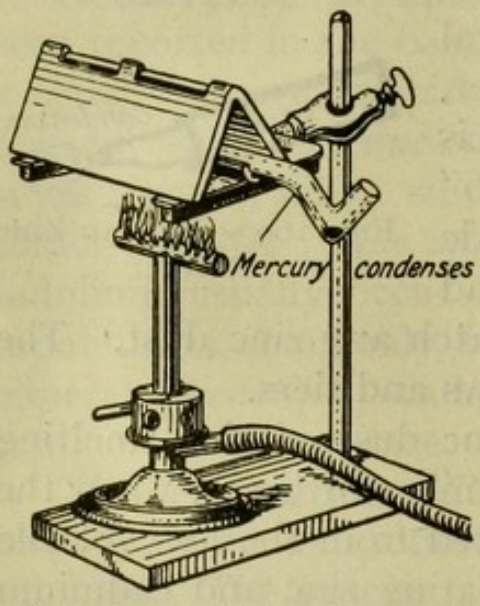


FIG. 170.—Extraction of Mercury.

Different condensing arrangements are employed in different works. The mercury, for example, may be condensed in large chambers, as at Idria; or in a series of pear-shaped vessels—aludels—connected in rows nearly 50 feet long, as at Almaden. About six trains of aludels are connected with one roasting furnace. Crude mercury is sent into commerce in iron bottles holding about 75 lbs. of liquid metal. The mercury may be cleaned by

filtration through chamois leather ; and purified by distillation from iron retorts. In the laboratory, mercury is often purified by running a fine spray of mercury down a long column of dilute nitric acid (specific gravity 1·1), followed by distillation *in vacuô*.

§ 4. The Properties of Zinc, Cadmium, and Mercury.

Cadmium and zinc are white metals. Mercury is a silvery-white metal liquid at ordinary temperatures. It freezes into a malleable solid at −38·85°. Mercury does not tarnish in air. Both cadmium and zinc are slowly oxidized by moist air ; and in water containing air in solution, the metals are oxidized with the formation of basic carbonates. Both metals are attacked by dilute hydrochloric and sulphuric acids, giving hydrogen ; nitric acid gives oxides of nitrogen. Cadmium is insoluble in alkaline hydroxides, but zinc dissolves, giving off hydrogen.

Mercury forms two oxides: Mercurous oxide, Hg_2O, and mercuric oxide, HgO. There is a series of salts corresponding with each oxide :

Mercurous oxide, Hg_2O	Mercuric oxide, HgO
,, chloride, HgCl	,, chloride, $HgCl_2$
,, nitrate, $HgNO_3$	,, nitrate, $Hg(NO_3)_2$
,, sulphate, Hg_2SO_4	,, sulphate, $HgSO_4$
,, sulphide, Hg_2S	,, sulphide, HgS

Mercury is not attacked by hydrochloric acid ; concentrated sulphuric acid acts very slowly in the cold ; but when heated, **mercuric sulphate,** $HgSO_4$, sulphur dioxide, and some mercury sulphide are formed. Concentrated nitric acid rapidly attacks mercury, forming **mercuric nitrate** and oxides of nitrogen. Dilute nitric acid acts slowly, giving another nitrate, **mercurous nitrate,** particularly if the metal be in excess. The two nitrates are not the same, for the latter gives a white precipitate of mercurous chloride, HgCl, with dilute hydrochloric acid, while the former does not. Mercurous nitrate has an ultimate composition corresponding with $HgNO_3$; and mercuric nitrate, $Hg(NO_3)_2$. In a general way the mercurous salts are formed

when the mercury is in excess, and the mercuric salts when the acid is kept in excess. Alkali hydroxides have no appreciable action on mercury.

Amalgams.—Mercury is a good solvent for some of the metals. Solutions of the metals in mercury are called "amalgams." The phenomena attending the solution of the metals in mercury appear to be closely analogous with the solution of different substances in water. A considerable amount of heat is often developed, as is the case when sodium or potassium metals are dissolved in the liquid metal. Gold and silver dissolve readily in mercury, and this fact is utilized in the extraction of gold. The mercury can be distilled off, the non-volatile metal remains in the retort. *Tin analgam* is soft, and is used in making mirrors. *Amalgams of gold, copper, and zinc* are used in dentistry for stopping teeth. *Zinc amalgam* is but slowly attacked by sulphuric acid, and amalgamated zinc is used in making batteries. The zinc dissolves only when the circuit is closed.

Uses of zinc, cadmium, and mercury.—Zinc is used in making the anode plates of batteries and in making certain utensils. It is also a constituent of certain alloys: brasses, German silver, bronze, etc. (*q.v.*). Galvanized iron is iron covered with a protective coating of zinc to prevent rusting. In one process of galvanizing, the iron is first cleaned with acid or sand blast, and subsequently dipped in molten zinc; in another process of galvanizing, the zinc is deposited electrolytically, similar to electroplating. Mercury is used in making certain medicinal preparations—blue pills and mercurial ointments; and in making amalgams and in the manufacture of scientific instruments—thermometers, barometers, etc. Cadmium is used in making certain fusible alloys.

§ 5. The Oxides of Zinc, Cadmium, and Mercury.

Zinc monoxide, ZnO; **and cadmium monoxide,** CdO. —The monoxides of zinc and cadmium are formed when the metals are burnt in air: $2Zn+O_2=2ZnO$. Zinc oxide, under the commercial name "zinc white," is manufactured by heating

zinc in air and passing the fumes into condensing chambers where the oxide collects. Zinc oxide is used in place of white lead as a white pigment where the blackening of white lead is objectionable; it is also used in the manufacture of rubber goods—tyres for motor-cars, etc. Zinc oxide appears yellow when hot, white when cold. Cadmium oxide, CdO, has a rich brown colour. Zinc oxide does not melt in the oxyhydrogen blowpipe, but, like lime and magnesia, the oxide is vividly incandescent under these conditions; it afterwards appears phosphorescent in the dark.

Zinc hydroxide, $Zn(OH)_2$; **cadmium hydroxide,** $Cd(OH)_2$.—These hydroxides cannot be produced by the action of water on the oxides, but they are precipitated when an alkaline hydroxide is added to a solution of a zinc or a cadmium salt. Zinc hydroxide, unlike cadmium hydroxide, is soluble in an excess of the alkaline hydroxide, forming salts of the type, $Zn(OK)_2$, called **zincates.** The same salt is formed when zinc metal is dissolved in potassium hydroxide. Both hydroxides are soluble in ammonia, not because of the acidic character of the hydroxide, but because of the formation of a soluble complex ammonio-zinc oxide. Both oxides are basic, and yield salts on treatment with acids.

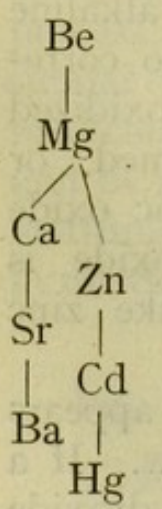
Mercurous oxide, Hg_2O.—Mercurous oxide, is formed as an unstable dark brown powder when mercurous chloride, HgCl, is digested with an alkaline hydroxide: $HgCl+KOH=KCl+HgOH$; and as a black powder when an alkaline hydroxide is added to soluble mercurous salts. No corresponding hydroxide is known. Instead of being oxidized in air, mercurous oxide is decomposed when warmed, or when exposed to air in the light, forming mercuric oxide and mercury: $2Hg_2O=2HgO+2Hg$. Mercurous oxide is feebly basic, but it exhibits no acidic qualities like zinc oxide.

Mercuric oxide, HgO.—At first sight, this oxide appears to exist in two distinct modifications—red and yellow. If a mercuric salt be treated with an excess of alkaline hydroxide in the cold, mercuric hydroxide is probably formed, but this immediately decomposes into a yellow mercuric oxide. If the

precipitation be made from hot solutions, *orange* mercuric oxide is obtained. The difference in colour is not due to a difference in the composition of the two oxides, for both furnish 7·4 per cent. of oxygen. Mercurous oxide under the same conditions gives but 4·8 per cent. of oxygen. The difference in colour of the red and yellow mercuric oxides is probably due to the state of subdivision of the precipitate: the larger the granules, the redder the tint. If mercuric oxide be prepared by the ignition of the nitrate, or by calcining the metal in air, nearly at its boiling-point, the oxide is red and distinctly crystalline; the yellow oxide becomes red when heated to about 400°. When heated, the red oxide darkens in colour and finally appears almost black; the red colour returns on cooling. If heated above the temperature at which the oxide appears to blacken, it decomposes into mercury and oxygen. The yellow oxide is slightly soluble in water, and the solution has an alkaline reaction with basic, but no acidic, qualities. On account of the ease with which mercuric oxide parts with its oxygen, it is an active oxidizing agent. The yellow oxide is more active than the red, probably owing to its finer state of subdivision.

§ 6. The Magnesium-Zinc Family of Elements.

The elements beryllium, magnesium, zinc, cadmium, and mercury, form a family related in many ways with one another, and with the metals of the alkaline earths. Beryllium is so scarce that a mere reference to it will be sufficient. The family relationship, however, is not so well marked as it is with the alkaline earths. Beryllium and magnesium form a kind of sub-group; zinc, cadmium, and mercury form another sub-group. The metals beryllium and magnesium appear to link the alkaline earths with zinc, cadmium, and mercury. The scheme indicated in the margin is sometimes used to illustrate the idea. There may be a missing member between cadmium and mercury, since cadmium is much more closely related to zinc than it is to mercury. The vapours of all the



elements appear to be composed of monatomic molecules. The physical properties of the metals are summarized in the table :—

TABLE XIX.—PHYSICAL PROPERTIES OF THE MAGNESIUM-ZINC METALS.

—	Beryllium.	Magnesinm.	Zinc.	Cadmium.	Mercury.
Atomic weight	9·1	24·32	65·37	112·40	200·0
Specific gravity	1·64	1·75	6·9–7·2	8·6	13·6
Atomic volume	5·5	13·8	9·34	13·0	15·4
Melting-point	over 960°	632°	418·2°	320·2°	−38·85°
Boiling-point	—	1120°	916°	780°	357·3°

The metals are not oxidized so readily as those of the alkaline earths. Beryllium does not bear such a close relationship to magnesium, zinc, and cadmium, and while mercury has a great many important similarities, it has also many important differences—thus, (1) it does not readily combine with oxygen ; (2) its hydroxide is unstable and difficult to make ; (3) the black sulphide is virtually insoluble in nitric acid ; and (4) it forms two chlorides, one of which—HgCl—resembles silver chloride—AgCl.

Some of the chemical relationships between this family of elements have already been discussed. The sulphates are soluble and isomorphous. The hydroxides are not made by direct union of the oxide with water, and the water is easily expelled from the hydroxides by heating. This is not the case with the hydroxides of the alkaline earths. The sulphides increase in stability as the molecular weight increases. The sulphides of the first two elements, for instance, are not formed in the presence of water; zinc sulphide is stable in alkaline solutions, but is dissolved by even feebly acidulated solutions ; cadmium sulphide is dissolved by concentrated but not by dilute acids ; whereas mercury sulphide is scarcely attacked by boiling nitric acid. The chlorides become less and less stable in passing from beryllium to mercury.

Questions.

1. Compute formulæ for two mercuric oxides which furnish on analysis: (*a*) mercury 92·6, oxygen 7·4 per cent.; (*b*) mercury 95·2, and oxygen 4·8 per cent. Describe an apparatus by which these measurements can be made.

2. Red oxide of mercury is heated (1) alone, (2) with carbon, (3) with hydrogen. What products are formed, and what weight of each would be obtained if 10 grms. of mercuric oxide were used? (Hg=200, C=12.)—*London Univ.*

3. State what you know of magnesium and its commoner compounds.—*London Univ.*

4. What metals are most nearly allied with magnesium? State the general characters of the group, and in what respects the compounds of these metals differ from the compounds of calcium.—*London Univ.*

5. Write the names and formulæ of three minerals containing magnesium. How is magnesium obtained and purified? Describe the properties of magnesium.—*Madras Univ.*

6. Give some account of the way in which mercury is obtained from its ores, and the method of purifying the metal. What products are obtained when mercury is heated with boiling sulphuric acid?—*Adelaide Public Exam. Board.*

7. What is the ordinary mineral source of cadmium? How is the metal obtained? Compare its chemical and physical properties with those of zinc.—*Bombay Univ.*

8. How would you prepare a solution of hydrogen dioxide? What is its action on oxide of silver, baryta solution, and potassium iodide?—*Science and Art Dept.*

9. How would you prove that the specific gravity of mercury is 13·6? Give examples of common substances which are soluble in liquid mercury, and state how you would recover these substances if dissolved.—*Science and Art Dept.*

10. A piece of metal, weighing 1·296 grms., dissolved in dilute sulphuric acid, the solution evaporated to dryness, and the excess of acid expelled by heat gave 2·41 grms. of residual sulphate. Find the equivalent weight of the metal.—*Cambridge Senr. Locals.*

11. If the equivalent of magnesium be 12·1, explain fully how you would proceed in order to ascertain whether or not the equivalent and atomic weights are identical.—*Science and Art Dept.*

12. What substance is formed when mercury is heated in air? Describe all that happens when this product is heated strongly in a test-tube.—*Science and Art Dept.*

13. Describe and explain the production of mercury from its most commonly occurring ore, explaining the principle of the

process without much detail as to apparatus. How can mercury be completely purified from other metals ?—*Science and Art Dept.*

14. Explain fully how you would proceed in order to determine the combining weight or chemical equivalent of zinc or of magnesium. —*Delegacy of Local Exams.*

15. How do the two nitrates of mercury differ in properties and in composition ? How may mercury be obtained from mercuric nitrate, from mercuric chloride, from mercuric sulphide ?—*Delegacy of Local Exams.*

16. Starting from mercury, how would you prepare mercuric sulphate, mercuric chloride, mercurous chloride, mercuric nitrate, mercurous nitrate respectively ?—*Bombay Univ.*

17. What are the chief resemblances and what are the chief differences between well-known calcium compounds and well-known magnesium compounds ?—*London Univ.*

18. Describe the extraction of zinc from the mineral calamine. How would you prepare the sulphate and distinguish it from the corresponding magnesium compound ?—*London Univ.*

CHAPTER XXI

The Alkali Metals

§ 1. Potassium and Sodium Carbonates.

The ash of wood contains about 30 per cent. of potassium carbonate. In special districts it may be profitable to burn wood in pits and extract the ashes with water in wooden tubs. The clear liquid is evaporated to dryness in iron pots and calcined to burn away the organic matter. The residue is the so-called American *potash*, that is, pot-ashes. Instead of evaporating the aqueous extract to dryness, a purer product can be obtained by evaporating the liquid until the less soluble impurities crystallize out, and finally evaporating the mother liquid to dryness as before. White refined potash is sometimes called *pearl ash*. Potash is also obtained from the residue left after beet sugar has been fermented, and the alcohol removed by distillation. The liquid in the retort is evaporated to dryness, calcined, and extracted with water as before.

The potash found in plants is derived from the soil, and the potash in the soil is one product of the decomposition of rocks which form the earth's crust. The potash which herbivorous animals—*e.g.* sheep—draw from the land is largely exuded as an oily sweat from the skin, and called, after the French, *suint*. The suint accumulates in the wool so that it may form as much as one-third the weight of raw merino wool. The liquid in which wool is first washed contains most of the suint. This liquid can be evaporated to dryness and heated in iron pots or retorts. Potassium carbonate is extracted from the residue by lixiviation with water as indicated above.

The alkaline lakes of Nevada and South California give

sodium carbonate on evaporation. "Natural soda," also called *trona* or *urao*, has been extracted commercially at Queen's Lake, and deposits in Northern Egypt are extensively worked.

Historical.—While the ashes of land plants furnish potassium carbonate, the ashes of sea plants furnish a similar, but not identical, alkali—sodium carbonate. Both sodium and potassium carbonates were once included under the Arabian term **alkali.** In order to distinguish these two salts from ammonium carbonate, they were termed **fixed alkalies,** and ammonium carbonate was called **volatile alkali.** H. L. Duhamel du Monceau (1736) first clearly recognized the difference between potash and soda, and the two were distinguished by using the term **vegetable alkali** for potassium carbonate, and **mineral alkali** for sodium carbonate. When M. H. Klaproth (1796) showed that the vegetable alkali occurred in many minerals, the term *potash* (English), or *potasse* (French), was applied to this particular compound. The Germans use the term *kali*—derived from the Arabian term "kali," for ash. Klaproth also proposed to confine the term *natron* to mineral alkali, sodium carbonate. The English equivalent for natron is *soda*, and the French *soude*. The first letter of the word "kali" is used by all chemists as the symbol for potassium, and the first two letters of the word "natron" for sodium.

§ 2. Alkali Manufacture.

Before 1793, sodium carbonate was made from the ashes of seaweeds, and potash carbonate from the ashes of land plants. Several methods were known at that time for converting sea salt into sodium carbonate, *e.g.* K. W. Scheele, about 1770, converted salt into soda by treating a solution of salt with lead oxide and passing carbon dioxide into the filtered solution. When Napoleon closed the European ports to English and American ships the main sources of supply of sodium carbonate and potashes were cut off. To ease the demand, Napoleon offered a prize of 100,000 francs for a process

of manufacturing soda from common salt. The prize was won by N. le Blanc, 1794, who proposed a method of manufacture which has held its own for over 100 years, although it has had a serious rival in the ammonia-soda or Solvay's process; and both processes have to compete against electrolytic processes. Had it not been for the commercial value of the by-products of le Blanc's process, there can be little doubt that it would have been ousted long ago. As a matter of history, Collison patented a similar process in England some ten years earlier than le Blanc—viz. 1782.

I. N. le Blanc's black ash process for sodium carbonate.—In studying the principle of le Blanc's process it will be convenient to take it in different stages:

(1) **Conversion of sodium chloride into sodium sulphate—salt-cake.**—The first stage in the process is to convert the sodium chloride into sodium sulphate by warming the chloride with sulphuric acid in large cast-iron pans. The reaction is represented: $NaCl+H_2SO_4=NaHSO_4+HCl$. The mixture is then raked on to the hearth of a furnace and roasted to convert the acid sulphate into the normal sulphate: $NaHSO_4+NaCl=Na_2SO_4+HCl$. The torrents of hydrogen chloride given off are led through condensing towers down which water trickles, and in this way hydrochloric acid is formed. The solid product of this reaction is sodium sulphate, also called salt-cake.

(2) **The conversion of salt-cake into black ash.**—The salt-cake is mixed with limestone and coal, and heated to a high temperature in a reverberatory furnace (black ash furnace); or in a furnace with a revolving cylinder so arranged that the hot gases from the furnace pass through the cylinder, Fig. 171. The cylinder contains the mixture of salt-cake, limestone, and coke, and the slow revolution of the cylinder ensures the thorough mixing of the contents. The sodium sulphate is reduced by the carbon: $Na_2SO_4+2C=Na_2S+2CO_2$. The resulting sodium sulphide reacts with the limestone, forming a mass which when treated with water furnishes calcium sulphide and sodium carbonate: $Na_2S+CaCO_3=CaS+Na_2CO_3$. The initial and end stages of the reaction are symbolized: $Na_2SO_4+CaCO_3+2C=Na_2CO_3+CaS+2CO_2$. The contents of the cylinder are

then discharged into iron trucks. The dark grey or brown porous mass so obtained is called **black ash.**

(3) **Extraction of sodium carbonate from black ash.**—The black ash is rapidly lixiviated with warm water, so that as little water as practicable will be used. The water passes through a series of tanks containing the pulverized ash. Fresh water passes through the tank containing the ash, which is almost all extracted; and the water, almost saturated, passes through the black ash fresh from the furnace. The tank liquid is allowed to settle, and then concentrated by evaporation

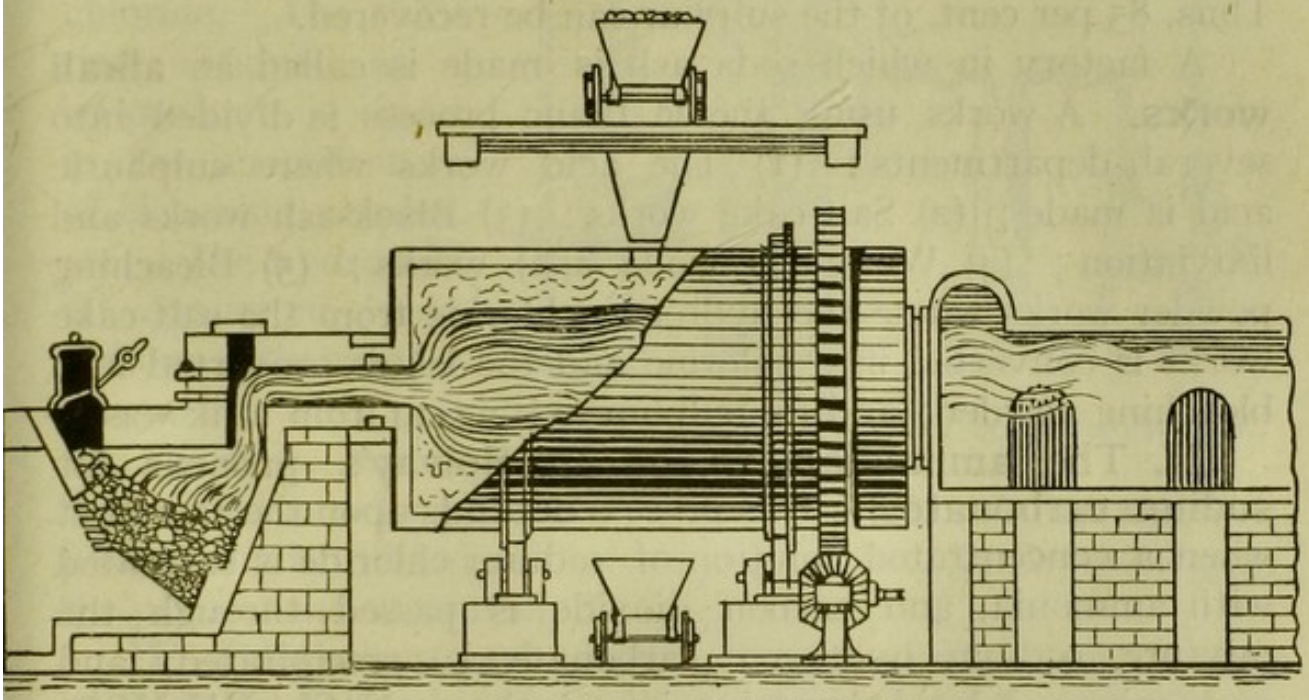


FIG. 171.—Revolving Black Ash Furnace.

in shallow pans heated by the waste heat from the black ash furnace. The product of the evaporation is then calcined; it is called crude soda ash. The latter is further purified by exposing it to a current of hot air in order to oxidize the sulphides to sulphates. The former imparts a slight yellow tinge to the mass. The soda ash, Na_2CO_3, is then crystallized from water if soda crystals (washing soda) are wanted—$Na_2CO_3.10H_2O$.

The action of water on black ash during the washing involves a complex series of chemical changes. The free lime of the black ash reacts with the sodium carbonate, forming sodium hydroxide and calcium carbonate; the calcium sulphide reacts

with sodium carbonate, forming sodium sulphide and calcium carbonate ; the oxygen of the air oxidizes the calcium sulphide to calcium sulphate, which in turn reacts with sodium carbonate, etc. All these reactions reduce the yield from the process. The tank liquid is sometimes treated with carbon dioxide so as to convert the caustic soda and sodium sulphide into sodium carbonate. The " tank waste " containing sodium sulphide is treated with carbon dioxide to liberate hydrogen sulphide. The hydrogen sulphide is burnt in a limited supply of air, so that most of the hydrogen but only part of the sulphur, burns. Thus, 85 per cent. of the sulphur can be recovered.

A factory in which soda ash is made is called an **alkali works.** A works using the le Blanc process is divided into several departments : (1) The acid works where sulphuric acid is made ; (2) Salt-cake works ; (3) Black-ash works and lixiviation ; (4) White-ash (soda ash) works ; (5) Bleaching powder works where the hydrogen chloride from the salt-cake works is converted into chlorine and the latter converted into bleaching powder ; and (6) Sulphur extraction from tank waste.

II. The ammonia-soda or E. Solvay's process for sodium carbonates.—This process depends upon the fact that when a concentrated solution of sodium chloride is saturated with ammonia, and carbon dioxide is passed through the mixture, sodium hydrogen carbonate is precipitated, and ammonium chloride remains in solution : $NaCl+NH_4HCO_3 \rightleftharpoons NaHCO_3+NH_4Cl$. If sodium carbonate is needed the bicarbonate is calcined : $2NaHCO_3=Na_2CO_3+H_2O+CO_2$. This carbon dioxide forms part of that used in the first stage of the operation. The mother liquid remaining after the separation of sodium bicarbonate is treated with lime obtained by burning limestone : $CaCO_3=CaO+CO_2$; and the ammonia is recovered : $2NH_4Cl+CaO=CaCl_2+H_2O+2NH_3$. The ammonia and carbon dioxide evolved in these two operations are used again. Thus calcium chloride is the only by-product which is not utilized. The process can be illustrated by connecting an apparatus, *A*, for generating ammonia, Fig. 172, and an apparatus, *B*, for making washed carbon dioxide with a tower, *C*, filled with a saturated solution of sodium chloride and fitted with four perforated iron

discs as shown in the diagram. The tower is provided with an exit tube dipping in a beaker of water. The solution is first saturated with ammonia, and then with carbon dioxide. In about an hour, crystals of sodium bicarbonate will be deposited on the perforated shelves.

III. Electrolytic processes.—The electrolytic processes of manufacture depend upon the formation of sodium hydroxide during the electrolysis of aqueous solutions of sodium chloride. The chlorine obtained as a by-product is used in the manufacture of bleaching powder, etc. The hydroxide is converted into sodium carbonate by treatment with carbon dioxide, which is obtained as a by-product in the fermentation industries, etc. Everything is utilized so that the cost essentially depends upon the price of the current used.

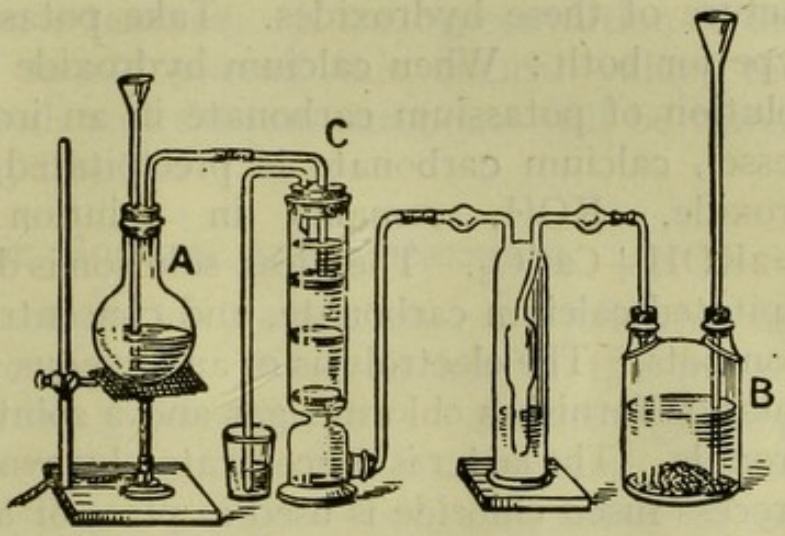


FIG. 172.—Illustration of Solvay's Process.

IV. Potassium carbonate.—Potassium carbonate cannot be made by Solvay's process because acid potassium carbonate is too soluble. A great deal of the potassium carbonate of commerce is made by le Blanc's process. It is also made from the potassium chloride or sulphate of the Stassfurt deposits by forcing carbon dioxide into a solution of the salts. The precipitate is a mixed carbonate of magnesium and potassium. When this is treated with steam, the magnesium carbonate forms an insoluble magnesium hydroxide, and the potassium carbonate can be recovered by lixiviation with water, and subsequent evaporation.

§ 3. Potassium and Sodium Hydroxides.

Preparation.—Sodium and potassium hydroxides cannot be conveniently made by calcining the corresponding carbonate

and digesting the residue with water as in the case of calcium hydroxide, because the two alkali carbonates do not decompose so readily as calcium carbonate. The preparation of the oxides of potassium and sodium is rather difficult and expensive. Hence, although the hydroxide can be made by the action of water on these oxides, it is far more economical to employ other methods of preparation. Two processes are used in the manufacture of these hydroxides. Take potassium hydroxide as a type for both: When calcium hydroxide is added to a boiling solution of potassium carbonate in an iron or silver or nickel vessel, calcium carbonate is precipitated, and potassium hydroxide, KOH, remains in solution: $Ca(OH)_2+K_2CO_3=2KOH+CaCO_3$. The clear solution is decanted from the precipitated calcium carbonate, and concentrated by heating it in iron pots. The electrolysis of an aqueous solution of potassium chloride furnishes chlorine gas and a solution of potassium hydroxide. The latter is concentrated by evaporation. In Acker's process fused chloride is used in place of an aqueous solution.

Theory of preparation.—The reaction between potassium carbonate and calcium hydroxide has many points of interest. It is best studied in the light of the theory of equilibrium, so useful in the study of chemical reactions generally. The four salts in solution are in equilibrium, and accordingly, the reaction is represented: $K_2CO_3+Ca(OH)_2\rightleftharpoons CaCO_3+2KOH$. An excess of solid calcium hydroxide is supposed to be present at the start so that as fast as calcium hydroxide is removed *from* the solution by reacting with the potassium carbonate, more passes *into* solution. Thus the concentration of the calcium hydroxide in the solution is kept constant. The solubility of calcium carbonate is very small, and, in consequence, any calcium carbonate in excess of the solubility constant will be precipitated as fast as it is formed. The reaction proceeds steadily from left to right because, all the time, calcium hydroxide steadily passes into solution, and calcium carbonate is steadily precipitated. But the solubility of calcium carbonate steadily increases with increasing concentrations of potassium hydroxide. There is a steady transformation of the potassium carbonate into potassium hydroxide

in progress. The concentration of the potassium carbonate is steadily decreasing, while the concentration of the potassium hydroxide is steadily increasing. Consequently, when the potassium hydroxide has attained a certain concentration, so much calcium carbonate will be present in the solution that the reaction will cease. Hence, the concentration of the potassium carbonate should be such that it is all exhausted before the state of equilibrium is reached. If the concentration of the potassium hydroxide should exceed this critical value, the reaction will be reversed, and calcium carbonate will be transformed into calcium hydroxide.

§ 4. Metallic Sodium and Potassium.

Discoveries in science are very often made by following up hints received from analogies. The isolation of the metals potassium and sodium is a good illustration. At the beginning of the nineteenth century, the so-called alkalies and alkaline earths—magnesia, lime, and potash—were considered to be elementary substances. Lavoisier proved that some things resembling the earths—*e.g.* tin oxide, iron rust, mercuric oxide—could be resolved into two substances, oxygen and a metal. By analogy, it was inferred that it might be possible to resolve the alkalies and the alkaline earths into the corresponding metals and oxygen. After it had been shown that the electric current could resolve water and certain other salts into their elements, H. Davy tried if the electric current would work in an analogous manner on caustic soda and caustic potash. As a result, Davy isolated the metal potassium on October 6, 1807, and sodium a few days afterwards. This discovery was soon followed by the isolation of barium, strontium, and calcium. By analogy, it was further inferred that all amorphous powders—alumina, magnesia, etc.—possessing similar properties, were metallic oxides. As a result, when a new earth is now discovered, chemists believe, by faith, that it is the oxide of a metal even in cases where the supposed metal has never been isolated.

Davy exposed a piece of solid potassium hydroxide to the atmosphere for a few seconds, so that a conducting film of

moisture formed on the surface. The piece of potash was then placed on an insulated disc of platinum connected with the negative pole of a battery, and a platinum wire connected with the positive pole was brought in contact with the upper surface of the potash. Davy adds :

> Under these circumstances a vivid action was observed to take place. The potash began to fuse at both its points of electrification. There was a violent effervescence at the upper surface ; at the lower, or negative surface, there was no liberation of elastic fluid ; but small globules having a high metallic lustre, and being precisely similar in visible character to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surface. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle, the basis of potash.

If a cavity be cut in the potash and a little mercury be placed therein, this may be used as the cathode, and an amalgam of potassium or sodium will be obtained when the mercury is made the cathode, as illustrated in Fig. 173.

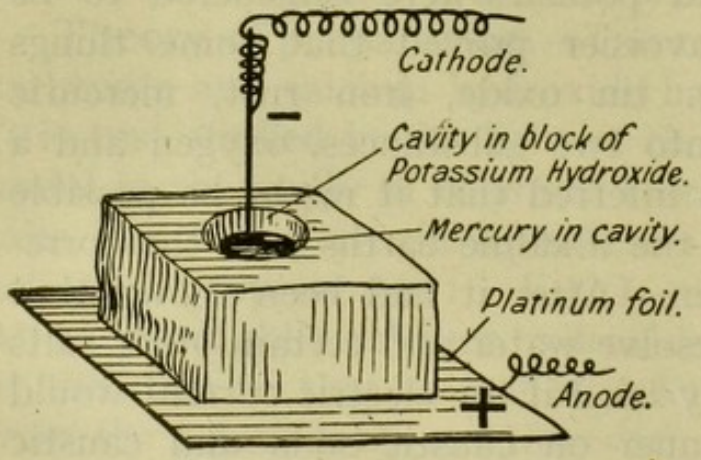


FIG. 173.—Imitation of Davy's Experiment on Electrolysis of Potassium Hydroxide.

Soon after Davy's discovery, J. L. Gay-Lussac and L. J. Thénard (1808) prepared the metal by heating metallic iron with potash at a white heat : $4KOH+3Fe=Fe_3O_4+2H_2+4K$. The potassium metal vaporized, and condensed in a copper receiver containing rock oil to prevent the oxidation of the metal.

In modern works, where cheap electrical energy is available, modifications of Davy's original process—electrolysis of fused potassium hydroxide—are used for preparing sodium industrially, *e.g.* H. Y. Castner's electrolytic process (1890). Metallic sodium is prepared by a similar process substituting sodium for potassium hydroxide.

H. Y. Castner's electrolytic process for sodium.—This may be illustrated by the laboratory model shown in Fig. 174. The sodium hydroxide, contained in an iron bottle, is melted by means of a ring of gas jets placed underneath ; and kept about 20° above the melting-point (310°) of sodium hydroxide. The iron cathode rises through the bottom of the iron bottle, and is maintained in position by a cake of solid sodium hydroxide in the lower part. The cake is kept cold because it is surrounded by a jacket through which cold water flows. The anode is an iron cylindrical pot as shown in the drawing. A cylindrical receiver is supported in the fused alkali above the cathode. When a current of about 50 amperes and 6 volts passes through the electrodes, the sodium and hydrogen liberated at the cathode collect under this cylinder. The hydrogen escapes through the cover, and the atmosphere of hydrogen in the cylinder protects the sodium from oxidation. At the lower end of the receiver is a cylindrical wire gauze guard which prevents the sodium which separates at the cathode from passing through. Castner skimmed off the sodium from

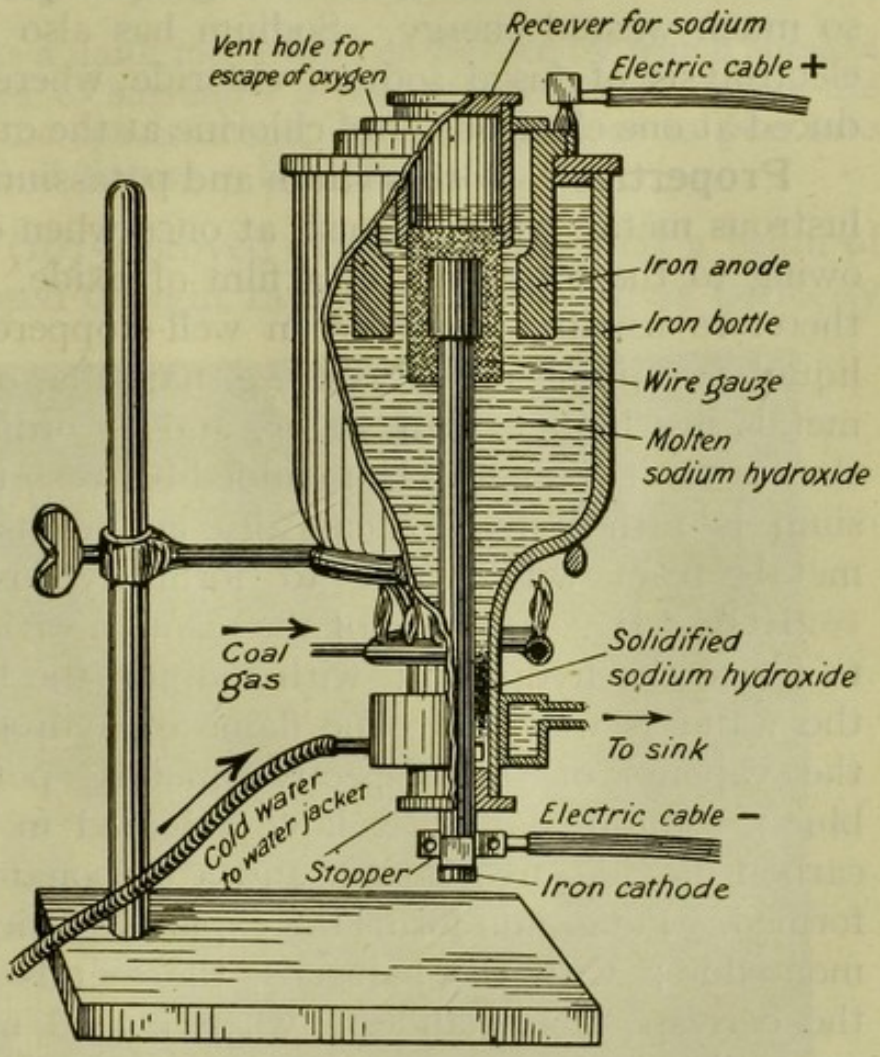


FIG. 174.—Castner's Electrolytic Process for Sodium as used for Illustrative Purposes.

time to time by means of a perforated ladle which retains the liquid metal, but allows the molten hydroxide to flow back. The oxygen liberated at the anode escapes *viâ* the vent. Hydrogen is a by-product in Castner's process, and if there be no commercial demand for this gas, its production represents so much wasted energy. Sodium has also been made by the electrolysis of fused sodium chloride, whereby sodium is produced at one electrode, and chlorine at the other.

Properties.—Both sodium and potassium are silvery-white, lustrous metals which tarnish at once when exposed to the air, owing to the formation of a film of oxide. These metals are therefore usually preserved in well-stoppered vessels, or in a liquid containing no oxygen, *e.g.* naphtha, or petroleum. The metals are lighter than water, and at ordinary temperatures they are soft enough to be moulded between the fingers. Potassium is rather more chemically active than sodium. Both metals react with water to form hydroxides: $2K+2H_2O=2KOH+H_2$. The heat of the reaction with potassium suffices to ignite the hydrogen; with sodium, the hydrogen ignites if the water is warmed. The flame of hydrogen is coloured by the vapours of the respective metals—potassium, lavender-blue; sodium, daffodil-yellow. Heated in an atmosphere of carbon dioxide, free carbon and a carbonate of the metal are formed. Potassium forms the explosive compound with carbon monoxide; with the halogens, the metals take fire, forming the corresponding halides; when heated in hydrogen, white crystalline **hydrides** are formed—KH and NaH; and in air, sodium and potassium burn, each metal forming a mixture of oxides. Perfectly dry air or oxygen has no appreciable effect upon the dry metals.

Uses.—An alloy of potassium and sodium, liquid at ordinary temperatures, is used for some high temperature thermometers above the boiling-point of mercury. Sodium is used in the manufacture of sodium cyanide and sodium peroxide, in drying oils, and in the manufacture of organic compounds.

Occurrence.—Potassium and sodium only occur in nature combined with other elements, but the compounds are widely distributed, being present in many silicate rocks, etc. Potassium

occurs as sylvine, carnallite, kainite, etc., in the Stassfurt deposits (*q.v.*). Sodium is present in sea-water, etc., and it occurs as rock salt (*q.v.*) and as Chili saltpetre (*q.v.*).

§ 5. Spectrum Analysis.

If there ever was a flank movement on Nature by which she has been compelled to surrender a part of her secrets, it was the discovery of the spectroscope, which enables us to peer into the very heart of Nature.—R. C. KEDZIE.

Isaac Newton (1675) proved experimentally that a beam of sunlight is composed of light rays of various colours perfectly

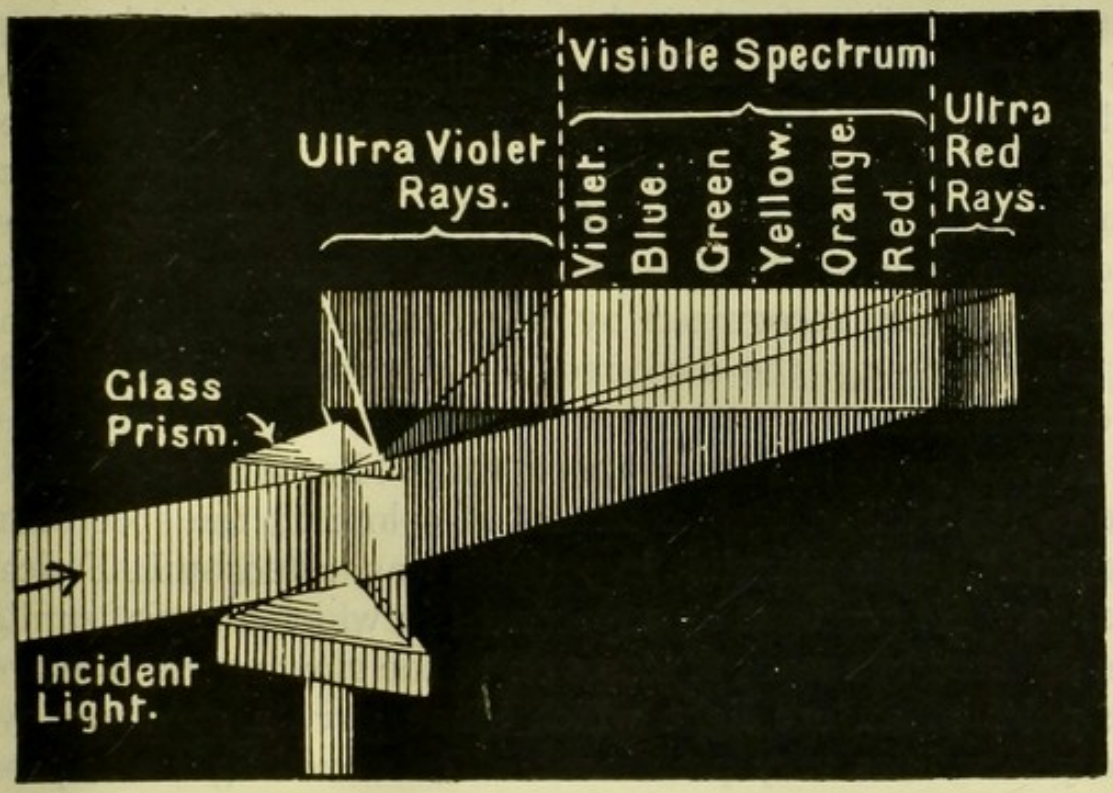


FIG. 175.—Newton's Experiment.

blended and ranging from red through orange, yellow, green, and blue to violet. This Newton did by passing the beam of sunlight through a glass prism, and projecting the beam on to a screen, Fig. 175. The violet, green, and blue rays are bent more in passing through the prism than the yellow, orange, and red rays. The beam of light after passing through the prism thus appears on the screen as an unbroken band of colours, which is called a **continuous spectrum.** Any beam of "white"

light can be used in place of sunlight, for instance, the light from an incandescent solid such as the limelight, Welsbach's mantle, incandescent carbon, etc.

W. H. Wollaston (1802) noticed that a beam of sunlight really furnishes a spectrum which is crossed by a large number of **dark lines**—some sharp and well defined, others more or less faint and nebulous. J. von Fraunhofer (1814–15) carefully mapped the relative positions of a number of these dark lines, and accordingly they are now generally called **Fraunhofer's lines.** It was also shown that incandescent vapours and gases furnish a **discontinuous or line spectrum,** that is, a spectrum composed of a few **bright lines** instead of a continuous band. The line spectra of some elements are comparatively simple, for they display but a few clear distinct coloured lines—*e.g.* sodium a yellow line ; thallium a green line ; indium a blue and an indigo line. Other elements have complex spectra containing numerous lines of varying intensity—*e.g.* barium, strontium, iron. The spectra of some elements, though complex, are easily recognized by the prominence and position of certain lines—*e.g.* the dark red line of rubidium, the blue line of cæsium, etc.

It was provisionally assumed that " Fraunhofer's lines are due to the lack of certain shades of colour in the spectrum of sunlight." This plausible hypothesis was tested by L. Foucault in 1849. He arranged an experiment in which a ray of sunlight was directed by means of lenses on to the glowing gases between the poles of an arc light which alone gave a spectrum with two yellow lines very prominent. The mixed light was passed through a prism. Foucault expected that the lacuna in the solar spectrum corresponding with the yellow lines of the glowing gases in the arc light would be filled by the latter ; and that the yellow portion of the solar spectrum would be continuous. To his astonishment, the dark lines of the solar spectrum corresponding with the " yellow lines " were more pronounced than before. Hence, the preliminary hypothesis cannot be true.

Foucault then suggested the hypothesis that " the incandescent gases in the arc light have the power of absorbing the

yellow from sunlight, as well as of emitting yellow light. The increase in the darkness of these lines is due to this absorbing power being greater than the emissive power." Foucault focussed the light from an incandescent carbon—which by itself gives a continuous spectrum—on to the incandescent gases between the carbon poles. Instead of getting the continuous spectrum of the incandescent carbon with yellow lines enhanced by the spectrum of the gases between the carbon poles, Foucault obtained a spectrum with the dark lines in the yellow portion. This experiment supported his hypothesis —the same kind of light which a gas gives out when heated will be arrested if the attempt is made to pass the light through the gas. Had Foucault known that the yellow lines were due to sodium, he would have recognized the origin of Fraunhofer's lines. This step was taken by G. Stokes, 1852. In 1859, R. Bunsen and G. Kirchhoff definitely settled the question. The subsequent history of spectrum analysis is but an illustration of the fact that when the right explanation of a phenomenon has been found, the facts seem to arrange themselves about the theory as naturally as the particles of a salt in a solution aggregate about the enlarging nucleus of a crystal.

Bunsen and Kirchhoff proved that **every element produces its own characteristic spectrum; and reciprocally, the presence of the vapour of an element can be inferred with certainty when the characteristic lines are present.** The spectrum of an element is so definite and characteristic that it has been seriously proposed to use this as part of the definition of an element. The spectrum of the incandescent vapour of a mixture of elements contains all the lines characteristic of each element in the mixture, and consequently it is possible to recognize each and all of them by measuring the position of the bright lines and comparing the lines with those of known elements. This method of detecting elements is called **spectrum analysis.** Bunsen and Kirchhoff were able to prove that the dark Fraunhofer's lines are due to the rays of light from an incandescent solid passing through vapours of various elements. In other words, Fraunhofer's lines are due to the rays of light from an incandescent sun passing

through the sun's atmosphere, and consequently the vapours of the elements whose line spectra correspond with the dark lines of the solar spectrum must be present in the sun's atmosphere.

By the aid of spectrum analysis, therefore, it has been possible to deduce the presence of a large number of known elements—some 34—in the sun's atmosphere from the coincidence of the bright lines furnished by elements in the laboratory with the dark lines in the solar spectrum. The halogen elements, nitrogen, oxygen, gold, mercury, and a few other elements, have not been detected in the sun. The spectrum of an unknown element—helium—was observed in the solar

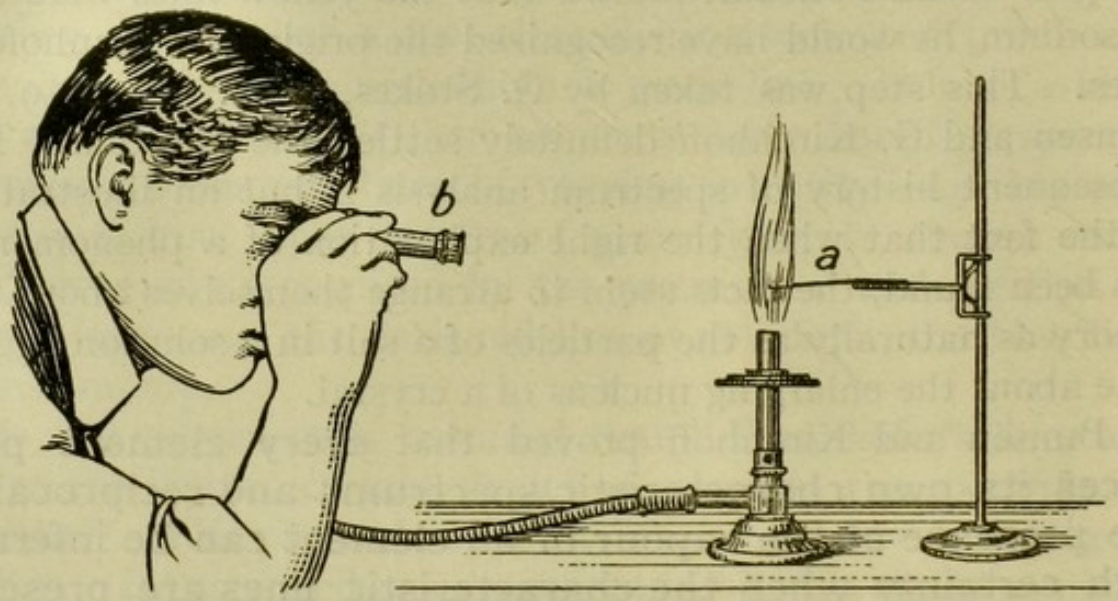


FIG. 176.—Examination of the Spectrum of a Direct-vision Spectroscope.

spectrum some thirty years before the corresponding element was discovered in the earth. The light from the fixed stars furnishes results similar to those obtained with sunlight. Spectral lines characteristic of hydrogen, helium, carbon, magnesium, calcium, and iron have been detected in nebulæ; and hydrogen and hydrocarbons have been recognized in comets.

The spectroscope.—Quite a large number of instruments have been devised for the examination of the spectra of different substances. The so-called direct-vision spectroscopes—*b*, Fig. 176—have a slit at one end to admit the light under

examination. The slit can be narrowed or widened by turning a suitable screw. The beam of light passes from the slit through a prism, and is thence directed to the eye-piece, where it is examined as illustrated in Fig. 174, where a piece of clean platinum wire, *a*, dipped in the solution under examination is held in the Bunsen's flame.

The delicacy of spectrum analysis.—The spectroscope is one of the most delicate means of detecting many substances, and it enables elements to be recognized with certainty when present in quantities far too small to produce an appreciable effect upon the most sensitive reagents known. Thus 1 c.c. of air contains approximately 0·0001 c.c. of neon, and the neon in $\frac{1}{20}$ c.c. of ordinary air, that is, 0·000005 c.c. of neon has been detected by means of the spectroscope. By means of the spectroscope also it is possible to detect the presence of 0·00006 milligram of strontium and of calcium ; 0·00001 milligram of lithium ; and 0·0000003 milligram of sodium. It is not likely that the elements rubidium and cæsium would have been discovered so soon had it not been for their striking spectra. The elements thallium, indium, and gallium were also discovered by the aid of the spectroscope.

§ 6. The Relations between the Alkali Metals.

The five elements, lithium, sodium, potassium, rubidium, and cæsium, called the alkali metals, exhibit an interesting gradation in the properties of the elements and their compounds in accord with the increase in their atomic weights, from member to member, in passing from lithium to cæsium. Lithium, rubidium, and cæsium are not important enough to claim much attention at this stage of our studies. The five metals are silvery white ; soft enough to be cut with a knife ; rapidly tarnish in air ; and decompose water at ordinary temperatures. They are all univalent ; and manifest a remarkable affinity for oxygen—cæsium and rubidium ignite spontaneously if placed in oxygen at the room temperature. The chemical activity of the alkali metals appears to increase steadily in

passing from lithium to cæsium. The gradation in the physical properties is illustrated in Table XX.

TABLE XX.—PHYSICAL PROPERTIES OF THE ALKALI METALS.

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Atomic weight . .	6·94	23·00	39·10	85·45	132·81
Specific gravity . .	0·534	0·9712	0·8621	1·532	1·87
Atomic volume . .	13·1	23·7	45·4	55·8	71·0
Melting-point . .	186°	97°	62·5°	38·5°	26·5°
Boiling-point . .	+1400°	877·5°	700°	696°	670°
Specific heat . . .	0·941	0·293	0·166	—	—

The elements have a remarkably low specific gravity, and a high atomic volume—atomic volume, by the way, is the quotient obtained by dividing the atomic weight of the element by the specific gravity. The oxides and hydroxides are all very soluble in water; they are markedly basic; they do not exhibit acidic qualities. The physical properties of the salts—solubility in water, molecular volume, optical properties, and the variation in the form of the crystals—show the same order of variation as the atomic weights of the elements. Lithium differs in many respects from the other members of the family. The salts of the alkali metals are nearly all soluble in water, although lithium, carbonate, phosphate, and fluoride are very much less soluble than the corresponding salts of the other members. The salts of sodium and lithium form stable hydrates with water, whereas potassium, rubidium, and cæsium salts are nearly all anhydrous. The salts are discussed when dealing with the chlorides, sulphates, etc.

Questions.

1. You are required to neutralize two quantities of 50 grms. each of sulphuric acid (H_2SO_4) diluted with water, the one with caustic soda, the other with sodium carbonate. Describe how you would do this, and how you would ascertain that neutralization had been effected. What difference would be noticeable between the two operations? and what quantity of product would be obtained in each case?—*London Univ. Matric.*

2. Outline the methods that may be used for preparing solid caustic soda. Give its properties, and its chief uses both in the laboratory and on a large scale.—*Adelaide Public Exam. Board.*

3. Describe how Sir Humphry Davy prepared the metals potassium and sodium. How could you distinguish a piece of barium from one of strontium ? The atomic heat of potassium is 6·2, what is its specific heat ?—*London Univ.*

4. Washing soda crystals have the following composition : $NaCO_3.10H_2O$. How much water is contained in a pound (16 ounces) of such soda ? (H=1, O=16, C=12, Na=23.)—*College Preceptors.*

5. An acid whose normal sodium salt is perfectly neutral, forms two classes of salt with monad metals. A mass of the acid, weighing 2·45 grms., is found to require 2 grms. of sodium hydroxide for complete neutralization. What conclusions would you draw from these data ?—*Cambridge Senr. Locals.*

6. Give two methods for causticizing sodium carbonate. To what uses is caustic soda applied ? How can sodium be obtained from it ?—*London Univ.*

7. What is the usual equation representing the action of strong sulphuric acid on metallic copper ? What volume of gas ought to be obtained by the solution of 76·2 grms. of copper, the gas being measured at 21° and 798 mm. ? (Cu=63·5. One litre of hydrogen at 0° and 760 mm. weighs 0·09 grm.) Represent by means of equations the various products (and mixtures of them) which might be obtained by passing a current of the above gas through a solution of sodium carbonate.—*London Univ.*

8. Describe the conversion of salt-cake into soda-ash, and the process of causticizing the ash so as to yield caustic soda. State the impurities commonly occurring in the commercial article.—*Science and Art Dept.*

9. You are supplied with 500 grms. of washing soda crystals with the object of making caustic soda therefrom. How would you proceed, and what weight of product would you expect to get ?—*Science and Art Dept.*

10. From what natural sources are potash compounds obtained ? Describe the mode of manufacture of potassium iodide, and potassium nitrate.—*Science and Art Dept.*

11. Describe how common salt may be converted into soda-ash, soda-crystals, and caustic soda.—*Science and Art Dept.*

12. Describe the general characteristics of metals as a class. Name the alkali metals. State whether the alkali metals and iron attack water and under what conditions.—*Cape Univ.*

13. Potassium, sodium, and silver are called monovalent elements. Why are they so called ? Describe and explain the preparation of potassium from potassium carbonate. How would you distinguish potassium from sodium ?—*London Univ.*

CHAPTER XXII

Copper, Silver, and Gold

§ 1. Copper—Occurrence and Properties.

History.—Copper appears to have been known from prehistoric times—the neolithic age. The "Copper age" followed the "Stone age." Copper appears to have been used for making utensils and instruments for war before iron. This is probably due to the fact that copper occurs native in a form requiring no metallurgical treatment. The ancients used the terms χαλκός (chalcos) and *aes* for copper, brass, and bronze, but the terms for copper and bronze are much confused by the old writers. Copper was afterwards called *aes cyprium* (*i.e.* Cyprian brass), since the Romans first obtained it from the Isle of Cyprus; the term *aes cyprium* was soon abbreviated to *cuprum*. Hence, the modern symbol "Cu." The seven metals—gold, silver, mercury, copper, tin, iron, and lead—known to the earlier chemists, were designated by the names and symbols of the seven greater heavenly bodies—Sun, Moon, Mercury, Venus, Jupiter, Mars, and Saturn. Thus the looking-glass of Venus ♀ symbolized copper. In some cases it is possible to see a fanciful reason why a particular metal was assigned to a particular heavenly body, but in other cases the connection is more obscure.

The properties of copper.—Copper has a characteristic reddish-brown colour by reflected light, but in transmitted light, thin layers are green. Copper is one of the best conductors of heat and electricity. These properties are modified if the metal be contaminated with minute traces of impurity. Dry air has no action on copper, but in the presence of atmospheric moisture and carbon dioxide, the metal becomes covered with a

green basic carbonate called *verdigris*; the atmosphere of towns containing sulphur oxides may also form green basic sulphates with the copper. Hydrochloric and sulphuric acids have little or no action on the metal in the cold; hot sulphuric acid dissolves copper rapidly, and hot hydrochloric acid attacks the metal slowly. Nitric acid—hot or cold, dilute or concentrated—dissolves the metal rapidly, forming copper nitrate. Ammonia acts on copper in the presence of air, forming a deep blue solution.

Copper forms two series of salts corresponding with cuprous oxide, Cu_2O; and with cupric oxide, CuO. Thus cuprous chloride, CuCl; and cupric chloride, $CuCl_2$; cuprous sulphide, Cu_2S; and cupric sulphide, CuS, are all well known.

Uses.—Next to iron, copper is the most useful metal. Enormous quantities are used in the electrical industries. It is also made into household utensils, boilers, etc. Copper nails, rivets, and sheeting are used for sheathing ships, because copper is but slowly corroded in moist air and in sea-water. Copper is one of the chief ingredients in small coins: *British copper coins* contain 95 per cent. of copper, 4 per cent. of tin, and 1 per cent. of zinc. Gold and silver coins of different nations usually contain 8–10 per cent. of copper. *Nickel coins* in Germany and the United States contain about 25 per cent. nickel, and 75 per cent. of copper. Copper is largely used in the manufacture of alloys. With zinc it forms *brass* (zinc 1, copper 2–5)—*common brass* has zinc 1, copper 2; *Dutch metal*, zinc 1, copper 4; *bell metal*, zinc 1, copper 3. *Bronze* is an alloy of copper (70–90 per cent.), zinc (1–25 per cent.), and tin (1–18 per cent.); it is used for making statues, coins, ornaments, etc. *Phosphor bronze* contains tin, copper, and a small percentage of phosphorus; *manganese bronze* contains about 0·3 per cent. of manganese. These alloys are tougher than ordinary bronze, and they are largely used for steamship propellers, because they resist very fairly the corrosive action of sea-water, and for certain parts of machinery. *German silver* contains copper (56–60 per cent.), zinc (20 per cent.), nickel (20–25 per cent.). It is used in making resistance coils (owing to its low electric conductivity), and for imitating silver. Alloys of copper and tin, *speculum metal* (tin 1,

copper 2) used for optical instruments; *gun metal* (tin 1, copper 9) was once used for making cannon. *Aluminium bronze* contains about 90 per cent. of copper; it is a hard yellowish-brown alloy, light, strong, and elastic. It is used for making the hulls of yachts, etc.

The occurrence of copper.—Metallic copper is found in many localities, *e.g.* considerable masses have been found in Michigan on the shores of Lake Superior; and small quantities in many other places—Cornwall, Siberia, Ural, Australia, Chili, etc. Compounds of copper are distributed in nature as oxide in *cuprite*, or ruby ore, Cu_2O; as sulphide in *chalcocite*, or copper glance, Cu_2S; as copper pyrites or *chalcopyrite*, $CuFeS_2$ or $Cu_2S.Fe_2S_3$. Copper also occurs in many places as basic carbonate, *malachite*, $CuCO_3.Cu(OH)_2$; and *azurite*, $2CuCO_3.Cu(OH)_2$. Copper silicates, arsenates, phosphates, etc., are also known to occur native. Copper has also been found in the feathers of some birds.

§ 2. Copper—Extraction.

The methods employed for winning copper from its ores depend upon the kind of ore used, and upon local conditions. Similar ores are seldom treated in the same manner in different localities. If the ore contains no sulphur—as is the case with the carbonates and oxides—the metal can be obtained by simply reducing the ore with coke in a furnace heated by a blast. Assuming that the ore to be melted is a typical chalcopyrite, the operations involved in extracting the copper are somewhat complex, because (1) a large number of impurities are present in the ore; (2) copper of a high degree of purity is needed; and (3) it will probably be profitable to recover gold and silver from the crude metal.

1. Roasting the ore.—The pyritic ore is first crushed, and it may or may not be necessary to concentrate the pyrites by washing away the earthy impurities. Part of the concentrated ore is then roasted, say, in a reverberatory furnace, Fig. 177, in order to convert the sulphides into oxides: $2CuFeS_2+6O_2=Cu_2O+Fe_2O_3+4SO_2$. It may or may not be convenient to use the sulphur dioxide for the manufacture of sulphuric acid.

2. Fusion for matte.—A mixture of roasted and unroasted ("green") ore and coke is charged into a furnace lined with firebricks and heated by a blast. The air blast burns the carbon to carbon monoxide: $2C+O_2=2CO$. Part of the cuprous oxide formed in the preceding operation is reduced to copper by the joint effect of the carbon and carbon monoxide: $Cu_2O+CO=2Cu+CO_2$. The copper unites with the sulphur of the unroasted ore: $3Cu+Fe_2S_3=3CuS+2Fe$; and some of the unreduced cuprous oxide forms cuprous sulphide: $3Cu_2O+Fe_2S_3=3Cu_2S+Fe_2O_3$. Any cupric sulphide present is reduced to cuprous sulphide. The ore probably contains silica, if not, some must be added when the furnace is charged. Part of the

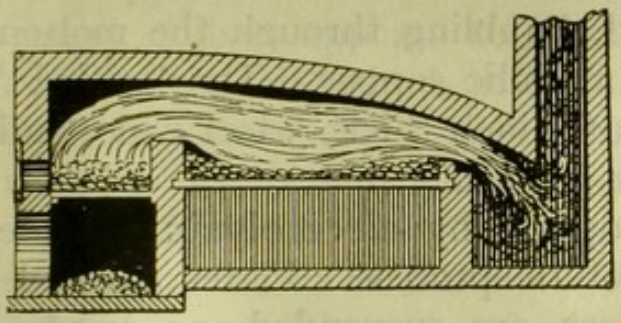


FIG. 177.—Reverberatory Furnace (Diagrammatic).

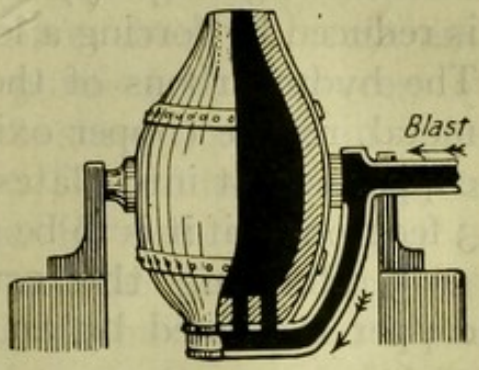


FIG. 178.—"Converter" Furnace (Diagrammatic).

iron unites with the silica to form a fusible slag; and part is reduced to ferrous sulphide, which remains admixed with the cuprous sulphide to form matte. Matte is a more or less impure mixture of cuprous and ferrous sulphides containing 45–75 per cent. of copper. The gold and silver and part of the arsenic and antimony in the ore remain with the matte. The furnace is then tapped, and the matte and slag are run into a trough. The lighter slag rises to the surface and flows over into a pit. The matte, which collects at the bottom of the trough, is drawn off from time to time.

3. The conversion of the matte into blister copper.—The molten matte is run into a tilting "converter" furnace lined with a mixture of quartz and clay, and arranged with openings in the bottom so that air can be blown through the molten matte, Fig. 178. The sulphur, iron, and many other

metals are oxidized. The volatile oxides are driven off, the iron oxide unites with the siliceous lining of the converter to form a slag. The iron and sulphur are oxidized first. As soon as appreciable quantities of copper commence to oxidize, the operator can tell from the appearance of the flame issuing from the converter that it is time to stop the blast. The furnace is then tilted, and the copper is run off. As the copper cools, the sulphur dioxide dissolved by the metal is expelled; this gives the metal a blistered appearance, hence, the product is called **blister copper.**

4. The conversion of blister into crude copper.—The blistered copper is melted on the hearth of a reverberatory furnace—*e.g.* Fig. 177—and any oxide dissolved by the copper is reduced by forcing a log of green wood into the molten mass. The hydrocarbons of the wood, bubbling through the molten metal, reduce copper oxide to metallic copper. The "poled" copper is cast into plates—about $\frac{3}{4}$-inch thick, 3 feet wide, and 3 feet long—if it is to be further purified.

5. Refining the crude copper by electrolysis.—Crude copper is refined by an electrolytic process. Plates of crude copper are suspended, as anodes, in a vat containing a solution of copper sulphate acidified with sulphuric acid. Thin sheets of pure copper, as cathodes, are suspended alternately with the anodes in the same bath, Fig. 179. A great number of these tanks or vats are arranged so that the current from a dynamo can be sent through them; when the current passes, copper dissolves from the anodes, and pure copper is deposited at the cathodes. The impurities in the crude copper either pass into solution—like iron—or are deposited—like lead, silver, and gold—as a sludge or "slime" at the bottom of the vat about the anode. The anode is enclosed in filter cloth bags to facilitate the collection of the "anode mud." Considerable amounts of silver

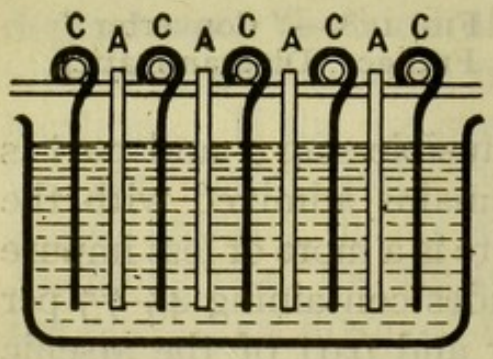


FIG. 179. — Diagrammatic Section of Tank for refining Copper electrically. A = anode. C = cathode.

and gold are obtained from the slimes or "anode mud." It is possible to get a very high degree of purity—*e.g.* 99·8 per cent. copper—by the electrolytic process. This quality of copper is needed for electrical purposes, since a trace of impurity may considerably reduce the electrical conductivity of the metal. Copper matte, blister copper, and even copper ores have been treated, more or less successfully, by a similar process.

§ 3. Silver—Occurrence and Properties.

History.—Silver has been known from ancient times. There are some allusions to silver in the Old Testament, and it was probably used as money as early as gold. The Phœnicians are supposed to have obtained their silver from Armenia and Spain. Silver appears to have been purified by a process of cupellation, but there is little evidence to show that the ancients knew how to separate silver from gold. The old terms for silver refer to its bright white colour—the Hebrew equivalent is derived from the verb "to be white," and the Greek term from ἀργός (argos), to be shining. The early chemists termed silver "Luna," or "Diana," and represented it by the symbol ☽ for the crescent moon—probably because of the pale silvery colour of moonlight.

Properties of silver.—Silver is a white lustrous metal. Powdered silver is grey and earthy in appearance. Silver is highly malleable and ductile. Sheets 0·00001 inch thick have been made. Molten silver absorbs oxygen, and the oxygen often escapes somewhat violently as the molten metal cools, thus producing "spitting." Silver conducts heat and electricity better than copper. Exposure to the air has no action on silver, but if the air be contaminated with hydrogen sulphide, the silver is blackened owing to the formation of a thin film of silver sulphide on the surface. Nitric acid—hot or cold, dilute or concentrated—readily dissolves the metal, forming silver nitrate. Hot concentrated sulphuric acid gives silver sulphate, but the metal is not perceptible attacked by the dilute acid. Hydrochloric acid acts very slowly, if at all, at ordinary temperatures, but at a red heat, hydrogen chloride forms silver chloride.

Uses.—British silver coinage has very nearly 92·5 per cent. of silver and 7·5 per cent. of copper. This is the standard of *sterling silver* for coinage and for silver plate regulated by law. The American dollar has about 90 per cent. of silver. Silver ornaments made from standard silver can be heated in air to oxidize the copper near the surface of the metal, the resulting copper oxide is removed by digestion with sulphuric acid. leaving a superficial layer of pure silver. The effect so produced is called "frosted silver." The so-called "oxidized silver" is made by dipping silver ornaments in a solution of an alkaline sulphide. A thin film of sulphide is thus formed on the surface.

Occurrence.—Native silver is occasionally found in large masses or crystallized in cubes or octahedra. It is also found associated with metallic copper, gold, etc. The principal ores of silver contain silver glance or *argentite*, Ag_2S, admixed with several other sulphides—antimony, arsenic, and copper. The chief silver ores are found in Mexico, Peru, Chili, Bolivia, Idaho, Arizona, Norway, Australia, etc. Much silver also occurs associated with lead in galena, and a great deal of the silver in commerce is extracted from argentiferous lead. Silver chloride, AgCl, occurs as *kerargyrite*, or horn silver.

§ 4. Silver—Extraction.

The methods employed for the extraction of silver are varied.

1. **Cyanide process.**—In the modern **cyanide process,** the crushed ore is treated with a solution of potassium or sodium cyanide—say NaCN, or NaCy. The cyanide reacts with the silver sulphide : $Ag_2S+4NaCy \rightleftharpoons 2NaAgCy_2+Na_2S$. The accumulation of sodium sulphide in the solution stops the reaction. When the solution is exposed to the air, however, the sodium sulphide is oxidized to sodium thiosulphate and sulphur. The reaction then progresses as indicated in the equation from left to right. Thus, the free access of air to the cyanide solution is an important factor in promoting the dissolution of silver. The silver is recovered from the solution by zinc precipitation.

2. **Smelting process.**—The object of the smelting process

is to concentrate the silver in lead. The ore is mixed with coke and limestone, and heated in a small blast furnace. A fusible silicate of iron and lime is formed as a slag, and the reduced metal accumulates in the bottom of the furnace. Slag and metal are run off from time to time. The "pigs" of lead are passed on for desilverization.

3. Electrolytic processes.—The electrolytic process indicated in our study of copper extraction is used for the separation of silver from argentiferous copper. In **B. Moebius' process** (1884), the electrolyte is a mixture of silver and copper nitrates acidified with nitric acid. A slab of impure silver is used as anode, and a plate of pure silver as cathode. Silver and copper are dissolved at the anodes, and silver is precipitated on the cathodes. The gold, if present, remains undissolved as a slime below the anode. The anodes are enclosed in filter bags to facilitate the collection of the "anode mud." The composition and concentration of the solution, as well as the current density are carefully regulated on account of the danger of depositing copper with the silver.

Parke's process for the desilverization of lead.—Silver and zinc form a number of crystalline compounds; these compounds all freeze at a higher temperature than molten lead, and they are specifically lighter than molten lead. Hence, if molten zinc be stirred in a bath of molten argentiferous lead, and the molten mixture be allowed to cool, a crust is formed on the surface containing a zinc-silver compound. Gold in the argentiferous lead also passes with the silver to the zinc. The zinc-silver crystals are ladled from the surface as they are formed until the lead itself begins to solidify. The process can be repeated until finally the remaining lead contains but 0·0005 per cent. of silver. The mixture of zinc, lead, etc., so obtained is heated on an inclined surface hot enough to melt the lead, but not the zinc alloy. The lead flows away, and the enriched scum remains. The zinc can be separated from the silver, gold, and lead by distillation. The residue in the retort containing the silver and gold is cupelled.

Refining gold and silver by cupellation processes.—The gold or silver is alloyed with an easily oxidizable metal, say,

lead. The alloy of lead is heated in a stream of air in a furnace with a shallow hearth made of bone ash. The lead is oxidized to litharge, PbO, which is then partly blown from the surface of the molten metal, and partly absorbed by the bone ash. When the gold or silver appears as a bright disc, the operation is stopped and the gold or silver removed. If both silver and gold be present, these metals remain alloyed after the operation, and they must be separated by some other process—say, "parting with sulphuric acid."

Parting with sulphuric acid.—In the old process of parting silver and gold, known as **quartation,** an alloy of gold and silver, containing less than 25 per cent. of gold, was treated with nitric acid. The silver dissolved as silver nitrate, and the gold remained behind undissolved as a brown powder. Parting with sulphuric acid is cheaper. Here the alloy is boiled with concentrated sulphuric acid, then with nitric acid. The gold is not attacked, and it remains behind as a brown porous mass. This is washed, dried, and fused into a compact mass with sodium carbonate and charcoal.

§ 5. Gold—Occurrence and Properties.

History.—Gold must have been one of the earliest of metals to attract the attention of primitive man, since it occurs free in nature, and is found in rocks and in the gravels of many rivers. Flint daggers with gilt handles have been reported from excavations in Egypt, and gold is mentioned in the earliest writings of civilized man. Representations of quartz crushing and gold refining processes are reported to have been found on Egyptian tombs dated 2500 B.C.; and a kind of map showing the gold-mining region 1350–1300 B.C. has been similarly reported. The gold mines of Nubia were worked extensively by the early Egyptians. Pliny described the amalgamation process for the extraction of gold. Cupellation processes for the purification of gold were described in the second century, and the same process is probably referred to by Jeremiah in the Old Testament, 600 B.C. The earliest words for gold in Hebrew and Egypt refer to its shining appearance. The early chemists

called gold *sol* (the sun) and represented it by the symbol of perfection ⊙ or ☼ ; not altogether on account of its appearance, but because they considered it to be the most perfect of the noble metals—the very king of metals.

Properties.—Gold in mass is yellow ; gold-leaf is green or blue in transmitted light ; and if precipitated in a fine state of subdivision the tint varies from red to dark brown. Very thin films of gold are crimson or purple in transmitted light. It is one of the most malleable and ductile of metals, sheets 0·000004 inch thick have been made. It is not quite so good a conductor of heat and electricity as silver and copper. Gold melts at 1062·4° ; and the molten metal appears green. Gold is not acted upon by air or oxygen at any temperature.

Solvents for gold.—Gold is but slightly, if at all, attacked by water, nitric, sulphuric, nor hydrochloric acids, although it is dissolved by aqua regia ; by water containing the halogens chlorine, bromine, or iodine in solution ; and by solutions which can generate the halogens. Gold is attacked by boiling ferric chloride solutions, hot selenic acid, telluric acid with sulphuric or phosphoric acid, alkaline sulphides and thiosulphates, perchlorates, perbromides, and periodides of the metals, iodic and periodic acids with hot sulphuric acids, and by reacting substances which give large quantities of oxygen—manganese dioxide or potassium permanganate or nitric acid with sulphuric acid—and aqueous solutions of potassium cyanide when exposed to the air. Gold is not appreciably attacked by solutions of the alkalies.

Uses.—British gold coinage contains 91·66 per cent. of gold and 8·33 per cent. of copper. This is called sterling or standard gold. The gold coinage of Sydney mint has the same amount of gold, but silver is used in place of copper, so that the Sydney sovereign is greenish-yellow. The amount of gold in alloys is usually expressed in terms of the *carat*. Here, 1000 parts are divided into 24 equal parts. Pure gold is 24-carat gold. The sovereign is a 22-carat alloy because it contains 22 parts of gold per 2 parts of other metals. The standard gold alloys recognized by law are 22-, 18-, 15-, 12-, and 9-carat, or parts of gold per 24 parts of alloy. Ware made by these standard alloys can be

"hall-marked." American gold coinage has 90 per cent. of gold and 10 per cent. of copper.

Occurrence.—Gold is generally found in a metallic condition in quartz veins, and in alluvial gravels, the latter represents the *débris* from the weathering of auriferous rocks. Native gold is never found pure, but specimens 99 per cent. purity are sometimes found; and one from Cripple Creek (Colorado) was reported to be of 99·9 per cent. purity. Metallic gold is very widely distributed in nature in quantities too small to be profitably extracted. Sea-water, for instance, is said to contain about $3\frac{1}{2}$ grains per ton. Granite, on the average, has about 0·37 part per million; sandstones, 0·03 part per million; limestones, 0·007 part per million. Gold also occurs in small quantities in clays, iron pyrites, and in almost all silver, copper, bismuth, lead, zinc, tellurium, and antimony ores. Gravels which need not be crushed can sometimes be profitably treated for gold—alluvial gold—if but 2 to 3 grains per ton be present, that is, one part of gold per 5 million parts of worthless material. The mean of the returns for the Rand is something less than half an ounce of gold per ton of material treated.

§ 6. Gold—Extraction and Refining.

Washing processes.—The amount of gold in a ton of ore is small, and in consequence, relatively large quantities of ore have to be treated. Gold is separated from alluvial gravel by mechanical washing. The specific gravity of gold is so much greater than that of the associated materials, that, when the mixture of sand and gravel is agitated with water in large pans or "cradles," and the rocky matters floated off, the fine particles of gold remain on the bottoms of the cradles as "gold dust." This primitive method of washing has been replaced by **placer mining,** in which the sand containing the gold is agitated in sluices, that is, in long flumes or troughs with transverse cleets along the bottom, and through which powerful streams of water flow. The water sweeps away the sand, and the heavier gold collects on the bottom of the sluices. In **hydraulic mining,** water under high pressure is directed against the "earth"

containing the gold. The "earth" and gold are washed into the sluices as in placer mining. In **vein mining,** the gold-bearing quartz is mined by blasting, etc.; the quartz is crushed to fine powder in stamper mills, and the gold extracted by one of the following processes:—

Amalgamation process.—The powder from the stamper mills is floated as a "slime" in a large trough through which water is continually flowing. The slime then runs over copper plates amalgamated with mercury. The particles of gold amalgamate with the mercury. After some time the plates are scraped, and the mercury removed from the scrapings by distillation. Gold remains behind in the retorts. The "tailings" which have passed over the copper plates can usually be profitably treated by the cyanide process, and more gold extracted.

Chlorination process.—Gold can be extracted from pyrites by the chlorination process. The ore is first roasted, then wetted, and exposed in revolving barrels to the action of chlorine gas. The gold forms auric chloride, $AuCl_3$, which is extracted by water, and precipitated from the solution by ferrous sulphate, or by hydrogen sulphide—followed by roasting of the precipitated sulphide.

Cyanide process.—The powdered ore is leached with a dilute (0·25 to 1 per cent.) aqueous solution of potassium cyanide, KCN, or KCy, while freely exposed to the atmospheric air. Under these conditions, gold is dissolved as a double cyanide: $4Au+8KCy+2H_2O+O_2=4KOH+4KAuCy_2$. Gold is precipitated from the solution either by the addition of zinc shavings: $2KAuCy_2+Zn=K_2ZnCy_4+2Au$; or by electrolysis. The gold is collected as a compact mass by fusion with sodium carbonate and charcoal.

Refining gold.—Gold is refined by electrolysis, and by cupellation and parting (p. 405). In the electrolytic process, the anode is the alloy to be purified; the electrolyte is a solution of gold chloride in hydrochloric acid, and the cathode is pure gold. On electrolysis, fairly pure gold is deposited on the cathode, silver forms silver chloride which remains as a deposit about the anode.

§ 7. Colloidal Gold and Silver.

If a solution containing 0·01 to 0·001 per cent. of gold chloride be made slightly alkaline by the addition of magnesia, and then a few drops of a reducing agent—formaldehyde, oil of turpentine, aqueous solution of acetylene, aqueous solution of phosphorus in carbon disulphide, carbon monoxide gas, sodium hyposulphite, $Na_2S_2O_4$, etc.—be added, the solution will probably acquire a ruby-red colour. Metallic gold is present in the form of minute particles which do not settle under the influence of gravity, and consequently remain suspended an indefinite time, and the solution can be filtered through paper unchanged. The solution is sometimes called **Faraday's gold,** because it was studied by M. Faraday in 1857. The gold is in colloidal solution because the clear solution appears opalescent by Tyndall's optical test, and the particles can be perceived by the ultra-microscope. Similarly, by the action of certain reducing agents on soluble silver salts, Carey Lea (1887) obtained coloured solutions containing **colloidal silver** from which finely divided silver was obtained coloured golden-yellow, ruby, blue, etc.

Purple of Cassius.—If a mixture of stannic and stannous chlorides be added to a very dilute solution of gold chloride, hydrated stannic oxide is precipitated and the gold chloride is reduced to the metal. The precipitate of stannic hydroxide may have tints varying from red to violet according to the concentration and composition of the solution. This precipitate is called purple of Cassius because A. Cassius wrote a pamphlet —entitled *De Auro*—describing its preparation in 1685. The mode of making this substance must have been known long before this, because it was used at that time for colouring glass and enamels. The colour of purple of Cassius is due to the precipitation of finely divided gold on the stannic hydroxide. Similar colours are made by precipitating gold on magnesium, calcium, and barium hydroxides, barium sulphate, zirconium oxide, alumina, lead sulphate, and china clay. Purple of Cassius remains as a residue when alloys of gold, and tin with a large excess of silver, are treated with nitric acid ; and when a

gold-tin alloy is vaporized in air. The tin burns to stannic oxide, and it is at the same time stained by the condensation of the vapour of metallic gold. The old view that purple of Cassius is a compound of tin oxide and aurous oxide has been abandoned.

§ 8. Copper, Silver, and Gold—Oxides and Hydroxides.

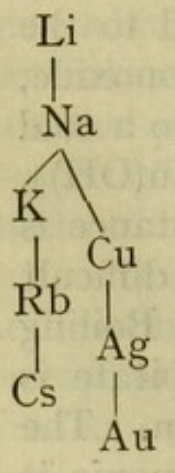
The three monoxides, Cu_2O, Ag_2O, and Au_2O, are here indicated in the order of their stability. **Cuprous oxide,** Cu_2O, is the most stable of the copper oxides. It is formed by heating copper or copper oxide in air to a high temperature; **silver oxide,** Ag_2O, decomposes between 250° and 300°; and aurous oxide, Au_2O, decomposes at about 250°. Similar remarks apply to the hydroxides. A series of well-defined salts corresponding with Ag_2O are known—**silver nitrate,** $AgNO_3$; **silver sulphate,** Ag_2SO_4, etc. With the exception of silver carbonate, Ag_2CO_3, these salts do not appear to be hydrolyzed by water. A few cuprous salts are known; and **aurous oxide,** Au_2O, like cuprous oxide, exhibits little tendency to form salts.

Cupric oxide, CuO, is formed as a black hygroscopic powder when copper is heated in air or in oxygen, or by the calcination of copper nitrate, carbonate, or hydroxide. When heated to a high temperature, cupric oxide cakes, fuses, and decomposes, giving a mixture of cuprous and cupric oxides, and finally cuprous oxide. Cupric oxide, when heated, is reduced to the metal by reducing agents—hydrocarbons, carbon monoxide, hydrogen, etc. When an alkaline hydroxide is added to a cold solution of a cupric salt, pale blue **cupric hydroxide,** $Cu(OH)_2$, is precipitated. If the liquid be boiled, a black substance is formed, possibly a mixture of $Cu(OH)_2$ and Cu_2O. It is difficult to wash away the alkalies from the blue precipitate. Boiling water converts it into cupric oxide. The blue precipitate is soluble in an excess of alkali, forming a blue solution. The solution of cupric hydroxide, $Cu(OH)_2$, in aqueous ammonia is called *Schweitzer's reagent.* It dissolves cellulose (cotton wool, filter paper, etc.). The cellulose is reprecipitated when the solution is acidified with hydrochloric acid.

Auric oxide, Au_2O_3.—Silver has been reported to form an **argentic oxide,** AgO, corresponding with cupric oxide. When a solution of potassium hydroxide is added to a boiling solution of gold chloride, a brown powder—auric oxide, Au_2O_3—is precipitated. If the solution is cold, an orange-coloured precipitate of **auric hydroxide,** $Au(OH)_3$, separates. This is dehydrated at 100°, forming AuO.OH ; at 160°, a dark chestnut brown auro-auric oxide, AuO, is formed ; and finally auric oxide, Au_2O_3. At 250° auric oxide decomposes into its elements. Auric hydroxide is soluble in an excess of alkali, forming a complex salt, **potassium aurate,** $KAuO_2$, which is precipitated by the addition of nitric acid. The aurates are crystalline salts somewhat unstable, and soluble in water. Auric oxide, Au_2O_3, dissolves in hydrochloric acid, forming a complex **hydrochloro-auric acid,** $HAuCl_4$, which forms a series of complex salts, **chloroaurates.** A **silver sesquioxide,** Ag_2O_3, has been reported.

§ 9. The Family Relationship of Copper, Silver, and Gold.

These three elements are generally classed together in so-called "systematic chemistry," and they are furthermore considered to be related with the alkali metals. The copper group of elements is generally linked with the alkali-metals by the scheme indicated in the margin, which starts with the elements with the lowest atomic weights. The fault with the scheme is that it makes the relationship appear far closer than is indicated by known facts. If we recall the relationship between the members of, say, the alkali metals, and the halogen families, the relationship between the individual members of this so-called family and the alkali metals is strikingly obscure. The student might well inquire why these elements are grouped together at all, and cogent reasons might be urged for grouping gold with platinum, silver with palladium, and copper with mercury. The reason why this is not done will appear when we take a general survey of all the



elements. Returning to the elements copper, silver, and gold, the physical properties may be tabulated :

TABLE XXI.—PHYSICAL PROPERTIES OF COPPER, SILVER, AND GOLD.

	Copper.	Silver.	Gold.
Atomic weight . .	63·6	107·88	197·2
Specific gravity . .	8·93	10·49	19·265
Atomic volume . .	7·07	10·28	10·11
Melting-point . . .	1082·6°	960·0°	1062·4°

In malleability, ductility, and tenacity, silver is intermediate between copper and gold. While the large atomic volume of the alkali metals was associated with great chemical activity and affinity for oxygen, the low atomic volume of these elements is related with their weak affinity for oxygen, etc. Copper, for instance, is alone oxidized in air. Silver appears to be uni-, bi-, and ter-valent, but copper is both uni- and bi-valent, and gold is uni- and ter-valent. Hence, these three elements have univalency in common with the alkali metals. Silver seems to be related with copper through a little known argentic oxide, AgO, where silver appears to be bi-valent, but the alkalies do not form oxides of this type ; with gold, through a little known silver sesquioxide, Ag_2O_3 ; and with the alkalies through argentous oxide, Ag_2O, and in the type of its salts. The haloids of the alkalies are all soluble in water, and are not hydrolyzed by water. Copper and silver form sparingly soluble haloids, and the haloids of copper and gold, not silver, are hydrolyzed by water. The oxides and hydroxides of the alkalies are strongly basic ; the oxides and hydroxides of copper and gold are feebly basic, and they accordingly form basic salts. The similarity of the following pairs of salts is significant : AgI and CuI ; AgBr and CuBr ; AgCl and CuCl ; Ag_2S and Cu_2S, as well as the oxides Ag_2O and Cu_2O. The alkali metals do not form complex salts, whereas copper, silver, and gold, do.

§ 10. The Electrochemical Series of Elements.

Magnesium or zinc, as we have seen, will displace hydrogen from dilute acids : $Mg+H_2SO_4=MgSO_4+H_2$; magnesium will also precipitate metallic zinc from a solution of a zinc salt : $Mg+ZnSO_4=MgSO_4+Zn$. Zinc, in turn, will precipitate iron from iron salts ; iron will precipitate copper from copper salts ; and copper will precipitate silver from silver salts. By treating the different metals in this manner, it has been found possible to arrange them in a series such that any metal in the list will displace those which follow it, and be displaced by those which precede it, thus :

$$Mg \rightarrow Al \rightarrow Mn \rightarrow Zn \rightarrow Cd \rightarrow Fe \rightarrow Co \rightarrow Ni \rightarrow Sn \rightarrow Pb \rightarrow Bi \rightarrow \text{etc.}$$

Again, when zinc is treated with dilute acids under suitable conditions in a voltaic cell (Fig. 40), so as to eliminate disturbing effects, the reaction produces an electric current of a certain strength. If the zinc be replaced by certain other metals—aluminium, magnesium, etc.—the strength of the current is increased ; and conversely, if the zinc be replaced by other metals—cadmium, iron, cobalt, etc.—the strength of the current is diminished. It is thus possible to arrange the elements in a series representing the strength of the current (in volts) developed between the metals and solutions of their salts.

The order here is virtually the same as the above list showing the order in which the elements displace one another from their salts. The list of the elements so arranged is called **the electrochemical series.** A short series is illustrated in Table XXII.

It will be noticed that the series only refers to the action of the *free* elements, and it has no direct reference to the mutual action of compounds of the elements upon one another.

The order may vary a little with different solutions ; secondary reactions may prevent the precipitation of the metal. In many cases, the displacement is so complete that the reaction is employed in quantitative analysis—*e.g.* cadmium or iron will precipitate tin quantitatively from a solution of tin chloride acidified with hydrochloric acid ; and cadmium or

zinc will precipitate silver from a solution of silver sulphate acidified with sulphuric acid. The further apart the metals in the series, the greater the amount of heat liberated when the displacement occurs, *e.g.* when zinc precipitates silver than when it precipitates tin. Similar remarks apply, *mutatis mutandis*, to the speed of precipitation. A similar table would be obtained if the elements were arranged in the order of their chemical activity. Thus, the earlier members on the list oxidize or rust on exposure to the air; oxides of the metals succeeding manganese are reduced to metals when heated in a stream of hydrogen, while the metals which precede manganese, under the same conditions, may be reduced to lower oxides, but not to the metallic condition. The oxides of the metals mercury to platinum may be decomposed by simply heating. The metals preceding hydrogen on the list can give hydrogen when treated with acids, although secondary actions may simultaneously lead to the formation of some product other than hydrogen. The metals succeeding hydrogen do not usually displace hydrogen from the acids. With the possible exception of tin and lead (metals close to hydrogen) the free elements preceding hydrogen are rarely found in nature excepting possibly in meteorites. That arises from the fact that natural waters containing carbonic and other acids in solution attack these metals; consequently, even if these elements were produced

TABLE XXII.—ELECTROCHEMICAL SERIES OF THE ELEMENTS.

Potassium	"Metals."
Sodium	
Barium	
Strontium	
Calcium	
Magnesium	
Aluminium	
Chromium	
Manganese	
Zinc	
Cadmium	
Iron	
Cobalt	
Nickel	
Tin	
Lead	
Hydrogen	
Antimony	
Bismuth	
Arsenic	
Copper	
Mercury	
Silver	
Palladium	
Platinum	
Gold	
Silicon	"Non-metals."
Carbon	
Boron	
Nitrogen	
Selenium	
Phosphorus	
Sulphur	
Iodine	
Bromine	
Chlorine	
Oxygen	
Fluorine	

by subterranean agents—volcanic or otherwise—they must succumb to attack by natural waters.

Questions.

1. How may metallic copper be converted into (*a*) cupric oxide, (*b*) cupric sulphate? How may the difference in composition between cupric oxide and cuprous oxide be demonstrated experimentally?—*Victoria Univ.*

2. If you were provided with the following substances, viz. sulphuric acid, nitric acid, hydrochloric acid, zinc, copper, and marble, what gases could you prepare? Write a brief account of their properties, and state how they could be distinguished from each other. Write the names and formulæ for the products of each action.—*London Univ.*

3. Describe in detail the methods you would adopt in the laboratory to prepare the following substances in the pure state from metallic copper: cupric oxide, cuprous oxide, cuprous chloride, cupric sulphate.—*London Univ.*

4. Describe the method of obtaining copper, and name its most important alloys.—*Science and Art Dept.*

5. What are the chief sources of silver? Describe how the metal is obtained from argentiferous lead.—*Science and Art Dept.*

6. Describe the preparation and the properties of the chlorides and oxides of copper.—*Delegacy of Local Exams.*

7. What is meant by the equivalent of an element? How would you determine experimentally the equivalent of (*a*) copper, (*b*) chlorine? What other considerations must be taken into account in order to fix the atomic weight of one of these elements? —*Board of Educ.*

8. Give a brief general account of the metal copper, its occurrence in nature, methods of extraction, and typical salts.—*Sydney Univ.*

9. What happens when nitric acid is poured on metallic copper, and the resulting substance heated? How would you proceed to prepare metallic copper from the residue?—*Cape Univ.*

10. Given a sovereign, how would you obtain from it pure gold and pure copper?—*Cape Univ.*

11. If supplied with metallic copper, how would you prepare the following compounds: cupric sulphate, cupric chloride, cuprous chloride, cuprous oxide? Describe the appearance of each of these substances, and the effect, if any, of water on each.—*Panjab Univ.*

12. In what respects do the salts of copper resemble those of mercury? How would you ascertain whether a given salt of copper is a cuprous or cupric salt?—*London Univ.*

13. Commercial lead frequently contains small quantities of silver. How can this latter metal be economically extracted ?—*London Univ.*

14. Of what use are the salts of silver in photography ? State how the silver print is made permanent in a photograph.—*Science and Art Dept.*

15. Describe the behaviour of a piece of silver with (*a*) nitric acid, (*b*) hydrochloric acid, and (*c*) sulphuric acid.—*Science and Art Dept.*

16. What substances are produced when potash and lime are added to separate portions of hydrochloric acid ; and when nitric acid is poured upon a penny piece ?—*Science and Art Dept.*

17. How is zinc extracted from its ores on a large scale ? Define the term *alloy* and *amalgam*, giving an example of each.

18. How would you prepare specimens of zinc oxide and of zinc sulphide from zinc carbonate ? What weight of zinc sulphide can be obtained from 100 grms. of zinc carbonate ?

19. How is hydrogen sulphide obtained ? Sketch and explain the working of the Kipp's apparatus used for supplying hydrogen sulphide in the laboratory. Explain by means of equations what changes take place when hydrogen sulphide is passed into (*a*) copper sulphate solution, (*b*) chlorine water.—*Cambridge Univ.*

20. How is metallic copper extracted from its ores ? Given metallic copper how would you prepare from it two oxides and two chlorides ? What are the properties of these compounds ?—*Cambridge Univ.*

CHAPTER XXIII

The Ionic Hypothesis

§ 1. Faraday's Laws of Definite Electrolytic Action.

It will now be interesting to study electrolysis—pp. 76 and 125—in a little more detail, and, in order to fix a unit for measuring quantities of electricity it has been agreed to call the amount of electricity which is required to deposit 0·001118 grm. of silver a **coulomb**. If copper sulphate be used in place of silver nitrate, then a coulomb of electricity will deposit 0·03555 grm. of copper. By placing an electrolytic cell containing a solution of silver nitrate or of copper sulphate in the path or circuit of a current of electricity, it is possible to find the quantity of electricity which has passed through the circuit by weighing the amount of silver deposited in the silver nitrate cell or of copper in the copper sulphate cell. The cell specially designed for such measurements is called a **silver voltameter** or a **copper voltameter** respectively. For instance, if 1·08 grms. of silver be deposited in a silver voltameter, $1{\cdot}08 \div 0{\cdot}001118 = 965{\cdot}4$ coulombs of electricity must have passed through the circuit.

M. Faraday (1834) found that the amount of chemical work done by an electric current is directly proportional to the quantity of electricity which passes through the electrolyte. If 96,540 coulombs lead to the separation of 108 grams of silver, $2 \times 96{,}540$ coulombs will lead to the separation of 216 grams of silver, and so on. Similar results are obtained with other electrolytes. Hence, said Faraday, "**the chemical decomposing action of a current is constant for a given quantity of electricity.**" Or "the quantity of chemical decomposition

is exactly proportionate to the quantity of electricity which has passed " through the electrolyte.

Provided there are no disturbing secondary actions, the amount of electro-decomposition is not affected by the strength (or intensity) of the current, the time the current is passing, the concentration of the solution, the nature of the dissolved substance, nor by the temperature. The same quantity of electricity will always liberate the same quantity of the elements stated. The accuracy of the law is said to have been established for " currents so small that a century would be required for the separation of a milligram of hydrogen," and in large electrochemical works, the law is continually being verified by the passage of millions of coulombs. In every case, the law describes the phenomena exactly.

Again, let a current be *simultaneously* passed through six cells containing respectively dilute sulphuric acid, aqueous

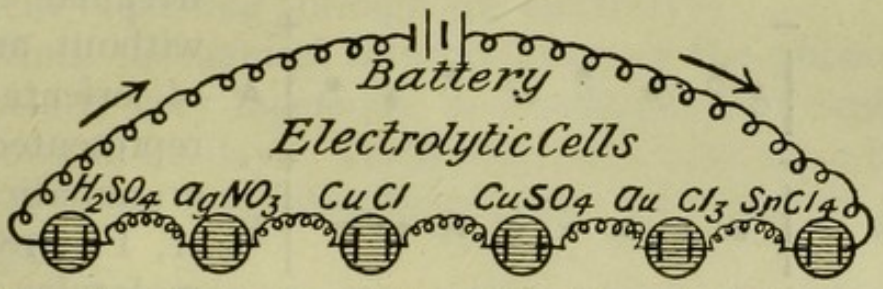


FIG. 180.—Experiment illustrating Faraday's Laws.

solutions of silver nitrate, cuprous chloride (acidified solution), cupric sulphate, gold chloride, and stannic chloride. The experiment is conducted by arranging the electrolytic cells as illustrated in the plan, Fig. 180. After about half an hour's electrolysis the amounts of the different elements collected at the cathode can be weighed or measured. The results will be very nearly:

	Dilute H_2SO_4		$AgNO_3$	CuCl	$CuSO_4$	$AuCl_3$	$SnCl_4$	
	Cathode.	Anode.						
	Hydrogen.	Oxygen.	Silver.	Copper.	Copper.	Gold.	Tin.	
Amt. found	0·0266	0·2126	2·9370	1·6900	0·8440	1·7476	0·7554	gr.
If H=I .	1	8	108	63·5	31·8	65·7	29·3	,,
Atomic wt.	1·01	16	107·9	63·6	63·6	197·2	119	,,
Valency .	1	2	1	1	2	3	4	,,

Accordingly, chemically equivalent quantities of the different

elements (that is, atomic weight ÷ valency) are liberated by the passage of the same quantity of electricity. Consequently, the **electrical equivalent of an element is numerically the same as the chemical equivalent.**

The consequence of Faraday's famous discovery that chemically equivalent quantities of matter carry equal quantities of electricity, reminds us at once of Dulong and Petit's generalization respecting the thermal capacity of atoms for heat. In the case of electricity, we see that chemically equivalent quantities of matter have the same capacity for electricity.

§ 2. Grotthus' Attempt to picture the Mechanism of Electrolysis.

C. J. T. Grotthus (1805) imagined that the molecules of a salt in solution are distributed throughout the solvent in an irregular manner without any signs of orientation, as represented diagrammatically at *A*, Fig. 181. The molecules, in the presence of a pair of oppositely charged electrodes, range themselves in "chains," like little magnets. The positively charged ions—cations—are directed towards the negatively charged cathode, and the negatively charged ions—anions—to the positively charged anode, *B*, Fig. 181. If the charges on the electrodes are great enough, the molecules in immediate contact with the electrodes will decompose, *C*, Fig. 181, and the charge on one of the ions will be neutralized

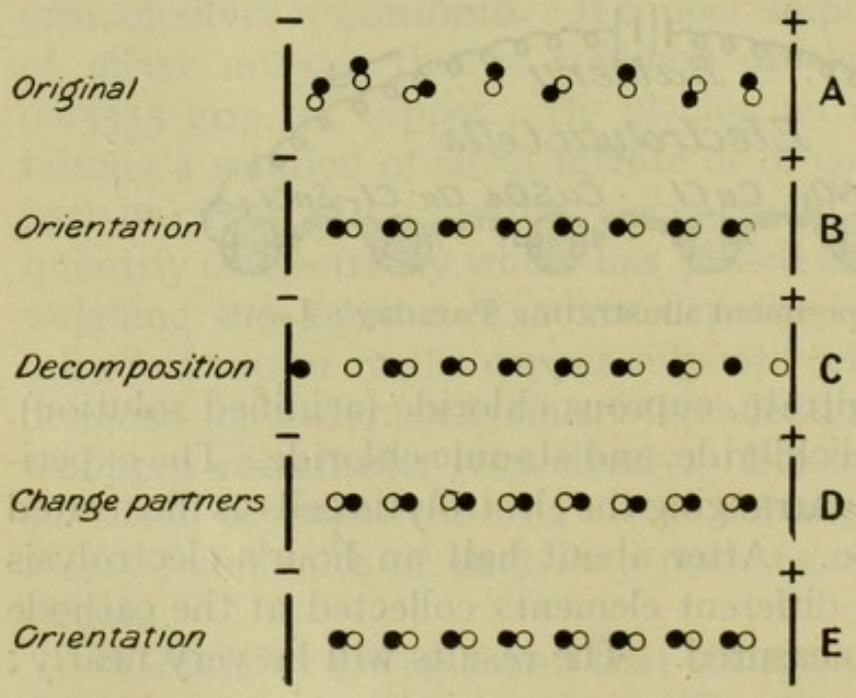


FIG. 181.—Diagrammatic Representation of Grotthus' Hypothesis.

by the charge on the electrodes. And the other ion will unite with the neighbouring molecule and liberate an ion with a similar charge. The free ion attacks the next molecule, and so the process is continued throughout the " chain."

To fix the idea, consider the end of the molecular " chain " at the cathode. There a negatively charged ion is set free when the positively charged ion has been neutralized at the cathode. This " negative " ion associates with the adjacent molecule of the chain ; this molecule decomposes, forming a new molecule, liberating, at the same time, a negatively charged ion which associates with the next molecule of the chain, *D*, Fig. 181. This successive decomposition and recombination goes on throughout the chain of molecules from electrode to electrode. The new molecules so formed turn about, and are again ranged in a " chain " resembling *B*, as shown at *E*, Fig. 181. A cycle of changes of this nature is supposed to be going on all the time the current is passing through the electrolyte.

Grotthus' mechanical interpretation of the phenomenon of electrolysis is very ingenious, and satisfactorily explained the facts known in his day. Three objections have since been urged against it ; but the objections may be " due to misunderstandings."

First, if the electricity be conducted by " Grotthus' chain," it is claimed that no current can flow until the electromotive force driving the energy is equivalent to the energy represented by heat of formation of the molecules undergoing decomposition *in the solution*. When a sufficient electromotive force is applied at the electrodes the decompositions and recompositions of the molecules might proceed in the way described by Grotthus. No such critical electromotive force, however, has been found to be necessary for the passage of a current through electrolytic solutions. The smallest electromotive force hitherto tried causes a current to flow when it is applied to copper electrodes immersed in a solution of copper sulphate. The total energy consumption is then nothing but that due to the " resistance " of the cell.

Second, it is found that solutions of electrolytes, like metallic wires, conduct electricity in such a way that the rate at which

electricity passes through the system is proportional to the electromotive force. This is true, whatever be the magnitude of the force, and consequently, if a certain amount of electrical energy be expended in breaking up the molecules, this proportionality cannot obtain. Hence, very little electrical energy can be expended in breaking up the dissolved molecules into their respective ions, and it has therefore been urged that "the ions cannot be held together by a force of finite value."

Third, we naturally expect those electrolytes whose atoms or radicles are held together by the weakest attractions would most readily decompose electrolytically. This is by no means the case. For instance, mercuric chloride is much less stable than sodium chloride, and yet the latter is much more readily decomposed by an electric current.

Several chemists, dissatisfied with Grotthus' hypothesis, suggested that another explanation of the mechanism of electrolysis be given a trial, and the alternative ionic hypothesis now occupies an important place in the text-books on the theory of chemistry.

§ 3. The Ionic Hypothesis of Solutions and Electrolysis.

The ionic hypothesis is to be regarded as a "daring stroke of scientific speculation" which is very fashionable. It assumes that when an electrolyte dissolves in water, it is split up into two particles; that the mere presence of the solvent leads to the fission of the molecules of the electrolyte into sub-molecules, each of which is charged with a definite amount of positive or negative electricity per chemical equivalent. The solution does not itself appear to be electrically charged, and hence it is assumed that an equal quantity of positive and negative electricity is developed by the rupture of the molecules of the electrolyte during the process of solution. By a modification of Faraday's definitions (p. 77), the "sub-molecules" are called ions, and consequently: **ions are atoms or groups of atoms which carry a definite positive or negative charge of electricity, and they are formed by the dissociation of the electrolyte in the solution. Each molecule, on dissociation, furnishes two kinds of ions with equal**

and opposite charges of electricity. To avoid confusing the phenomenon of dissociation in which the products are not charged electrically, with the dissociation of a molecule into electrically charged ions, the term **ionization** is reserved for the latter phenomenon.

Each positive charge of electricity is represented by a small dot at the top-right hand corner of the symbol for element or radicle, and each negative charge by a dash similarly placed. Thus, a silver ion is represented by $Ag^{\cdot}$, a sulphate ion by SO_4'', etc. The ionization of hydrochloric acid is represented in symbols: $HCl \rightleftharpoons H^{\cdot} + Cl'$; of sodium chloride, $NaCl \rightleftharpoons Na^{\cdot} + Cl'$; of zinc sulphate, $ZnSO_4 \rightleftharpoons Zn^{\cdot\cdot} + SO_4''$; and of zinc chloride, $ZnCl_2 \rightleftharpoons Zn^{\cdot\cdot} + 2Cl'$.

In view of the great chemical activity of metallic sodium in contact with water, it might be objected that it is not profitable to postulate the existence of the element sodium in contact with water without chemical action. This objection is said to "rest on a misunderstanding," because *electrically charged ions* of sodium in an aqueous solution of sodium chloride are very different from *neutral atoms* of metallic sodium. The ions of sodium carry large charges of electricity. It is urged that "chemists know practically nothing about the properties of atoms carrying large charges of electrical energy," and also that "the chemical activity of an electrically charged sodium atom is much less than a neutral atom of sodium." In other words, the presence of the electrical charge on the sodium ion keeps the ordinary chemical activities of the atom in abeyance. This means that whenever a chemical difficulty arises in the application of the ionic hypothesis the assumption is made that "neutral atoms or atomic groups and ions are different substances," because the properties of a substance are determined as much by the energy it contains as by the kind of matter. In this way, the ions have been invested with such imaginary properties as may be needed to keep the ionic hypothesis in accord with facts. Quite an elaborate system, fairly consistent with itself, has been founded on the above postulates. Neither the ionic nor the chain hypothesis has proved an adequate explanation of the facts, and although the majority of chemists favour the ionic

hypothesis, yet it is recognized that it has many defects which will render a change necessary when chemists can think of a better.

There is supposed to be a definite relation between the concentration of the solution and the fractional part of the solute which has undergone ionization. Take the case of sodium chloride.

When a salt—say, sodium chloride—is dissolved in water, some of the dissolved molecules are, by hypothesis, ionized, and the ions immediately begin to recombine to form molecules. The speeds of the two reactions ionization and de-ionization are supposed to behave analogously with opposing reactions, and a state of equilibrium is reached when the number of molecules reformed by the combination of the ions is equal to the number of molecules ionized in the same time. Symbolically,

$$NaCl \rightleftharpoons Na^{\cdot} + Cl'$$

Ionization→ ←De-ionization.

Still further, when the two poles of a battery—say platinum electrodes—are dipped in the salt solution as indicated in Fig. 41, all the chlorine ions, carrying a negative charge, are attracted to the anode or positively charged electrode, and the positively charged sodium ions are attracted to the cathode or negatively charged electrode. As each ion comes in contact with the electrode with a charge of opposite sign to its own, the ion is relieved of its charge, and thereby reverts to an ordinary atom of chlorine or sodium. The chlorine atoms do not appreciably attack the water or the electrode, but unite in pairs to form molecules of chlorine gas. As soon as the liquid in the vicinity of the anode is saturated with chlorine, this gas bubbles to the surface of the liquid. Similarly, the sodium ions are relieved from their charges at the cathode, and the resulting sodium atoms immediately attack the water, forming hydrogen gas and sodium hydroxide: $2Na + 2H_2O = 2NaOH + H_2$; the hydrogen bubbles off as a gas, and the solution of sodium hydroxide accumulates about the cathode.

The equilibrium between the unionized molecules and the ions is disturbed by the annihilation, so to speak, or the removal

of ions at the electrodes. The difference of potential at the electrodes is maintained by the battery, and the supply of ions is kept up by the steady ionization of the salt as fast as the ions are de-electrified at the electrodes, until practically the whole of the salt in the solution has been electrolyzed. Thus, it has been said that "the ions do not transport the electricity of the battery, but their own." The charged ions are already present in the solution before connection is made with the battery.

If ionization is a real phenomenon, it is to be expected that the greater the number of ions in a solution, the better will it conduct electricity, for the ions alone carry the current. Accordingly it is *assumed* that **the number of ions which take part in conducting the electric current at any particular concentration of the solution is proportional to the conducting power of the solution.** Hence, the degree of ionization of a substance can be measured by the conducting power of the solution provided the same weight of solute is maintained between the electrodes in every case. With this limitation it is found that the conducting power of a solution gradually increases with dilution up to a certain maximum point, when no further change occurs, it is inferred that the less the concentration of a solution the greater the degree of ionization of the solute until, when all the solute is ionized, no further change can occur.

§ 4. Acids and Bases according to the Ionic Hypothesis.

Acids.—Over fifty years ago Gerhardt defined acids to be "salts of hydrogen"; the ionic hypothesis expresses a similar idea another way: "all acids, when dissolved in water, furnish hydrogen ions." Although many substances not usually called acids when completely ionized furnish hydrogen ions—*e.g.* potassium hydrogen sulphate, $KHSO_4$, etc.—yet their acidic properties are due to the presence of $H^{\cdot}$ ions, and consequently it has been said that "there is only one acid, and that is the $H^{\cdot}$ ion." The general and characteristic properties of acids are assumed to be the general and characteristic properties of $H^{\cdot}$ ions, and thus the $H^{\cdot}$ ions are said to have a sour taste, redden blue litmus, conduct electricity in solutions containing

them, behave as univalent radicles, etc. The basicity of an acid is fixed by the number of $H^{\cdot}$ ions furnished by the complete ionization of one molecule of the acid. Thus monobasic hydrochloric acid, HCl, furnishes one $H^{\cdot}$ ion, $HCl \rightleftharpoons H^{\cdot} + Cl'$; and dibasic sulphuric acid furnishes two $H^{\cdot}$ ions: $H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4''$. Sulphuric acid also furnishes the ions $H^{\cdot}$ and HSO_4' so that it behaves also as a monobasic acid when it forms the so-called "acid sulphates"; carbonic acid, H_2CO_3, also furnishes the ions $H^{\cdot}$ and HCO_3', as well as $2H^{\cdot}$ and CO_3''. Many substances contain hydrogen, and they are not regarded as salts of hydrogen because they do not furnish $H^{\cdot}$ ions, *e.g.* methane, CH_4; ammonia, NH_3; alcohol, C_2H_5OH, etc.

The action of a metal, say zinc, on an acid is usually represented by the equation: $Zn + 2HCl = ZnCl_2 + H_2$; the ionic hypothesis assumes that: $Zn + 2H^{\cdot} + 2Cl' \rightleftharpoons Zn^{\cdot\cdot} + 2Cl' + H_2$. Since the Cl' ions are but little affected by the change, the last equation reduces to $Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2$. The action is thus independent of the negative ion, for it involves little more than a transfer of the positive electric charges from the two hydrogen ions to the zinc. When the solution of zinc chloride is concentrated by evaporation, the $Zn^{\cdot\cdot}$ and $2Cl'$ ions recombine to form zinc chloride. It does not matter which equation be used to represent the action of zinc on the acid—both describe the known facts, one equation in the language of the ionic hypothesis, and the other in the language of the molecular theory. The facts will stand for ever, the language used in describing the facts will change with the prevailing or fashionable hypothesis.

Bases.—Just as an acid has been defined to be a substance which can furnish hydrogen ions when dissolved in water, so bases, according to the ionic hypothesis, are substances which yield HO' ions when dissolved in water. The basic properties of bases are due to the OH ions, and in this sense it has been said that "there is only one base, and that is the OH ion." The general and characteristic properties of the bases are supposed to be the general and characteristic properties of the OH' ions. Thus the OH' ions are said to have a soapy feel, turn red litmus blue, conduct electricity in a solution containing

them, etc. The acidity of a base is fixed by the number of OH' ions it furnishes on complete ionization of a molecule of the base. Thus, the uniacid bases, like sodium hydroxide, ionize : $NaOH \rightleftharpoons Na^{\cdot} + OH'$; and the biacid bases, like barium hydroxide, ionize : $Ba(OH)_2 \rightleftharpoons Ba^{\cdot\cdot} + 2OH'$.

§ 5. The Strengths of Acids and of Bases.

The strength of an acid or base refers to the extent to which the acid or base exhibits acidic or basic properties respectively. The terms "affinity," "avidity," and "activity" are sometimes employed synonymously with "strength," but there are objections to each of these. The term "strength," too, is often used where "concentration" is really meant. "Concentration" refers to the "quantity of matter in unit volume" expressed in, say, "grams per litre," etc.

The chemical activity of different solutions containing equivalent amounts of different acids has been referred to the concentration of the $H^{\cdot}$ ions in the solution. The concentration of the $H^{\cdot}$ ions depends upon the degree of ionization of the different acids. Hence the relative strengths of the acids can presumably be expressed in terms of the electrical conductivity of equivalent solutions. The speed of a reaction dependent upon an acid is thus connected with the concentration of the $H^{\cdot}$ ions. If the rates at which equivalent solutions of hydrochloric, sulphuric, and acetic acids react with zinc under like conditions, it will be found that the volume of hydrogen liberated per minute are as 100 : 70 : 0·5. These numbers can be taken to represent the relative strengths of these acids. The results agree with the degrees of ionization of the corresponding acids, which are related as 100 : 65 : 0·5. This means that in hydrochloric acid, a greater number of hydrogen ions are ready to react with the metal than with acetic acid, and consequently the available hydrogen in hydrochloric acid is more rapidly exhausted than with acetic acid, where but few ions are in a condition to react with the metal at any moment, and consequently the reaction progresses slowly for a long time ; as fast as the available ions are exhausted, new ions are formed by

the ionization of the molecule of acetic acid. The total number of hydrogen ions is the same in both cases, but the number in a condition to react with the metal at any moment is very different in all three cases.

Similarly, the strength of a solution containing equivalent quantities of the different bases is referred to the concentration of the OH′ ions in the solution. The strength of a base depends upon the degree of ionization, or on the concentration of the OH′ ions. The strength of a base can thus be determined from the electrical conductivity. In equivalent solutions, bases, like acids, differ very much in strength. The alkalies and alkaline hydroxides are very strong bases, for they are ionized to very nearly the same extent as hydrochloric acid in aqueous solution. Ammonia is a comparatively feeble base.

When a highly dissociated acid is mixed with a salt, the two react, forming another acid and salt. The change is reversible, and the reacting system is then a further illustration of the principle of opposing reactions. For instance, the action of dilute nitric acid on potassium hypochlorite (see p. 291), $HNO_3+KOCl=KNO_3+HOCl$. If both products are highly ionized, there will be no perceptible change in the system, but in the illustration just cited, hypochlorous acid is but feebly ionized, and, since the H· ions of the nitric acid, and the OCl′ ions of the potassium hypochlorite react to form feebly ionized hypochlorous acid, the result of the reaction in dilute solutions is ionized potassium nitrate, and feebly ionized hypochlorous acid :

$$\underbrace{H\cdot+NO_3'}+\underbrace{K\cdot+OCl'}\rightleftharpoons\underbrace{K\cdot+NO'_3}+HOCl$$

Similar remarks apply, *mutatis mutandis*, to the action of a salt on a base, and this explains how feebly ionized ammonium hydroxide is formed in relatively large quantities when highly ionized solutions of potassium hydroxide and ammonium nitrate are mixed together. The reaction proceeds almost to the end :

$$\underbrace{NH_4\cdot+NO_3'}+\underbrace{K\cdot+OH'}\rightleftharpoons\underbrace{K\cdot+NO_3'}+NH_4OH$$

When the base is insoluble, it will be precipitated and the reaction will proceed to an end quite apart from the degree of

ionization of the reacting compounds. This is the case, for example, with ferric, aluminium, zinc, and other hydroxides :

$$Fe^{\cdots}+3Cl'+3Na^{\cdot}+3OH'=3Na^{\cdot}+3Cl'+Fe(OH)_3$$

The action of sulphuric acid on sodium chloride (p. 134), which results in the formation of hydrochloric acid, seems to prove that sulphuric acid is stronger than hydrochloric acid ; again, when hydrochloric acid is added to a solution of silver sulphate, silver chloride is precipitated. The hydrochloric acid expels the sulphuric acid from its combination with silver : $Ag_2SO_4+2HCl=2AgCl+H_2SO_4$, and it seems as if hydrochloric acid is stronger than sulphuric acid. These two conclusions are contradictory, and there must therefore be a fallacy in our reasoning. We have wrongly assumed that the two acids were competing for sodium and for silver under similar conditions. This is not the case. When hydrochloric and sulphuric acids compete for the sodium, the hydrochloric acid, being volatile, escapes from the system as fast as it is formed ; while the non-volatile sulphuric acid alone remains behind. Again, when sulphuric and hydrochloric acids are competing for silver, the hydrochloric acid carries the silver away from the sulphuric acid as an insoluble precipitate of silver chloride. Still further, hydrosulphuric acid is notoriously a very feeble acid, and yet it can displace relatively strong acids from combinations with the metals. Thus, it will precipitate lead sulphide from solutions of lead chloride ; copper sulphide from solutions of copper sulphate, etc. Here again the feeble acid does its work by removing the metal from the solution as an insoluble sulphide.

To compare the relative strengths of the acids, and, *mutatis mutandis*, of the bases, it is necessary that the comparison be made under conditions where the reacting acids and the products of the reaction are in the same physical condition—say, all in solution. Thus, if an equivalent of a solution of sodium hydroxide be mixed with an equivalent of a solution of sulphuric and of hydrochloric acids, the two acids can compete for the one base under the same conditions, and hence the stronger acid will

be able to unite with more sodium than the weaker acid. It is found experimentally that the same result is obtained when equivalent quantities of sodium hydroxide, sulphuric acid, and hydrochloric acid are mixed together as when equivalent quantities of sodium sulphate and hydrochloric acid, or equivalent quantities of sodium chloride and sulphuric acid, are mixed, provided, of course, the whole of the system has been allowed to stand long enough for equilibrium. This fact is represented by the equation : $2HCl+Na_2SO_4 \rightleftharpoons 2NaCl+H_2SO_4$.

The proportions of a base shared between two acids, or of an acid between two bases, cannot be determined by the ordinary methods of chemical analysis without disturbing the equilibrium of the mixture. The distribution of an acid between two bases, or of a base between two acids, must be determined by physical processes which do not interfere with the solution. In illustration, the heat of neutralization of sodium hydroxide by sulphuric acid is 31·38 Cals. ; and by hydrochloric acid, 27·48 Cals. If, therefore, on mixing hydrochloric acid with sodium sulphate, all the sulphuric acid were displaced by the hydrochloric acid, the thermal effect resulting from the decomposition of the sodium sulphate and the formation of the sodium chloride would be $27{\cdot}48-31{\cdot}38=-3{\cdot}9$ Cals. J. Thomsen found that the thermal value of the reaction is $-2{\cdot}6$ Cals. Hence it follows that $-2{\cdot}6 \div -3{\cdot}9$ or about two-thirds of the hydrochloric acid combines with about two-thirds of the base to form sodium chloride ; and about one-third of the sulphuric acid combines with the other third of the base to form sodium sulphate. A similar result was obtained with a mixture of sodium chloride and sulphuric acid. Consequently, in the competition of sulphuric and hydrochloric acids for sodium under comparable conditions, the hydrochloric acid can hold twice as much of the base as the sulphuric acid, and consequently, hydrochloric acid is nearly twice as strong as sulphuric acid.

Similar results have been obtained by measuring the specific gravity, etc. The relative strengths of the different acids have also been determined in a similar way. The actual numbers obtained by the different methods are not always quite the

same, possibly because of the different conditions under which the experiments are made. The results obtained by three different methods are shown in Table XXIII.

TABLE XXIII.—RELATIVE STRENGTHS OF ACIDS.

Acid.	Thomsen's thermal process.	Specific gravity process.	Electrical conductivity.
Hydrochloric acid .	100	98	100·0
Nitric acid . . .	100	100·0	99·6
Hydrobromic acid .	89	95·0	100·0
Sulphuric acid . .	49	66·7	65·1
Phosphoric acid . .	25	—	7·3
Acetic acid . . .	3	1·23	0·4

§ 6. The Neutralization of Acids and Bases.

The term " neutral " has been used somewhat vaguely, implying that the substance is neither acidic nor basic. The test for acidity or basicity depended upon the behaviour of the solution towards a solution of litmus. If other indicators are used, the conclusions might be different, because a substance might appear acidic towards one indicator, and neutral towards another. The ionic hypothesis, as we have seen, refers acidity to the presence of hydrogen ions, and alkalinity to the presence of OH' ions, and the term " neutrality " refers to the case where the concentration of both ions are the same, or both ions are absent. We have seen that water is a constant product of the reaction between the solution of an acid and of a base: $HCl+KOH \rightleftharpoons KCl+H_2O$; $H_2SO_4+2NaOH \rightleftharpoons Na_2SO_4+2H_2O$, etc. These reactions are, no doubt, slightly reversible, but the formation of feebly ionized water leads to the removal of the OH' and the $H^{\cdot}$ ions from the solution, and the reaction is almost completed:

$$\underbrace{H^{\cdot}+Cl'}+\underbrace{K^{\cdot}+OH'} \rightleftharpoons \underbrace{K^{\cdot}+Cl'}+H_2O$$

What is here stated with respect to hydrochloric acid and

potassium hydroxide applies, *mutatis mutandis*, to any strongly ionized acid and base ; and consequently, the neutralization of strongly ionized acids and bases involves little more than the formation of water : $H^{\cdot}+OH' \rightleftharpoons H_2O$, because the other ions present before the acids and bases are mixed remain after the reaction is over. If, however, the water be evaporated from the solution, the ions recombine to form the salt, and the result of the reaction is then correctly symbolized : $HCl+KOH \rightleftharpoons KCl+H_2O$. This reaction probably also occurs if very concentrated solutions or solids are mixed, whereas **the neutralization of acids and bases in dilute solutions involves the formation of water, not salt molecules.**

The heat of neutralization.—This view is further supported by the fact that with dilute solutions of the strong acids and bases, the thermal value of the process of neutralization—heat of neutralization—is the same. For example,

	NaOH	KOH	$Ca(OH)_2$	$Ba(OH)_2$
Hydrochloric acid .	13·7	13·7	13·8	13·8 Cals.
	HCl	HBr	Hi	HNO_3
Sodium hydroxide .	13·7	13·8	13·7	13·7 Cals.

Hence, the heats of neutralization of dilute solutions of the strong acids and bases do not depend upon the specific nature of the acid or base ; the formation of water in these reactions is accompanied by the evolution of approximately 13·7 Cals. of heat.

The law only describes the thermal effect attending the neutralization of solutions sufficiently diluted to ensure complete ionization of acid, base, and salt ; it presupposes that no new electrically neutral molecules are formed. If the acid and base are but partially ionized, the heat of neutralization is not only determined by the heat of formation of water—13·7 Cals.—but it is also determined by the thermal value of the energy required to complete the ionization of acid and base. Hence, with feebly ionized acids and bases, deviations from 13·7 Cals. are to be expected. Such is the case with aqueous ammonia, hydrofluoric acid, etc. It also follows that if two completely ionized salts are mixed, there will be no thermal change provided

the salts are completely ionized before and after the mixing, and no other electrically neutral molecules are formed. The fact that "if two neutral salt solutions at the same temperature are mixed together, no change of temperature occurs" was discovered by H. Hess in 1841, and is called **Hess' law of thermo-neutrality**. The ionic hypothesis indicates clearly the conditions which must be fulfilled before Hess' law of thermo-neutrality is applicable.

§ 7. Hydrolysis.

The term "hydrolysis" is applied to the phenomenon which occurs when a salt reacts with water to form the free base and free acid, or free acid and a basic salt. **Hydrolysis is thus a reversion of the process of neutralization.** Thus, with zinc sulphate in aqueous solution,

$$H_2SO_4 + Zn(OH)_2 \rightleftharpoons ZnSO_4 + 2H_2O$$

Neutralization → ← Hydrolysis.

In some cases the amount of hydrolysis is not appreciable, while in other cases the hydrolysis is very marked. With bismuth or antimony salts, for example, bismuth trichloride, $BiCl_3$, with a small quantity of water gives a syrupy liquid, but with a large amount of water a white precipitate is formed—bismuth oxychloride, BiOCl. Thus:

$$BiCl_3 + H_2O \rightleftharpoons 2HCl + BiOCl$$

Hence, from the principle of opposing reactions, owing to the sparing solubility of the oxychloride, it separates from the sphere of the reaction, and, to maintain the equilibrium conditions represented by the equation, more bismuth trichloride separates until finally the hydrolysis is so complete that practically all the bismuth is precipitated.

The hydrolysis of zinc salts.—The electrical conductivity of the purest water yet made is very slight, but it can be detected; it is 0·000000038: this number means that a column of water one centimetre long will not conduct an electrical current so well as a column of mercury of equal cross section

and extending more than 30 times round the earth. Accordingly, it is inferred that the purest water yet made is slightly ionized : $H_2O=H^{\cdot}+OH'$, and that water is thus an amphoteric oxide. It is estimated that 18 grams of such water contains about $\frac{1}{10000000}$th of a gram of $H^{\cdot}$ ions, and $\frac{17}{10000000}$ths of a gram of OH' ions. If all or part of one or other of these two ions be removed, more water molecules will ionize in order to keep the equilibrium value constant. The percentage ionization of a few weak acids deduced from conductivity measurements for $\frac{1}{10}$-N solutions with HCl as standard of reference, is :

Hydrochloric acid	91·400
Carbonic acid	0·174
Hydrosulphuric acid	0·075

Zinc sulphate is completely ionized in dilute solution, $ZnSO_4 \rightleftharpoons Zn^{\cdot\cdot}+SO_4''$. The $Zn^{\cdot\cdot}$ ions pair with the OH' ions of the water to form feebly ionized $Zn(OH)_2$ molecules ; more water is ionized in order to maintain the equilibrium value $H_2O \rightleftharpoons H^{\cdot}+OH'$; and these actions continue until the concentration of the zinc hydroxide has attained the equilibrium value : $Zn(OH)_2 \rightleftharpoons Zn^{\cdot\cdot}+2OH'$. When that occurs, a considerable proportion of the OH' molecules have been withdrawn from the solution to form molecules of zinc hydroxide, and an excess of the $H^{\cdot}$ ions in solution are " paired," so to speak, with the SO_4'' ions of the zinc sulphate. The scheme may be represented :

$$\begin{array}{ccc} ZnSO_4 & \rightleftharpoons & Zn^{\cdot\cdot}+SO_4'' \\ & & + \quad + \\ 2H_2O & \rightleftharpoons & 2OH'+2H^{\cdot} \\ & & \rightleftharpoons Zn(OH)_2 \quad \rightleftharpoons H_2SO_4 \end{array}$$

An aqueous solution of zinc hydroxide thus behaves in many ways like a solution of sulphuric acid—*e.g.* turns blue litmus red, etc. If an alkali, say sodium hydroxide, be added to the solution of zinc sulphate, the OH' ions of the base unite directly with the $H^{\cdot}$ ions of the acid to form water, and if just sufficient

OH' ions be added to remove all the $H^{\cdot}$ ions of the acid, the solution will contain nothing more than would be obtained by dissolving sodium sulphate in water; the zinc hydroxide is removed from the solution by precipitation when its concentration exceeds the solubility coefficient.

The hydrolysis of sodium carbonate.—Similar principles can be applied to the hydrolysis of sodium carbonate. Sodium carbonate in dilute aqueous solutions is completely ionized: $Na_2CO_3 \rightleftharpoons 2Na^{\cdot} + CO_3''$. Water, as we have seen, is but slightly ionized: $H_2O \rightleftharpoons H^{\cdot} + OH'$. The carbonate ions, CO_3'', react with the $H^{\cdot}$ ions of water to form feebly ionized carbonic acid, H_2CO_3; more water molecules ionize so as to maintain the equilibrium value: $H_2O \rightleftharpoons H^{\cdot} + OH'$; and the process continues until the concentration of the carbonic acid molecules has attained the equilibrium value: $H_2CO_3 \rightleftharpoons 2H^{\cdot} + CO_3''$. When that occurs, a considerable proportion of the $H^{\cdot}$ ions from the water have been "withdrawn" from the solution to form carbonic acid molecules, and an excess of OH' ions remain in solution, "paired," so to speak, with the $Na^{\cdot}$ ions of sodium hydroxide. The scheme may be represented:

$$\begin{array}{ccccc} Na_2CO_3 & \rightleftharpoons & 2Na^{\cdot} & + & CO_3'' \\ & & + & & + \\ 2H_2O & \rightleftharpoons & 2OH' & + & 2H^{\cdot} \\ & & \rightleftharpoons & & \rightleftharpoons \\ & & 2NaOH & & H_2CO_3 \end{array}$$

An aqueous solution of sodium carbonate behaves in many ways like a solution of sodium hydroxide—turns red litmus blue, etc.—and the ionic hypothesis thus refers this action to the presence of an excess of OH' ions. If an hydrochloric acid solution be added to a solution of sodium carbonate, the $H^{\cdot}$ ions of the acid unite directly with the OH' ions in the solution to form water, and if just sufficient HCl be added to remove the OH' ions, the solution will contain nothing more than $Na^{\cdot}$ and Cl' ions such as would be obtained by dissolving sodium chloride in water. The CO_3'' ions of carbonic acid, and the Cl' ions of

the hydrochloric acid, are competing for the $Na^{\cdot}$ ions, but carbonic acid is very feeble in comparison with hydrochloric acid; and carbon dioxide formed by the *dissociation*, not ionization, of the carbonic acid is volatile under the conditions of the experiment and escapes from the solution.

The language of the ionic hypothesis has penetrated analytical chemistry, more particularly the qualitative analysis taught in our schools. As a result, tests for metals and acid radicles are described as tests for the ions. Since both the chlorides and hydrochloric acid are supposed to furnish chlorine ions: $HCl \rightleftharpoons H^{\cdot} + Cl'$, or $NaCl \rightleftharpoons Na^{\cdot} + Cl'$, it is assumed that the test for hydrochloric acid or for a chloride is a search for chlorine ions. The silver nitrate solution used in making the test is supposed to be ionized: $AgNO_3 \rightleftharpoons Ag^{\cdot} + NO_3'$; consequently, when silver nitrate is added to sodium chloride solution, the mixed solution momentarily contains $Ag^{\cdot} + NO_3' + Na^{\cdot} + Cl'$; but, since silver chloride is but very slightly soluble in water, it precipitates at once. Silver chlorate, $AgClO_3$, is soluble in water, and accordingly, when silver nitrate is mixed with a solution of, say, potassium chlorate, there is no precipitation, and the solution contains four different kinds of ions:

$$AgNO_3 + KClO_3 \rightleftharpoons K^{\cdot} + ClO_3' + Ag^{\cdot} + NO_3'$$

Hence, silver nitrate is a test for chlorine ions, but not for chlorate ions. Here again it matters very little whether the facts be described in terms of the ionic hypothesis or in terms of the basic and acidic radicles. The choice can only be decided by personal opinion so long as the ions remain hypothetical units.

Questions.

1. State the law of Faraday. A current passes through solutions of silver nitrate and hydrochloric acid. Ten grams of silver are deposited. How many grams of chlorine are set free?—*Sheffield Scientific School, U.S.A.*

2. What is Faraday's Law of Electrolysis? Illustrate it by two examples.—*London Univ.*

3. The two wires from a galvanic battery are attached each to a plate of platinum; describe what happens when these two

plates are immersed in a solution, coloured with litmus, of (*a*) sodium chloride, (*b*) copper sulphate, (*c*) sodium sulphate.—*Staffs. County Schol.*

4. How is copper sulphate prepared ? Without employing heat, how would you prepare metallic copper from copper sulphate crystals ?—*Cape Univ.*

5. State Faraday's electrolytic law, and give some account of the modern views held regarding the nature of the electrolytic changes which occur in solutions through which a current is passing.—*Science and Art Dept.*

6. Enunciate Faraday's electrolytic law. Explain how you would proceed to determine its validity by experiment.—*London Univ.*

7. What products are formed in each case when an electric current is passed through solutions (in water) of the following compounds : HCl, Na_2SO_4, $Pb(NO_3)_2$, KI ? Explain the meaning of the terms " electropositive " and " electronegative " as applied to the elements.—*London Univ.*

8. Explain the terms " cation," " anion," " electrolyte " ; and describe in detail the results when solutions of copper sulphate, sodium sulphate, and potassium iodide respectively are electrolyzed. —*Adelaide Public Exam. Board.*

9. A current of electricity is passed through a solution of common salt. The electrodes are near each other and the solution is well stirred. What would you expect to be present in the solution after the passage of the current if (1) the solution is cold, (2) the solution is hot ? How would you demonstrate the truth or otherwise of your conjecture ?—*Bombay Univ.*

10. Write a brief account of the theory of electrolytic dissociation. How does this theory explain electrolysis, and the neutralization of acids by bases ?—*Cape Univ.*

11. Write a short essay on the hydrolysis of salts.—*Institute Chem.*

12. What weight, in grams, of (1) iron and (2) aluminium, would theoretically be required to remove (*i.e.* precipitate) the copper completely from a solution containing 1 kilogram of crystalline copper sulphate ($CuSO_4.5H_2O$) ? (Cu=63, Zn=65, Al=27, O=16, S=32, H=1.)—*Sydney Univ.*

13. Two copper plates of the same weight are connected, one with the positive and the other with the negative pole of a voltaic battery, and immersed side by side in a solution of copper sulphate. If, after a time, the plates are removed, dried, and reweighed, they are no longer found to weigh alike. Account for this, and explain how, by the continued action of the current, the equality of the plates could be re-established.—*Science and Art Dept.*

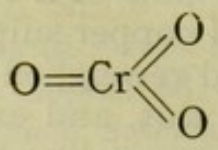
CHAPTER XXIV

Chromium and Compounds

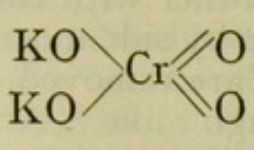
§ 1. Chromic Acid—The Chromates and Dichromates.

Chromite.—This mineral is also called *chrome ironstone*, or *chrome iron ore*. It is a native *ferrous chromite*, $FeCr_2O_4$, or $Fe(CrO_2)_2$, contaminated with silica, alumina, magnesia, etc. It resembles magnetite in general appearance, for it has an iron-black colour, with a brownish tinge. Good marketable chromite contains the equivalent of at least 50 per cent. Cr_2O_3, and not more than about 10 per cent. of silica. Most of the chromium compounds of commerce are derived from this ore.

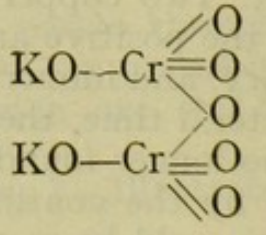
Potassium and sodium chromates.—If the finely ground chromite be intimately mixed with potassium or sodium carbonate, and roasted in an oxidizing atmosphere, the reaction which occurs is probably that represented by the equation: $4FeCr_2O_4+8K_2CO_3+7O_2=8K_2CrO_4+8CO_2+2Fe_2O_3$, if potassium carbonate be used. The yellow mass can be lixiviated with water, and the solution filtered. **Potassium chromate** separates in yellow crystals when the solution is concentrated by evaporation. If the solution be treated with sulphuric acid in slight excess, the solution furnishes orange-red crystals of **potassium dichromate.** The two salts have compositions corresponding with the formulæ:



Chromium anhydride, CrO_3.



Yellow potassium chromate, K_2CrO_4.



Orange-red potassium dichromate, $K_2Cr_2O_7$.

The latter can be converted into the former by treatment with potassium hydroxide : $K_2Cr_2O_7+2KOH=2K_2CrO_4+H_2O$; and the former can be converted into the latter by treatment with acid as just indicated

$$2K_2CrO_4+H_2SO_4=K_2SO_4+H_2O+K_2Cr_2O_7$$

The analogy between chromic trioxide and sulphur trioxide, and between, say, potassium chromate and sulphate, is rather striking. A number of other analogies, more or less remote, can be traced between sulphur and chromium ; and in consequence many class chromium with the sulphur elements.

Chromium trioxide, CrO_3.—When a concentrated aqueous solution of potassium dichromate is treated with concentrated sulphuric acid, long scarlet needle-like crystals separate when the solution is cooled. The crystals can be filtered through glass wool and drained on a porous earthenware tile ; then washed with concentrated nitric acid to remove the sulphuric acid and sulphates ; and dried in a current of dry warm air. The resulting crystals of chromium trioxide, CrO_3, are very deliquescent, and dissolve in water, forming a red solution which is probably **dichromic acid,** $H_2Cr_2O_7$, formed by the reaction : $2CrO_3+H_2O=H_2Cr_2O_7$. The acid H_2CrO_4 has not been isolated. Chromic trioxide, CrO_3, is thus called **chromic anhydride,** and the aqueous solution **chromic acid,** although the trioxide crystallizes out again when the aqueous solution is evaporated. Chromium trioxide decomposes when heated to 250° into chromic oxide Cr_2O_3, and oxygen : $4CrO_3=2Cr_2O_3+3O_2$. Chromium trioxide is a vigorous oxidizing agent, owing to the readiness with which it seems to part with oxygen and form chromic oxide, Cr_2O_3. Thus, alcohol dropped on to the oxide takes fire ; where ammonia gas impinges on the crystals, the trioxide is reduced with incandescence ; paper is charred at once ; carbonaceous matter is oxidized to carbon dioxide, etc.

One oxygen in chromic trioxide can be replaced by two chlorine atoms. Thus, when potassium dichromate is distilled with a mixture of sodium chloride and sulphuric acid, a dark red liquid is obtained with the composition CrO_2Cl_2, and called **chromyl chloride.** Neither bromine nor iodine form similar

compounds. Hence the reaction is characteristic of both chlorine and of chromium.

Chromates and dichromates.—Ammonium dichromate, $(NH_4)_2Cr_2O_7$, is made by the evaporation of a mixed solution of chromium trioxide and of aqueous ammonia. When the crystals are heated, free nitrogen, water, and chromic oxide are obtained : $(NH_4)_2Cr_2O_7=Cr_2O_3+4H_2O+N_2$. This is an interesting way of making nitrogen gas, but of no commercial importance. **Lead chromate,** $PbCrO_4$, is a bright sulphur-yellow salt precipitated by adding potassium chromate to the solution of a lead salt. It is used as a pigment under the name " chrome yellow." By boiling lead chromate with aqueous ammonia or potassium hydroxide, a **basic lead chromate,** $Pb(OH)_2PbCrO_4$, called " chrome red," is formed. This also is used as a pigment. **Barium chromate,** $BaCrO_4$, is formed in a similar manner, and is used as a pigment ; the dichromate has not been made. The precipitation of barium chromate from a solution of a barium salt by adding a soluble chromate or dichromate ; or conversely, the precipitation of chromium as barium chromate by adding a soluble barium salt, enables the amount of barium or of chromium in a solution to be determined. At 18° a litre of water only dissolves 0·0038 gram of barium chromate ; 1·2 grams of strontium chromate ; and 16·68 grams of calcium chromate. **Silver chromate** and **mercurous chromate** are both red salts. The chromates are often made by the addition of soluble dichromates to a solution of the salt in question.

Potassium dichromate as an oxidizing agent.—Potassium dichromate is used in volumetric analysis in virtue of its oxidizing properties when in contact with a reducing agent, *e.g.* ferrous sulphate, $FeSO_4$. Since potassium dichromate has a formula equivalent to $K_2O.2CrO_3$, and ferrous sulphate a formula equivalent to $FeO.SO_3$, the $2CrO_3$ of the dichromate on reduction furnish $2CrO_3=Cr_2O_3+3O$; and the ferrous oxide, FeO, of the ferrous salt is converted into Fe_2O_3, it follows that one molecule of potassium dichromate is equivalent in oxidizing properties to three atoms of oxygen, and it can therefore oxidize six molecules of ferrous sulphate. Hence the equation can be written : $6FeO.SO_3+K_2O.2CrO_3=3Fe_2O_3+Cr_2O_3+6SO_3+K_2O$.

The action takes place in an acidified solution, so that the ferrous sulphate is oxidized to ferric sulphate, $Fe_2(SO_4)_3$, the potassium oxide forms potassium sulphate, K_2SO_4, and the chromic oxide, chromic sulphate, $Cr_2(SO_4)_3$. In all, thirteen SO_4 radicles are needed, but six SO_4 radicles already come from the ferrous sulphate, hence, seven molecules of sulphuric acid are needed. The full equation thus becomes : $6FeSO_4+K_2Cr_2O_7+7H_2SO_4=3Fe_2(SO_4)_3+Cr_2(SO_4)_3+K_2SO_4+7H_2O$. Similarly, one molecule of potassium dichromate can oxidize three molecules of sulphurous acid, H_2SO_3, to sulphuric acid, H_2SO_4, and the equation is accordingly written :

$$K_2Cr_2O_7+3H_2SO_3+H_2SO_4=Cr_2(SO_4)_3+K_2SO_4+4H_2O.$$

When heated with hydrochloric acid, chlorine is produced ; the action is analogous to that indicated in our study of the action of oxidizing agents on hydrochloric acid.

Volumetric analysis.—When standard dichromate solutions are employed for titrating solutions containing ferrous iron, the dichromate solution is run from a burette until a drop of the solution being titrated, when removed at the end of a glass rod, gives no blue coloration when brought in contact with a drop of a solution of potassium ferricyanide resting on a slab of white wax or porcelain. Such an indicator for the end of a reaction is called an **external indicator** or *spot test* as contrasted with the **internal indicator** of p. 171. The student has in all probability learned in the laboratory that ferrous salts give a deep Prussian blue coloration with solutions of potassium ferricyanide, while ferric salts give a dirty green or brown coloration with the same reagent ; and that ferrous salts give a light blue coloration, and ferric salts a dark blue with potassium ferrocyanide.

In calculations involving oxidations with solutions of dichromate, there is no need for a bewildering array of equations. The important thing to remember in the above discussion is that **one molecule of the dichromate, $K_2Cr_2O_7$, furnishes one K_2O, and one Cr_2O_3 molecule, which are dissolved by the excess of acid, and the remaining three oxygen atoms of the dichromate are available for oxidation.** Since a

normal solution contains the "hydrogen equivalent of an element or compound expressed in grams per litre," and since three oxygen atoms are equivalent to six hydrogen atoms, one molecule of the dichromate is equivalent to six hydrogen atoms, and a normal solution of potassium dichromate will thus contain one-sixth the molecular weight, that is, $\frac{1}{6}$ of 294·4=49·1 grms. per litre ; and a decinormal solution will contain $\frac{1}{10}$ of 49·1=4·91 grms. per litre.

EXAMPLE.—Suppose in titrating 50 c.c. of a solution of ferrous iron, 40 c.c. of a $\frac{1}{10}$ N.-dichromate solution were needed, how much ferrous iron is present in the solution ? From the above discussion we have seen that one molecule of the dichromate is equivalent to six atoms of ferrous iron, hence, one-sixth of a molecule of the dichromate is equivalent to one atom of ferrous iron (or one molecule of ferrous oxide), and hence a litre of decinormal dichromate will be equivalent to 5·6 grms. of ferrous iron (or 7·2 grms. of ferrous oxide). Consequently, 1 c.c. of $\frac{1}{10}$ N.-dichromate represents 0·0056 grm. of ferrous iron (or 0·0072 grm. of ferrous oxide), and 40 c.c. of the standard solution are thus equivalent to $40 \times 0{\cdot}0056 = 0{\cdot}224$ grm. of ferrous iron per 50 c.c. of the given solution.

The amount of ferrous iron in a given solution can be readily determined in this manner. If the solution contains ferric salts, these can be reduced to the ferrous condition by the action of zinc in an acid solution, or by means of hydrogen sulphide, or sulphur dioxide, or stannous chloride. When all the ferric salt is reduced to the ferrous condition no red coloration will be obtained with an alkali thiocyanate solution, whereas if any ferric salt is present a brownish-red colour will be produced. The ferrous salt so obtained can be titrated with dichromate, and the corresponding amount of ferric oxide computed from the relation : $2FeO + O = Fe_2O_3$. The excess of the reducing agents must be removed before the titration, although a slight excess of stannous chloride does not affect the dichromate.

§ 2. Chromic Salts.

When potassium dichromate is heated with, say, ammonium chloride, sulphur, etc., the salt is reduced, and the insoluble

mass remaining after washing with water is **chromic oxide,** Cr_2O_3, used as a green pigment—*Guignet's green*, etc. If an aqueous solution of the dichromate be reduced with say sulphur dioxide, and then treated with ammonia or an alkaline hydroxide, blue gelatinous **chromic hydroxide,** $Cr(OH)_3$, is precipitated. The precipitate dissolves in acids, forming the corresponding salts. **Chromic sulphate,** $Cr_2(SO_4)_3$, forms a series of alums analogous with the alums proper. The hydroxide also dissolves in bases, say, alkali hydroxides forming **chromites,** *e.g.* ferrous chromite. Hence, chromic oxide is both an acidic and a basic oxide. If aqueous solutions of the chromic salts are treated with ammonium sulphide, chromic hydroxide is precipitated. If chromic sulphide is formed at all it is immediately hydrolyzed by the water.

§ 3. Metallic Chromium.

Occurrence.—Metallic chromium does not occur free in nature. It occurs combined with oxygen in *chrome ochre*, which is chromium sesquioxide, Cr_2O_3, associated with more or less earthy matters. *Chromite*, $Fe(CrO_2)_2$, is the chief ore of chromium. It also occurs as lead chromate in crocoite or *crocoisite*, $PbCrO_4$. Traces occur in many minerals—*emerald, jade, serpentine*, etc.

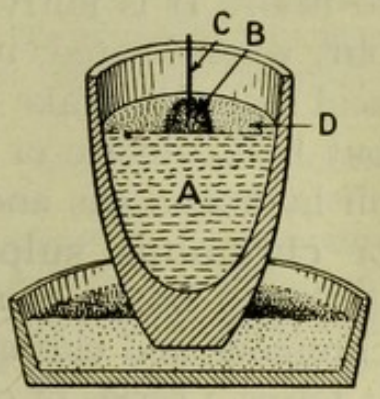


FIG. 182.—Alumino-Thermic Process for Reduction of Oxides.

Preparation of the metal.—Chromium metal can be prepared by reducing chromium sesquioxide with carbon in the electric furnace; or better, by the **alumino-thermic process,** which is also called, after its inventor, the **H. Goldschmidt's process** (1905). An intimate mixture of chromium sesquioxide and aluminium powder, *A*, Fig. 182, is placed in a refractory clay crucible so that about two-thirds of the crucible is filled. A mixture of sodium or barium peroxide and aluminium powder is placed over this, as at *B*, Fig. 182. A piece of magnesium ribbon, *C*, is stuck into the latter mixture, and a layer of powdered

fluorspar, *D*, is placed over all. The crucible is then set in a tray of sand and the magnesium ribbon, *C*, ignited. When the flame reaches the peroxide mixture, *B*, the aluminium is oxidized with explosive violence, and care must be taken to protect the face and hands accordingly. The heat of the combustion of the aluminium in the ignition mixture, *B*, starts the reaction between the chromic oxide and the aluminium. The chromic oxide is reduced to metal, and the aluminium is oxidized to alumina: $Cr_2O_3+2Al=2Cr+Al_2O_3$. When the crucible is cold, a button of metallic chromium will be found on the bottom. The slag is nothing but fused alumina which has crystallized so as to form a kind of artificial corundum. This is called *corubin*, to distinguish it from natural corundum. In Goldschmidt's works at Essen, about 100 kilograms of chromium are produced at a single charge. The reduction takes place in less than half an hour. Manganese is produced in a similar manner. Titanium, alloyed with iron—ferro-titanium—is produced by the same process.

Properties.—Chromium is a very hard metal and difficult to fuse. It is fairly resistant to air at ordinary temperatures, but, when heated, it burns to the sesquioxide, Cr_2O_3. Nitric acid seems to make the metal passive, as is the case with iron, but hydrochloric or sulphuric acid dissolves the metal, giving off hydrogen gas and forming solutions of **chromous chloride** or **chromous sulphate**: $Cr+2HCl=CrCl_2+H_2$. Chromium is thus a **basic element,** since it forms two series of salts—chromous and chromic—and it is also an **acidic element,** since it forms a series of chromates and chromites analogous in some ways with the sulphates and sulphides derived from the element sulphur, *e.g.* calcium sulphate, $CaSO_4.2H_2O$, is isomorphous with the chromate, $CaCrO_4.2H_2O$.

Chromium was discovered by L. N. Vauquelin, in 1797, while examining a " new " mineral (crocoisite) from Siberia.

Uses.—**Ferro-chromium** alloys are made containing over 60 per cent. of chromium, and less than 2 per cent. of carbon by smelting high-grade chromites in the electric furnace. Ferro-chromium is used in the manufacture of chrome-steel. Chrome-steel is a hard, tough, and dense metal with a high tensile strength.

Steel with 1 to 1½ per cent. of carbon and 2½ to 4 per cent. of chromium is so hard that it cannot be worked by ordinary hardened tool steels—for example, it is drill proof. It can, however, be welded to iron, and rolled into sheets, etc. It is used in the manufacture of burglar-proof safes, cutlery, stamp-mill shoes, crusher jaws, knuckles for car couplings, etc. It is superior to every known metal for the wearing parts of crushing and pulverizing mills. Alloys of chromium, nickel, and iron are used for the armour plates of war-ships. The alloy is hard and elastic, and even if a projectile does penetrate the armour plating the metal does not crack.

Chromite is used in making refractory bricks. Potassium and sodium chromates are used in dyeing ; in the manufacture of pigments (chrome yellow, chrome red, Guignet's green, etc.) ; in tanning leather, etc. Chromic trioxide is used in place of nitric acid in some voltaic batteries, etc.

Questions.

1. Describe in sufficient detail how the following substances could be isolated with the aid of potassium dichromate : oxygen, chlorine, chrome alum, chromium trioxide, chromyl chloride.—*London Univ.*

2. From what sources are chromium and its compounds obtained ? How is the metal manufactured, and what are its properties and uses ? What are the most important compounds of chromium ? Indicate the uses of any which are commonly employed in the industries or in the laboratory. With what other elements is chromium most nearly related and why ?—*Bombay Univ.*

3. Compare the general chemical behaviour of chromium trioxide (CrO_3) with that of chromium sesquioxide (Cr_2O_3) and explain generally how compounds corresponding to the one may be transformed into those corresponding to the other.—*Cambridge Senr. Locals.*

4. Describe the method of making potassium dichromate. Explain the action of excess of sulphurous acid on a solution of this salt containing free sulphuric acid.—*London Univ.*

5. Describe the preparation and chief reactions of the chromates of potassium.—*London Univ.*

6. On heating an unknown quantity of potassium dichromate with a concentrated solution of hydrogen chloride, and passing the

evolved gas into a solution of potassium iodide, 1·25 grms. of iodine was liberated: what was the weight of the dichromate used? (K=39, I=272, Cr=52.)—*London Univ.*

7. Give a short account of the processes by which the following substances are manufactured: quicklime, sodium carbonate, caustic soda (sodium hydroxide), potassium chlorate, potassium chromate.—*Delegacy Local Exams.*

8. 0·737 grm. of a ferric salt after reduction with stannous chloride in the presence of hydrochloric acid required 15 c.c. of $\frac{1}{10}$ N.-dichromate solution for re-oxidation. What amount of iron is present in the ferric salt?

9. What weight of potassium dichromate is required to convert a gram of ferrous iron into ferric iron?

10. A gram of ferrous sulphate $FeSO_4.7H_2O$, when dissolved in dilute sulphuric acid, required 36 c.c. of $\frac{1}{10}$ N-potassium dichromate before a drop of the solution being titrated ceased to give a blue coloration with potassium ferricyanide. Compare the theoretical with the measured amount of iron in the ferrous sulphate crystals.

11. What is chrome iron ore? Explain how potassium chromate is prepared from this body. How may potassium chromate be converted into potassium dichromate?—*Science and Art Dept.*

12. What is the action upon potassium dichromate of (*a*) sulphuric acid, (*b*) sulphurous acid, (*c*) sulphuretted hydrogen, and (*d*) soda? Give equations in all cases.—*Science and Art Dept.*

CHAPTER XXV

Manganese and its Compounds

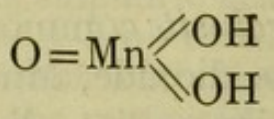
§ 1. Manganese Dioxide and the Manganous Salts.

Manganese dioxide, MnO_2.—The mineral *pyrolusite* commonly contains from 70 to 90 per cent. of manganese dioxide, MnO_2, contaminated with more or less iron, alumina, silica, lime, baryta, and, maybe, cobalt. When heated, manganese dioxide loses oxygen and first changes to **manganese sesquioxide,** Mn_2O_3, and then to **mangano-manganic oxide,** Mn_3O_4. Cold concentrated hydrochloric acid gives a dark brown liquid, and very little chlorine is evolved. The cold solution may contain **manganese trichloride,** $MnCl_3$, and possibly also a little **manganese tetrachloride,** $MnCl_4$; these salts have been isolated, but they are rapidly decomposed in the presence of water. In any case, chlorine gas is evolved when the liquid is warmed, and **manganous chloride,** $MnCl_2$, remains in solution. The manganese dioxide thus acts as an oxidizing agent on the hydrochloric acid. When heated with sulphuric acid, a solution of **manganese sulphate,** $MnSO_4$, is formed and oxygen gas is evolved: $2MnO_2+2H_2SO_4 \rightarrow 2MnSO_4+2H_2O+O_2$. The manganous salts are mostly pale rose colour.

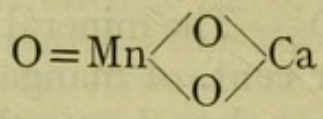
When manganese chloride is treated with an alkaline hydroxide in the absence of air, a colourless **manganous hydroxide** is precipitated—$Mn(OH)_2$—but if ammonium salts be present, a soluble complex salt is formed. A green **manganic hydroxide,** $Mn(OH)_3$, is precipitated when ammoniacal solutions of manganous hydroxide are exposed to air. **Manganous sulphide, manganous carbonate,** and **manganous phosphate** are precipitated by adding to a solution of a manganous

salt ammonium sulphide, sodium carbonate, or ammonium phosphate respectively.

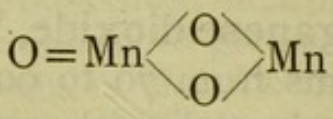
When an aqueous solution of a manganous salt is treated with an alkaline hypochlorite, or with chlorine or bromine water, a brown precipitate of $MnO_2.H_2O$ is formed. It is supposed to be a **manganous acid,** H_2MnO_3; and the "brown mud" which is formed when air is blown through a solution containing a mixture of lime and manganous chloride—*manganese mud*—is supposed to contain the calcium salt of manganous acid, viz. **calcium manganite,** $CaMnO_3$. **Manganese sesquioxide** is sometimes regarded as the manganese salt of the same acid, thus:



Manganous acid, H_2MnO_3.



Calcium manganite, $CaMnO_3$.

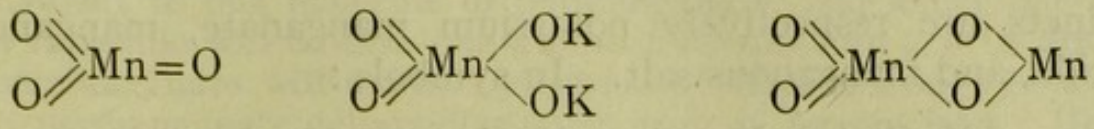


Manganese manganite, $MnMnO_3$.

§ 2. Manganates and Permanganates.

Manganates.—When manganese dioxide is fused with potassium or sodium hydroxide, in the absence of air, a part of the manganese is converted into potassium manganate, K_2MnO_4: $3MnO_2+2KOH=K_2MnO_4+Mn_2O_3+H_2O$. If air be present, and if some oxidizing agent—potassium nitrate or chlorate—be associated with the mixture, the manganese dioxide can be nearly all converted into potassium manganate: $2MnO_2+4KOH+O_2=2K_2MnO_4+2H_2O$. The fused mass has a dark green colour, and when diluted with a small quantity of water, it furnishes a dark green solution from which dark green crystals of **potassium manganate,** K_2MnO_4, can be obtained by allowing the solution to evaporate, at ordinary temperatures, *in vacuô*. Sodium manganate can be made by a similar process, using sodium in place of potassium compounds; and it can also be made by fusing manganese dioxide and other manganese compounds with sodium peroxide. The **sodium manganate,** $Na_2MnO_4.10H_2O$, has a composition resembling Glauber's salt, $Na_2SO_4.10H_2O$. The manganates are supposed to be derived from **manganic acid,** H_2MnO_4, which in turn is considered to

belong to **manganic anhydride,** MnO_3, also called **manganese trioxide**. By analogy with the sulphates, the graphic formula of potassium manganate is written :



Manganese trioxide, MnO_3. Potassium manganate, K_2MnO_4. Manganous manganate, $MnMnO_4$.

The molecular formula of manganese dioxide is not known, it is usually written MnO_2. It can be regarded as a manganese manganate, $MnMnO_4$. If the green solution of potassium manganate be gently warmed, or largely diluted with water, the green changes to pink, and some manganese hydroxide is precipitated. The change does not occur in alkaline solutions, but if a small trace of acid is present the action is quite rapid. For instance, if carbon dioxide be passed through the green solution the pink colour is developed, and the solution deposits dark purple almost black crystals of **potassium permanganate,** $KMnO_4$. The reaction is symbolized :

$$K_2MnO_4 + H_2CO_3 = K_2CO_3 + H_2MnO_4$$

Potassium permanganate is the salt of **permanganic acid,** $HMnO_4$, which in turn is derived from **permanganic anhydride,** Mn_2O_7, also called **manganic heptoxide**.

Oxidizing action of the permanganates.—Potassium permanganate is not acted upon by pure sodium or potassium hydroxides in aqueous solutions, but the commercial alkaline hydroxides generally contain sufficient impurities to reduce some of the permanganate. When heated with an alkali, potassium permanganate reverts to potassium manganate :

$$4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2$$

if a reducing agent be present, the alkaline permanganate solution is further reduced to manganese dioxide :

$$4KMnO_4 + 2H_2O = 4MnO_2 + 4KOH + 3O_2$$

In acidified solutions, the reduction proceeds still further, and a manganous salt is formed. Thus :

$$4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$$

There are thus three stages in the reduction of potassium permanganate corresponding with the separation of 1, 3, and 5 atoms of oxygen per molecule of salt; the decomposition products are respectively potassium manganate, manganese dioxide, and manganous salt. In symbols:

$$Mn_2O_7 \rightarrow 2MnO_3 + O;\ Mn_2O_7 \rightarrow 2MnO_2 + 3O;\ Mn_2O_7 \rightarrow 2MnO + 5O$$

The first takes place in alkaline solutions; the second in alkaline and neutral solutions; and the third in acid solution.

Ferrous sulphate, $FeSO_4$; sulphurous acid, H_2SO_3; hydrogen peroxide, H_2O_2; oxalic acid, $H_2C_2O_4$, etc., in an acid solution reduce potassium permanganate to a manganous salt, at the same time these substances are themselves oxidized. With hydrogen peroxide, oxygen is evolved:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + 8H_2O + K_2SO_4 + 5O_2$$

Since the solution of the manganous salt is almost colourless, if a solution of potassium permanganate containing a known amount of the salt per litre, be added from a burette, the permanganate is decolorized as fast as it is added to the reducing agent, until all the latter has been oxidized. The appearance of a permanent pink coloration due to the permanganate shows that all the reducing agent is destroyed. No indicator is required. The solution must be kept acid or a precipitate of hydrated manganese dioxide will be formed.

Volumetric analysis.—Here again there is no need to obscure the principles by complex equations in calculations connected with potassium permanganate in volumetric analysis. The important thing to remember is that **two molecules of permanganate, $2KMnO_4$, furnish one K_2O and $2MnO$ which are kept in solution by the excess of acid; the remaining five atoms of oxygen are available for oxidation.** For the same reasons as those indicated in connection with potassium dichromate, since one molecule of permanganate has the equivalent of five hydrogen atoms, a normal solution will contain one-fifth of the molecular weight of the salt expressed in grams per litre, that is, $\frac{1}{5}$ of $158 = 31{\cdot}6$; and a $\frac{1}{10}$ N-permanganate will contain $3{\cdot}16$ grms. of the permanganate per litre.

EXAMPLE.—How much iron is present in a litre of a solution of ferrous sulphate when 25 c.c. of it are oxidized completely by 10 c.c. of N-permanganate? Here, five atoms of ferrous iron are equivalent to one molecule of permanganate, and hence one-fifth of a molecule will oxidize one atom of ferrous iron; or a litre of N-permanganate will oxidize 56 grms. of ferrous iron; or 1 c.c. of N-permanganate will oxidize 0·056 grm. of ferrous iron. Hence 25 c.c. of the given solution contains the equivalent of 0·56 grm. of ferrous iron, and a litre will have $40 \times 0{\cdot}56 = 22{\cdot}4$ grms. of ferrous iron.

§ 3. Manganese.

The element has been made by mixing manganese dioxide and aluminium powder and proceeding by Goldschmidt's process as described for chromium. The oxide is reduced by the aluminium. The metal resembles iron in many respects, and it dissolves readily in acids, forming manganous salts.

Manganese is a basic element forming at least two series of salts—manganous and manganic—and it is an acidic oxide forming the manganates and permanganates. The valency of manganese is noteworthy, since it acts as a bi-, ter-, quadri-, sexi-, and septi-valent element. Manganese also forms an unusual number of definite oxides, more indeed than any other element.

Manganous oxide, MnO	Basic, forms manganous salts somewhat resembling zinc salts.
Mangano-manganic oxide, Mn_3O_4	Neutral or mixed oxide; probably a salt analogous with magnetic oxide of iron.
Manganese sesquioxide, Mn_2O_3	Basic, forms manganic salts somewhat like alumina.
Manganese dioxide, MnO_2	Basic peroxide and acidic; forms manganites.
Manganese trioxide, MnO_3	Acidic, forms manganates isomorphous with chromates.
Manganese heptoxide, Mn_2O_7	Acidic, forms permanganates isomorphous with perchlorates.

Metallic manganese resembles metallic iron and chromium; all three elements and aluminium form similar alums; the manganates, chromites, and ferrites are related in constitution

and general properties. Manganese bears but little analogy with chlorine, although it is sometimes classed with the halogens. The likeness between manganese and chlorine begins and ends with the highest oxides—the permanganates and perchlorates.

History.—Manganese appears to have been used by the ancient Egyptians and Romans for bleaching glass. Pliny mentions its use for this purpose under the name "magnes." B. Valentine and many later chemists believed "wad" to be an ore of iron. J. H. Pott (1740) proved that pyrolusite proper does not contain iron, and prepared a number of salts from it. K. W. Scheele (1774) made an important investigation on manganese (*vide* chlorine), and T. Bergmann (1774) concluded from Scheele's experiments that pyrolusite contained a new metal which was afterwards isolated by J. F. John in 1807.

Occurrence.—The metal manganese does not occur free in nature. The chief minerals are the oxides *pyrolusite*, MnO_2; *braunite*, Mn_2O_3; *hausmannite*, Mn_3O_4; *manganite*, $Mn_2O_3.H_2O$. The carbonate, $MnCO_3$, is often associated with siderite ($FeCO_3$); manganese also occurs as sulphide, *manganese blende*, MnS. *Wad* is an impure mixture of manganese oxides often found in damp low-lying places, it is supposed to be a decomposition product of manganese minerals. Minute quantities of manganese occur in water, plants, and animals; and traces also appear to be the colouring agent of many amethyst coloured minerals.

Uses.—Manganese is used in the manufacture of manganese bronze (*q.v.*), and also in the manufacture of iron and manganese steel. Manganese alloyed with iron, **ferro-manganese,** can be made by reducing the oxides with carbon in an ordinary blast furnace, or in an electric furnace. Ferro-manganese is used for reducing the iron oxide formed in the Bessemer's converter, and for counteracting the deleterious effects of phosphorus and sulphur. The resulting manganese oxides pass into the slag. Since ferro-manganese contains about 4 or 6 per cent. of carbon, it is used for recarbonizing Bessemer's steel. Manganese steel is particularly hard and free from air blebs. It is used in the manufacture of burglar-proof safes, dredge pins, shoes and crusher plates, ore crushing mills;

Heusler's alloys contain copper, aluminium, and manganese (55 : 15 : 30). They are magnetic.

Manganese dioxide is used as an oxidizing agent ; in the manufacture of chlorine and bromine, decolorizing glass stained a yellowish tinge by the traces of " ferric silicate " present, the violet colour of manganese silicate masks the complementary yellow tint of the iron. Manganese dioxide is also used as a " drier " for paints and varnishes ; as a depolarizer in battery cells ; colouring pottery bodies and glazes ; etc. Wad is used in the manufacture of paint. A crude mixture of sodium manganate and permanganate is made by fusing sodium hydroxide with pyrolusite, and sold as a disinfectant under the name " Condy's fluid." Its " disinfecting " qualities depend upon its oxidizing properties.

Evaluation of manganese dioxide.—If manganese dioxide (or potassium dichromate) be heated with hydrochloric acid, chlorine is evolved, p. 137. If chlorine be passed into an aqueous solution of potassium iodide, iodine will be liberated. It is comparatively easy to determine the amount of free iodine in a given solution by taking advantage of the fact that sodium thiosulphate, $Na_2S_2O_3.5H_2O$, p. 319, reacts quantitatively with free iodine in such a way that two molecules of the thiosulphate with two atoms of iodine produce two molecules of sodium iodide and one molecule of a salt called sodium tetrathionate, $Na_2S_4O_6$. In symbols: $Na_2S_2O_3.5H_2O + I_2 \rightarrow Na_2S_4O_6 + 2NaI$, Hence, 248 grms. of thiosulphate correspond with 127 grms. of iodine. Since one atom of iodine is equivalent to one atom of hydrogen a normal solution of sodium thiosulphate will contain 248 grms. (one gram-molecule) per litre. When the potassium iodide solution containing free iodine is titrated with $\frac{1}{10}$ N-thiosulphate, the colour due to the free iodine becomes paler and paler towards the end of the titration, a couple of drops of a solution of starch is then added, and the titration continued until the resulting blue coloration disappears.

EXAMPLE.—0·3 grm. of pyrolusite was treated as above described and 250 c.c. of a solution of iodine in potassium iodide were obtained. When 50 c.c. of this solution, on titration, required 10 c.c. of $\frac{1}{10}$

N-thiosulphate. Every molecule of manganese dioxide liberates a molecule of chlorine (p. 140); $MnO_2+4HCl=2H_2O+MnCl_2+Cl_2$; and a molecule of chlorine liberates a molecule of iodine from potassium iodide; $Cl_2+2KI=2KCl+I_2$; hence a molecule of the dioxide represents a molecule of iodine, or two molecules of the thiosulphate: $2Na_2S_2O_3.5H_2O+I_2=2NaI+Na_2S_4O_6$. Hence a gram-molecule of the thiosulphate represents half a gram-molecule of manganese dioxide; or, 1000 c.c. of the $\frac{1}{10}$ N-thiosulphate represents $\frac{1}{10}$ of $\frac{1}{2}$ of 87 = 4·35 grms. of the dioxide or 1 c.c. represents 0·00435 grm. of MnO_2; or 10 c.c. represents 0·0435 grm. of MnO_2. Hence 250 c.c. contains iodine equivalent to 0·2175 grm. of MnO_2 per 0·3 grm. of pyrolusite; or the sample contains 72·5 per cent. MnO_2.

Questions.

1. Manganese chloride is found on analysis to contain: manganese 43·63 per cent., chlorine 56·36 per cent.—total 99·99. Calculate its simplest formula (atomic weight of manganese = 55, of chlorine = 35·5).—*London Univ.*

2. Five grams of pink calcite yielded 0·4386 grm. of Mn_3O_4. What proportion of MnO did the calcite contain?—*College Preceptors.*

3. How could you prepare the chloride, sulphide, and the sulphate of manganese from black oxide of manganese?—*Science and Art Dept.*

4. Write down the formulæ of the oxides of manganese, and show in what manner potassium permanganate is related to any of these. What are the uses of potassium permanganate?—*Sydney Univ.*

5. What is the usual naturally occurring source of manganese compounds? From this source how are manganous sulphate, manganous chloride and potassium permanganate prepared?—*Bombay Univ.*

6. Calculate the volume of chlorine measured at 15° and 740 mm. obtainable by the dissolution of 10 grms. of pure manganese dioxide in an excess of hydrochloric acid.—*Science and Art Dept.*

7. Express by equations the action of potassium permanganate acidified with sulphuric acid on aqueous solutions of the following substances: sulphurous acid, hydrogen peroxide, ferrous sulphate, oxalic acid.—*London Univ.*

8. How would you volumetrically determine the strength of a solution of hydrogen peroxide? Give equations of the changes which occur.—*Science and Art Dept.*

9. The native dioxide is the common ore of manganese. How

from this body can you obtain (1) manganese sulphate, and (2) potassium permanganate ?—*London Univ.*

10. How is potassium permanganate prepared ? Why is its formula written $KMnO_4$ rather than $K_2Mn_2O_8$?

11. Give the formulæ for potassium manganate and potassium permanganate. Describe, with equations, the action of sulphurous acid and of hydrogen peroxide upon acidified solutions of the latter salt.—*London Univ.*

12. If 10 grms. of potassium permanganate were distilled with a concentrated solution of hydrogen chloride, and the evolved gas passed into a solution of sulphur dioxide, what amount of sulphuric acid would be formed ? (Mn = 55.)—*London Univ.*

13. Given a solution of potassium permanganate, explain how the following substances can be obtained with its aid : manganese dioxide, manganese sulphate, chlorine, and oxygen.—*London Univ.*

14. How is sodium sulphite prepared ? What crystals are deposited from its concentrated solution saturated with sulphur dioxide ? What is the effect of treating it with hydrochloric acid and warming ? What is the effect of adding to its solution a solution of permanganate of potash ?—*London Univ.*

15. Explain the term *available oxygen* as applied to potassium permanganate and potassium dichromate respectively ; also *available chlorine* as applied to bleaching powder.—*London Univ.*

16. What happens when potassium nitrate is heated (*a*) alone, (*b*) with sulphuric acid, (*c*) hydrochloric acid, (*d*) charcoal, (*e*) lead, (*f*) manganese dioxide, (*g*) chromic oxide, (*h*) copper ?—*London Univ.*

17. What weight of pyrolusite containing 70 per cent. of MnO_2 will be required for the liberation of the iodine contained in 10 grms. of potassium iodide ? What weight of potassium hydroxide solution containing 20 per cent. of potassium hydroxide will be required to decolorize the iodine thus liberated ?—*London Univ.*

18. What are the chief substances containing manganese which find application in the arts or manufactures ? Explain how they are obtained, and what use is made of them.—*Delegacy Local Exams.*

19. What weight of potassium permanganate in dilute sulphuric acid solution would be acted upon by 25 grms. of a 1 per cent. solution of hydrogen peroxide ? (Atomic weight of potassium = 39, of manganese = 55.)—*Staffs. County Schol.*

20. If you were provided with sulphuric acid, common salt, nitre, and manganese dioxide, what substances could you prepare ? —*Staffs. County Schol.*

21. Show that the equivalent of potassium permanganate in acid solutions is one-tenth its molecular weight.

22. What weight of potassium permanganate is required to convert a gram of ferrous iron into ferric iron ?

23. If 0·2 grm. of iron, after dissolving in dilute acid while protected from the oxidizing action of air, required 35·6 c.c. of $\frac{1}{10}$ N-permanganate solution to get a permanent pink solution, what amount of iron is present in the given sample ?

24. When ferric salts are reduced to the ferrous condition by zinc and sulphuric acid, prior to the permanganate titration, why must zinc be absent before the titration is commenced ?

25. Represent by equations the reactions which take place when manganese dioxide is subjected to the action of (*a*) heat, (*b*) hydrochloric acid, (*c*) sulphuric acid, and describe the tests you would employ to identify the gaseous products.—*Science and Art Dept.*

26. Explain how manganese dioxide is recovered from manganese chloride by Weldon's process.—*Science and Art Dept.*

CHAPTER XXVI

Iron, Nickel, and Cobalt

§ 1. Iron—Occurrence, Preparation, and Properties.

History.—Several fabulous stories have been told describing how meteoric iron falling to the earth was sent from heaven as a gift of the gods to man. Iron implements have been used from prehistoric times. An iron implement, found during some blasting operations in the Pyramid at Gizeh (Egypt), is probably 5000 years old. The use of steel in China has been traced as far back as 2220 B.C. In olden times, iron was symbolized by ♂, the spear and shield of Mars, the god of war—probably in allusion to its use in making weapons of war. The methods for extracting and working iron were probably discovered later than those for copper and bronze. Iron is frequently mentioned in the sacred writings. The process of smelting iron is supposed to have originated in the East, and the Hindoos acquired considerable skill in the manufacture of wrought iron. The Chalybes—an ancient nation living near the Black Sea—is supposed to have been the first to smelt iron. Hence, the old term *chalybs* for steel, and our modern *chalybeate* for "ferrugineous." The more recent method of smelting by means of the blast furnace is said to have been introduced in Germany about 1350; and in Great Britain about 1500. Charcoal was first used as the reducing agent; in 1618, D. Dudley commenced using coal; and in 1713, Darby used coke. Coke and coal gradually displaced the use of charcoal. Some charcoal is still used where wood is cheap, *e.g.* in a few places on the Continent and in America.

Occurrence.—Small quantities of metallic iron occur in

some basaltic rocks. An unusual mass, over 25 tons, has been found on the Disko Island, Greenland. Since iron rapidly corrodes when exposed to a humid atmosphere, native iron is not at all common. Nearly all meteorites or aërolites contain iron associated with other metals—chiefly copper, cobalt, and nickel. Ferric oxide, Fe_2O_3, is widely distributed in nature as *red hæmatite*, red ore, or specular iron ore. *Brown hæmatite* represents a class of hydrated oxides which may be represented by the general formula : $Fe_2O_3.nH_2O$, where n represents the variable amount of water in different varieties—*limonite* is generally taken to be $Fe_2O_3.3H_2O$, that is, $Fe(OH)_3$; *göthite*, $Fe_2O_3.H_2O$; and *bog iron ore* which occurs in Ireland belongs to this class. *Magnetite*, Fe_3O_4, is also called loadstone, and magnetic oxide of iron. *Siderite*, $FeCO_3$, is a ferrous carbonate. *Iron pyrites*, FeS_2, and *chalcopyrites* or cupriferous pyrites, $CuFeS_2$, are not worked directly for iron on account of the difficulty involved in eliminating sulphur from the product. Very few clays, soils, and granite rocks are free from small quantities of iron. Iron plays an important part in the nutrition of the higher animals and plants, since this element seems necessary for their healthy growth.

The action of acids.—Iron dissolves in dilute acids ; sulphuric acid furnishes **ferrous sulphate** and hydrogen ; and hydrochloric acid furnishes **ferrous chloride** and hydrogen. With cold dilute nitric acid, hydrogen is not evolved, but the acid is reduced to ammonia, and this reacts with the excess of nitric acid to form ammonium nitrate. With hot nitric acid, ferric nitrate and nitrogen oxides are formed. With concentrated nitric acid (specific gravity 1·45), the iron does not dissolve. The iron in contact with the concentrated acid appears to have changed, for it behaves differently from a piece of the same sample of iron which has not been in contact with concentrated nitric acid. The sample which has not been in contact with the strong acid will precipitate copper from copper sulphate solutions, lead from lead nitrate, and silver from silver nitrate ; the other sample will not. The inert iron is said to be in the passive condition. **Passive iron** does not dissolve when dipped in dilute nitric acid. Other oxidizing agents,

chromic acid, hydrogen peroxide, will make iron passive. Chemists are not yet agreed as to the cause of passivity, the general idea is that a thin film of oxide is formed on the metal by contact with the oxidizing agent. The passivity can be removed by scratching the surface of the iron, by heating it in a reducing gas, by strongly rubbing the surface, and by bringing the passive iron in contact with zinc while immersed in the dilute nitric acid. Other metals also exhibit passivity, *e.g.* cobalt, nickel, chromium, and bismuth.

The rusting of iron.—When commercial iron is exposed to a humid atmosphere for a short time, it soon becomes covered with a reddish-brown film which is called *rust*. Iron rust seems to be an indefinite mixture which on analysis furnishes numbers which vary according to the age of the rust, etc. Rust usually contains ferrous oxide, ferric oxide, carbon dioxide, and water. Analyses show that rust is probably a mixture of ferric oxide, hydrated ferrous and ferric oxides, and basic ferrous and ferric carbonates. If the rust has been long exposed to the air, the amount of ferric oxide is relatively large, and the amounts of ferrous oxide and carbon dioxide small. Rusting is a complex process, and workers are by no means agreed on the simple facts. Dry iron in dry air does not rust, moisture must be present before rusting can occur. Some deny, others affirm, that the presence of an acid and water are necessary. It is exceedingly difficult to free water and the surface of glass from carbon dioxide ; and silicic acid can be dissolved from the glass vessels used and from particles of slag in the iron. However, where careful attention has been taken to eliminate the disturbing factors, the evidence seems in favour of the conclusion that the presence of an acid is necessary for rusting ; that an acid is always present when the iron dissolves ; and it is highly probable that pure iron does not undergo appreciable oxidation when exposed to pure water and to pure oxygen. Films of moisture frequently condense on the surface of iron exposed to the air, and the moisture holds carbonic acid and oxygen in solution. The mechanism of the "atmospheric rusting" of iron may then proceed according to the following scheme : An acid ferrous carbonate, $Fe(HCO_3)_2$; or a basic

carbonate, $Fe(OH)(HCO_3)$, is first formed. The ferrous carbonate in contact with oxygen is oxidized to basic ferric carbonate, $Fe(OH)_2(HCO_3)$; or to $Fe(OH)(HCO_3)_2$; or both. The basic ferric carbonate is then hydrolyzed by the water forming ferric hydroxide, $Fe(OH)_3$; and the ferric hydroxide is subsequently more or less dehydrated, forming ferric oxide. Ferric oxide is more or less hygroscopic, so that once rusting has started, at any point, subsequent corrosion is quicker because the ferric oxide helps to keep the surface of the iron adjacent to the rust spot moist. Several other hypotheses have been suggested, and the subject is still *sub judice*.

Sacrificial metals.—We have seen that any metal in the electrochemical series can be made one plate of a cell against a metal lower down in the series. Zinc, for instance, can be made the positive plate against a negative plate of iron, tin, lead, etc. ; and iron the positive plate against a negative plate of tin, lead, etc. The further apart the elements in the series, the greater the electromotive force of the combination. *Tin plate* is iron or steel coated with a thin layer of tin. If a little moisture be precipitated on the surface in contact with both the iron and the tin, the moisture, with its dissolved carbonic acid, dissolves the iron producing salts of iron ; these ultimately form rust (*q.v.*). The iron is covered with a layer of tin to protect it from rust, but if there be a flaw in the protecting surface of tin so as to expose the underlying iron, rusting takes place more rapidly than if the iron had not been tinned at all. The tin remains untarnished. Zinc is also used as a protecting layer over the surface of thin iron plates—*galvanized iron*. The voltaic action developed when the protecting layer is damaged is much less than when tin is used. These facts can be illustrated by fitting up a cell like Fig. 183 with iron and tin plates, and another cell with iron and zinc plates. Water saturated with carbon dioxide is used in both cells. A feeble electric current will flow from the tin to the iron outside the cell in one case, and from the zinc to the iron in the other,

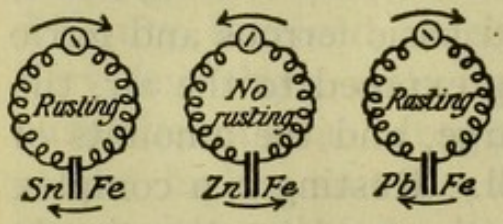


FIG. 183.

as illustrated graphically in the adjoining diagram. *In the iron : tin cell, iron dissolves and rusting occurs ; while in the the iron : zinc cell, the zinc dissolves and no rusting occurs as long as the circuit is closed.* These results might almost have been predicted from our study of Table XXII., p. 415. An iron : lead cell behaves like an iron : tin cell. Iron railings are often fixed in a bed of lead, the iron corrodes first and the lead remains intact. H. Davy (1824) once proposed to prevent the corrosion of the copper sheathing of ships by fixing pieces of metallic zinc here and there on the sheathing. The zinc was corroded and the copper preserved.[1] In all these cases it has been fancifully said that one metal is sacrificed to ensure the safety of the other ; and all the cases quoted are examples of galvanic couples : Fe:Sn ; Zn:Fe ; Fe:Pb ; and Zn:Cu.

§ 2. The Manufacture and Properties of Pig Iron.

The oxides and carbonates are the sources of commercial iron. These ores frequently contain a certain amount of clay, and the ores are then termed *clay ironstone.* The so-called *blackband ironstone* is a ferrous carbonate contaminated with clay and black coaly matters. The clay ironstones are usually calcined or roasted by stacking the ore with a small quantity of fuel in heaps, in stalls, or in shallow kilns. In the former case, combustion is started at one point and allowed to proceed throughout the whole mass. The temperature of the smouldering mass is sufficient to drive off most of the moisture, and carbon dioxide, and burn the organic matter and some of the sulphur and arsenic. The ferrous oxide is also oxidized to ferric oxide. This prevents the early formation of a fusible slag which would attack the lining of the furnace. Ferric oxide does not form a slag at so low a temperature as ferrous oxide. At the same time, the ore is made somewhat porous, and this facilitates its reduction to metallic iron at a later stage of the process.

The reduction of the calcined ore or of ferric oxide is effected

[1] The copper then ceased to poison the barnacles, and the bottom fouled as if the wood had not been sheeted with copper.

in a blast furnace. The blast furnace is a long cylindrical shaft fed with ore, fuel, and flux at the top by depressing the cone *C*, Fig. 184, near the throat of the furnace ; and supplied with a hot blast of air necessary for the combustion of the fuel through tuyères, *T*, at the bottom. The function of the blast furnace is to reduce the iron oxides to the metallic condition,

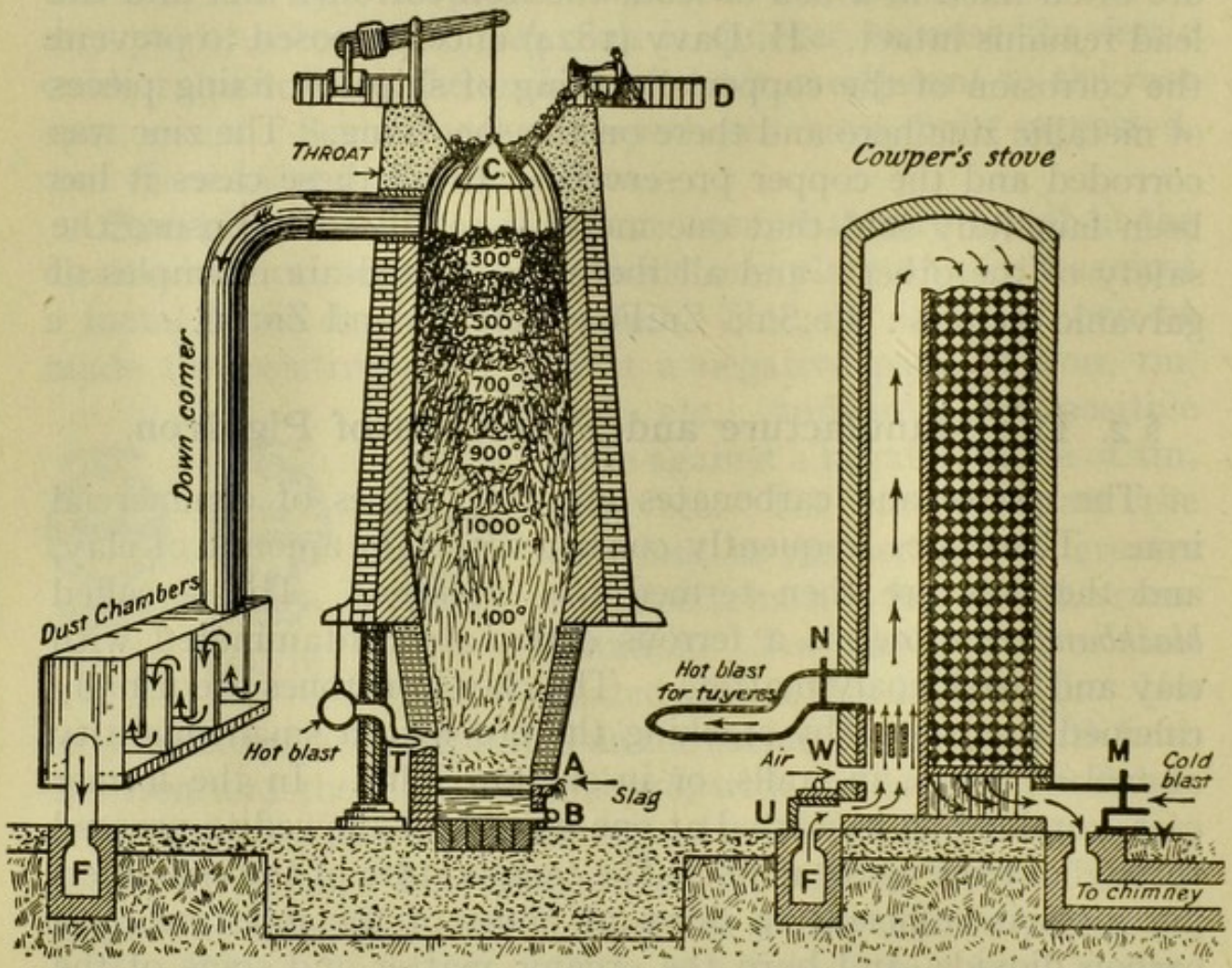


FIG. 184.—Blast Furnace (Diagrammatic).

and to free the iron so reduced from earthy impurities by forming a slag which is fusible at the temperature of the furnace. The metallic iron and slag are discharged at the bottom of the furnace and the gases pass away to the top and are there drawn off. The gases pass along the *down-comer* and enter the *dust chamber* where much of the dust is removed. The gas is mixed with air (*viâ W*), and burnt in Cowper's stove. This heats the checkered brickwork. The valves *U* and *V* are then closed, and the gas deflected into a second " stove," while cold air is

blown through the hot stove to the tuyères by opening the valves *M* and *N*.

The reactions in the blast furnace during smelting.—The chemical changes which take place in the blast furnace during the smelting of iron ore are somewhat complex. Hence, the following sketch must be regarded as a simplified description :—

1. **The ore.**—The ore, mixed with coke and limestone, is exposed, in the upper part of the furnace, to the action of reducing gases, principally carbon monoxide, ascending from the lower part of the furnace. The action commences between 200° and 500°, that is, as soon as the charge has commenced its downward descent : $Fe_2O_3+3CO \rightleftharpoons 2Fe+3CO_2$; and reduction continues with increasing velocity as the charge descends into the hotter part of the furnace. Most of the oxide is reduced before it has descended 10 feet below the level of the charge ; any oxide which has escaped reduction will then be reduced by the carbon : $Fe_2O_3+3C=3CO+2Fe$. The hot spongy iron meets the ascending carbon monoxide, and decomposes part : $2CO=CO_2+C$. The solid carbon is deposited amidst the spongy iron. The iron undergoes little change until it reaches the zone of fusion. The iron, however, absorbs or dissolves much carbon as it passes down the furnace. The melting-point of a mixture of iron and carbon is lower than that of pure iron, so that while the temperature of the blast furnace would not be sufficient to melt pure iron to the necessary fluid condition, the temperature required for iron with carbon in solution is easily maintained. The molten iron trickles down and collects in the well of the furnace below the tuyères. The iron takes up many other elements in addition to carbon during its descent in the furnace. Thus, silicon, sulphur, phosphorus, and manganese are partly absorbed by the iron, and partly by the slag.

2. **The ascending gases.**—The oxygen of the hot air blast burns the carbon of the hot coke : $C+O_2=CO_2$; and the carbon dioxide is at once reduced by the hot carbon : $CO_2+C=2CO$. The ascending gases warm up the descending charge. When the temperature reaches about 600°, the limestone begins to

decompose : $CaCO_3=CO_2+CaO$. Most of the carbon dioxide thus formed is at once reduced by the excess of carbon to carbon monoxide. At this stage, the reduction of the iron oxide to spongy metallic iron is practically complete. An excess of carbon monoxide is needed for the reduction because the reaction, $Fe_2O_3+3CO \rightleftharpoons 3CO_2+2Fe$, is reversible, and a condition of equilibrium would be attained when only a certain proportion of the ferric oxide is reduced. An excess of carbon monoxide favours a more complete reduction of the ferric oxide. There are quite a number of concurrent reactions taking place at the same time. If any water is present in the blast, it will be reduced : $H_2O+C=CO+H_2$; and the nitrogen of the air, brought in with the gas, forms a little cyanogen. The net result is a combustible gas, containing approximately :

CO	CO_2	N	H	Hydrocarbons.
25·3	10·5	58·1	4·3	1·6 per cent.

The combustible gas is utilized for heating the blast ; and if there be any surplus, it is used for heating the boilers which run the blowing engine ; for calcining the ore, and for general heating purposes. If coal be used in place of coke, some tar, etc., will separate from the gas and collect at the base of the downcomer.

3. **The slag.**—When the charge in the furnace has descended about 20 or 30 feet, and the temperature is about 600°, it has formed a mixture of spongy iron, earthy gangue, coke, and limestone or quicklime. Little further change occurs until the temperature is hot enough to melt the mixture. At this temperature, a fusible slag is formed containing approximately 55 per cent. SiO_2, 30 per cent. CaO, and 15 per cent. Al_2O_3. The fused slag trickles down into the well, and floats on the surface of the molten iron. The slag is drawn from the furnace at intervals, and, when cool enough, tipped on the slag heap. The slag is derived from the ash of the fuel from the earthy gangue of the ore, and the fluxes added with the charge to promote fusion. The composition of the slag varies with the quality of the iron, etc. Success in working the blast furnace depends largely upon the nature of the slag. Some types of

slag which do not disintegrate on exposure to the air are used as road metal and railway ballast; or mixed with some clay and moulded into bricks for paving and building purposes. Some varieties of slag are made into cement.

The properties of pig iron.—The molten metal which collects in the well is tapped at intervals—say, twice every twenty-four hours, and run into sand moulds, or into "chilled moulds," and allowed to solidify. The iron is then called pig iron. The "pigs" of iron are about 3 feet long, and 3 or 4 inches thick. In some cases the molten metal is run directly into a mixer, or into Bessemer's converter and made into steel. Ore, flux, and coke enter the furnace; molten iron, molten slag, and gaseous products leave the furnace. Fresh charges of ore, coke, and flux are added in definite proportions at regular intervals, and the smelting of the ore thus continues without interruption for months or years.

The pig iron is classed according to its quality. Ordinary pig iron contains from 1·5 to 4·5 per cent. of carbon. Higher proportions are sometimes present when the raw materials contain much manganese or chromium. The carbon of pig iron occurs in at least two different states—free and combined. Combined carbon is either in solution or present as a definite chemical compound, see "Steel." The mode in which the carbon is associated with the iron has a marked effect on its properties. The free carbon, interspersed as graphite through the pig iron, is well shown on the fractured surface of a broken pig. If pig iron be digested with hydrochloric acid, the graphite remains behind as an insoluble black powder, but the combined carbon unites with the hydrogen, forming various hydrocarbons, which colour the solution yellowish-brown, and give the escaping gas a characteristic unpleasant smell. The gas is also contaminated with hydrogen sulphide, silicide, and phosphide derived from the impurities—iron sulphide, silicide and phosphide—in the iron. The classification of pig iron is based on the relation of free to combined carbon. If much of the carbon be "free," the iron is called **grey pig iron**; and if much combined carbon be present, **white pig iron**; intermediate varieties are called **mottled pig iron**. The grey and mottled varieties

are further subdivided. Pig irons too are often graded according to their source, because certain districts work a specially pure or a specially foul ore, and this gives the iron from districts characteristic properties. The following analyses will illustrate the difference between the three varieties of pig iron :

	Grey.	Mottled.	White.
Combined carbon (C.C.)	0·90	1·80	3·00 per cent.
Free carbon (Gr.) . .	2·8	1·40	0·10 ,, ,,

The pig iron also contains silicon, sulphur, phosphorus, and manganese. Cast or pig iron is not malleable, nor can it be welded. It is used for casting articles—like stoves and ornamental iron—which are not likely to be subjected to shocks. Cast iron is the starting-point for the manufacture of wrought iron and steel.

§ 3. The Manufacture and Properties of Wrought Iron.

Wrought iron is made by melting pig iron with " scrap " iron on the bed of a reverberatory furnace, Fig. 177, lined with iron ore (Fe_2O_3). The reverberatory furnace—here called a *puddling furnace*—was first used for iron by H. Cort in 1784, although similar furnaces had been used by copper smelters for some time. Rogers, in 1816, improved the furnace by introducing a bed of iron oxide in place of siliceous matters previously used. Part of the carbon, silicon, sulphur, and phosphorus of the cast iron are oxidized by the furnace lining, and the metal melts to a fluid mass on the bed of the furnace (*melting stage*). The puddler then thoroughly mixes the charge so as to bring the molten metal into intimate contact with the iron oxide of the furnace bed. The puddler works the iron through an opening in the side of the furnace. The sulphur, phosphorus, and silicon are partly oxidized. Jets of flame soon appear on the surface of the molten metal—" puddler's candles " (*fluid stage*). The carbon is oxidized to carbon monoxide, which burns to carbon dioxide. The other impurities are also partly oxidized, and form a slag with the lining of the furnace (*boiling stage*). The iron then becomes " pasty," because purified iron melts at a higher temperature than the less pure iron. The molten mass

is stirred, puddled, and finally gathered into large " balls " or " blooms," each ball about 80 lbs. in weight (*boiling stage*). The balls are removed from the furnace, and squeezed nearly free from slag by working under a steam hammer. The iron is then rolled into sheets so as to give the finished product a fibrous structure.

While cast iron melts at about 1200°, wrought iron melts at about 1550°. Wrought iron softens at about 1000°, and it can then be forged and welded. Wrought iron is tough and malleable, and fibrous in structure ; cast iron is brittle, and it has a crystalline structure. Wrought iron can be rolled into plates, and drawn into wire. It is made into wire, nails, chains, anchors, horseshoes, agricultural implements, etc. It is not used so much as formerly, because it has been largely replaced by steel. When heated red hot and quenched in cold water, wrought iron does not harden ; steel under the same treatment becomes very hard.

§ 4. The Manufacture of Steel—Crucible and Cementation Processes.

The amount of carbon in steel is intermediate between that in cast iron and in wrought iron. Steel is made by decarbonizing cast iron, or by carbonizing wrought iron. The latter process gives the more reliable result, because wrought iron is less contaminated with other impurities. The principal methods of making steel are : (1) the cementation process ; (2) the crucible process ; (3) electric processes ; (4) Bessemer's acid and basic processes ; and (5) Siemens and Martin's acid or basic processes.

The cementation process.—Bars of specially pure varieties of wrought iron—*e.g.* Swedish iron—are packed with charcoal in boxes made of firebrick, and sealed with a lute of refuse from the troughs below the grindstones of the steel grinders. The boxes are heated in a furnace for 8 to 11 days at about 1000°. The time and temperature depend upon the amount of carbon to be incorporated with the wrought iron. The bars, when removed from the cold furnace, have a blistered appearance, hence the term *blister steel*. The bars are broken and sorted by

experts, who estimate the quality from the appearance of fractured surfaces. The blistered steel is then heated, and hammered into bars. The product is a high-class tool steel called *shear steel*. The only change in composition which can occur during the cementation is due to carbon, and some of the purest steels in commerce are made by this process. Blister steel is also melted in crucibles and cast into ingots for high-grade cast steels. The cementation process is being gradually displaced by cheaper processes.

During cementation, solid carbon slowly diffuses into the iron. Probably at the high temperature, gaseous carbon compounds play some part in the action. Maybe carbon monoxide is formed and occluded by the iron. The carbon monoxide is then decomposed : $2CO=CO_2+C$. The carbon dioxide escapes into the box of charcoal and there forms more carbon monoxide. This is again occluded by the iron, and the cyclic action : $CO \rightarrow CO_2 \rightarrow CO \rightarrow \ldots$ is repeated indefinitely. Possibly also some cyanogen compounds take part in the action.

The crucible process for cast steel.—Bars of wrought iron are melted with a definite amount of carbon in fireclay crucibles. The iron slowly changes into steel by absorbing carbon. The time required is about four hours. Experience has taught the melter how much charcoal is needed to bring the metal up to the required carbon content. The success of the operation depends upon the skill in the selection of the iron ; in the adjustment of the charge ; and on careful melting. Crucible steel is usually a high-grade tool steel used for razors, files, etc. A less pure product is made by heating a mixture of wrought iron with the necessary amount of cast iron. High-grade crucible steel is more expensive than Bessemer or open hearth steel. The term " cast steel " was originally reserved for crucible steel, but the term is sometimes used by vendors of steels made by cheaper processes.

Special steels of the self-hardening type are usually made by the crucible process, by alloying steel with small quantities of other metals ; these impart hardness, toughness, and strength. In districts where electric power is cheap, electric furnaces are coming into use for the manufacture of steel. Electric furnaces

may not succeed in ousting the Bessemer and open hearth processes ; but they promise to play an important part in the future of the steel industry, and possibly may displace some of the older processes of making special steel.

§ 5. The Manufacture of Steel—Bessemer's Process.

In 1852, Kelly patented a process in America, for purifying iron, based on the fact that if air be forced through a mass of molten pig iron, in a suitable vessel, the impurities which prevent the pig iron being ductile and malleable are removed, and a bath of molten metal, virtually wrought iron, is obtained. In 1855, H. Bessemer patented a converter very suitable for the process. After some litigation, the Bessemer Co. bought Kelly's interests. The metal in the furnace can be mixed with a known amount of spiegeleisen or ferro-manganese, containing a known amount of carbon. The steel is then at a sufficiently high temperature to permit of its being cast into moulds. In this way, in half an hour's time, 10 tons of steel can be prepared at but a small fraction of the cost of manufacture by the processes which precede. This method of making steel has virtually revolutionized the art.

In Bessemer's process about 10 tons of molten pig iron are run into a large egg-shaped vessel, called the *converter*. The converter can be tilted into any required position. It is provided with holes at the bottom through which a powerful blast of air can be blown. The converter is made of wrought-iron plates, and lined with a bed made of silica and clay. A general idea of the structure of a converter can be gathered from Fig. 178 which shows part of the inside and part of the outside. Molten pig iron is run into the converter, and a powerful blast of air in fine jets is forced through the mass of molten metal. The temperature rises owing to the heat evolved by the oxidation and combustion of the impurities—the carbon, sulphur, and manganese. The carbon forms carbon monoxide which burns at the mouth of the converter. The flame is accompanied by a brilliant shower of sparks. The other oxides form a slag with the furnace lining. Experience and the appearance of the

flame tells the operator when to stop the blast. The right amount of spiegeleisen is then added to make a metal of definite composition. The blast is again turned on for a moment, and the metal is then cast into moulds to form blocks of Bessemer steel.

Thomas and Gilchrist's basic process.—The sulphur and phosphorus are not removed by Bessemer's process just indicated. In 1878, Thomas and Gilchrist showed that, if the converter be lined with, say, dolomite (basic lining), and some lime be added to the charge of pig iron, and the blast continued a little longer, the oxides of phosphorus, sulphur, and silicon formed are absorbed by the furnace lining. The operation is otherwise conducted as before. The lining, after use, is called *Thomas's slag*, and it is used as a fertilizer on account of the phosphorus it contains. If the lining is siliceous the operation is called the *acid Bessemer's process ;* and if the lining be dolomite, the *basic Bessemer's process.*

§ 6. The Manufacture of Steel—Siemens and Martin's Open Hearth Process.

E. Martin (1864) made steel by fusing pig iron admixed with wrought-iron scrap in an open sand basin ; and W. Siemens (1863) by treating pig iron and pure hæmatite ore in a similar manner. The idea thus originated with the latter, though the process is usually called the " Siemens-Martin," or the open hearth process. In this process, the furnace is charged with a mixture of pig iron, scrap (wrought) iron, and good hæmatite ore free from carbon. The mixture is melted in a shallow rectangular trough or hearth. The furnace is heated by producer gas. Both the gas and the secondary air for the combustion of the gas are pre-heated, so that a very high temperature can be obtained. A general idea of the process can be gathered from Fig. 185, which shows a section through the hearth. The air port is not shown in the diagram. The gas and air burn on the left, the flue gases travel down the flue on the right, and in doing so heat up two chambers below. The direction of the burning gas is then reversed. Gas and air pass

separately through the hot chambers, and the flue gases heat up another pair of chambers below the hearth. The direction travelled by the burning gas is reversed about every half-hour, and the heat of the flue gases is utilized in warming up chambers through which the unburnt gas and air will pass later on. The furnace is called *Siemens' regenerative furnace.* When a test shows that the metal contains the right amount of carbon, ferro-manganese is added as in the case of Bessemer's steel. If the bed of the furnace is made of siliceous materials—*acid process*—the proportion of carbon, silicon, and manganese are reduced during the treatment, but the amounts of sulphur and phosphorus remain fairly constant. In the *basic process*, the furnace is bedded with, say, dolomite, and there is a steady fall in the amount of phosphorus and sulphur during the treatment, just as was the case with the basic Bessemer's process of Thomas and Gilchrist.

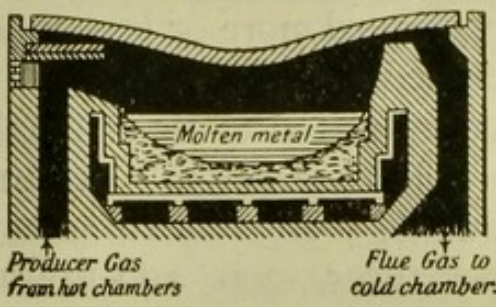


FIG. 185.—Hearth of Siemens-Martin's Process (Diagrammatic).

§ 7. The Properties of Steel.

It may be said in a rough kind of way that steel is intermediate between cast and wrought iron so far as the proportion of carbon is concerned. Thus :

			Steel.		
	Pig iron.	Wrought iron.	Hard.	Medium.	Soft.
Carbon . . .	3·0	0·06	0·9	0·4	0·1

There is, however, no hard and fast boundary line, and it does not seem possible to define steel satisfactorily without reference to its mode of manufacture.

The tempering and hardening of steel.—The sudden quenching of the steel while these changes are in progress may arrest or inhibit further change. Similarly, re-heating followed by sudden quenching may completely alter the structure, and accordingly also the properties of the metal. The hardness of

steel thus depends upon its composition and its history—the way the metal has been cooled, and on its subsequent heat treatment. A typical steel containing nearly 1 per cent. of carbon when heated to a high temperature and suddenly chilled, becomes so hard that it will scratch glass, and so brittle that it will not bend very far without breaking. The operation is called *hardening steel.* The hardenite of hardened steel is preserved more or less undecomposed when the steel is suddenly chilled—hence the term "hardenite." If the hardened steel be re-heated to its original high temperature, and slowly cooled —"letting down," or **annealing steel**—it becomes soft and ductile. By reheating hardened steel to certain definite temperatures—200° and upwards—and then cooling under definite conditions, steels can be obtained of varying, yet definite, degrees of hardness and ductility. This has been traced to changes in the constitution of the metal. The process of re-heating a hardened steel to a temperature far short of that employed when the steel was hardened is called **tempering steel.**

§ 8. Iron, Nickel, and Cobalt Oxides.

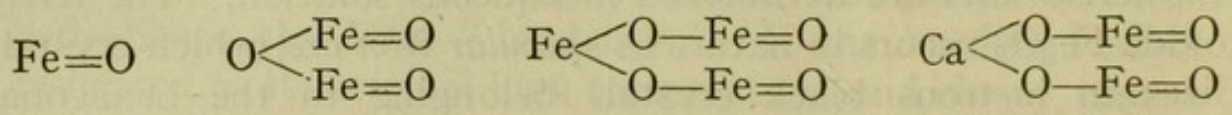
The monoxides.—White **ferrous hydroxide,** $Fe(OH)_2$, is precipitated when an alkaline hydroxide or ammonia is added to a solution of a ferrous salt, provided air be entirely absent; but if the solutions have dissolved air, the precipitate will have a greenish colour. The white precipitate rapidly absorbs oxygen, and passes into ferric hydroxide, $Fe(OH)_3$. Ferrous hydroxide and oxide dissolves in acids, forming ferrous salts. When nickel is similarly treated a pale green **nickelous hydroxide** is formed, and cobalt salts furnish blue or rose-red **cobaltous hydroxide.** When heated out of contact with air the corresponding monoxides are formed; and they also form cobaltous or nickelous salts with acids.

The sesquioxides.—A voluminous reddish-brown precipitate of **ferric hydroxide,** $Fe(OH)_3$, is formed when ammonia is added to a solution of a ferric salt. As in the case of aluminium hydroxide, $Al(OH_3)$, there is some doubt whether a real hydroxide

is formed. Several hydrated hydroxides are said to have been obtained by drying the precipitate at different temperatures, or by precipitating the hydroxide under special conditions. Some of the hydrates occur in nature. For instance, *limonite* has a composition corresponding very nearly with $2Fe_2O_3.3H_2O$; *göthite*, $FeO(OH)$ or $Fe_2O_3.H_2O$, has some analogies, with diaspore and manganite. Ferric hydroxide is a very weak base, and the ferric salts are hydrolyzed in aqueous solution. The ferric oxide Fe_2O_3 occurs in nature as *specular iron ore*, which crystallizes in lustrous black crystals belonging to the hexagonal system ; and in reddish masses of *hæmatite* isomorphous with corundum. **Ferric oxide** is a reddish-brown powder formed when ferrous sulphate, or carbonate, or hydroxide, or many organic salts of iron are calcined in air. It is stable at a red heat, but at a temperature above about 1000° it decomposes into Fe_3O_4. The powdered ferric oxide formed as just described, is used as jeweller's polishing powder—*rouge*—and as a pigment. The particular tint of the pigment depends upon the temperature of calcination, which, in turn, appears to determine the size of the grains of the ferric oxide. Both ferric oxide and the hydroxide are basic, and give rise to ferric salts when heated with acids. Some of the native oxides, and the oxide which has been heated to a high temperature dissolve in acids but slowly. Similar hydroxides are obtained with cobalt and nickel when chlorine is passed through water with the "-ous" hydroxides in suspension. The sesquioxides are formed by calcining the carbonates or nitrates in air.

Ferrosoferric oxide, Fe_3O_4.—Magnetic oxide of iron occurs free in nature in black octahedral crystals which are magnetic. It is the most stable oxide, and is formed when iron or iron oxides are heated in air or oxygen. According to Moissan, there are two modifications of ferrosoferric oxide, the one is formed by heating ferric oxide from 350° to 400° in a current of hydrogen or carbon monoxide ; and the other by reactions at a high temperature, *e.g.* the combustion or iron in oxygen. The former is attacked by nitric acid, and has a specific gravity of 4·86 ; the latter is not attacked by the same acid, and has a specific gravity 5·0 to 5·1. The phenomenon is thus analogous

with the general effect of high temperatures on oxides like alumina, chromic oxide, ferric oxide, etc. Ferrosoferric oxide is not a basic oxide, since it forms a mixture of ferric and ferrous salts when treated with acids. It is probably a " compound " oxide, analogous with mangano-manganic oxide, Mn_3O_4, and red lead, Pb_3O_4. The relations of the iron oxides thus far considered will appear from the graphic formulæ :



Ferrous oxide. Ferric oxide. Ferrosoferric oxide. Calcium ferrite.

Ferrosoferric oxide, according to this hypothesis, is a ferrous ferrite, $Fe(FeO_2)_2$. Several other ferrites are known corresponding with the unknown **ferrous acid,** $HFeO_2$. Thus **calcium ferrite,** $Ca(FeO_2)_2$, that is, $CaO.Fe_2O_3$, is made by precipitating a neutral solution of ferric chloride with lime water.

Cobalto-cobaltic oxide, Co_3O_4, is formed in a similar way to ferrosoferric oxide, and it has probably the same constitution. There is some doubt about the existence of the corresponding nickel compound, although it is reported to be formed when moist oxygen is passed over nickel chloride heated to about 400°.

§ 9. Cobalt and Nickel.

History.—The word " kobalt " occurs in the writings of B. Valentine and Paracelsus to denote a goblin supposed to haunt a mine—from the German *kobald*, an evil spirit ; the term was also applied to what were called " false ores," that is, ores which did not give metals when treated by the processes then in vogue for the extraction of the metals ; and also to ores which had an objectionable smell (1554). The term was gradually confined to the minerals used for colouring glass blue, and which are still used for making smalt. In 1735, Brandt stated that the blue colouring principle is due to the presence of a metal which he called " cobalt rex," hence our " cobalt."

Nickel seems to have been known to the Chinese in early times. In Europe, towards the end of the seventeenth century,

the German term *kupfer-nickel* (false-copper) was applied to an ore, which, while possessing the general appearance of a copper ore, yet gave no copper when treated by the general process then used for the extraction of copper. Nevertheless, the mineral was supposed to be an ore of copper. A. F. Cronstedt, 1751–1754, stated that kupfer-nickel contains a metal which gives a brown, not a blue colour, with glass. Cronstedt's views were not adopted until T. Bergman proved clearly that Cronstedt's " nickel " was a new element in an impure condition.

Occurrence.—Cobalt and nickel are nearly always found associated with one another. Both elements occur free in some meteorites. Cobalt occurs as a minor constituent in some minerals. It also occurs combined as arsenide in *smaltite* or cobalt speiss, $CoAs_2$; and as *cobaltite* or cobalt glance, CoAsS. Nickel occurs as *kupfernickel* or *niccolite*, NiAs ; *millerite*, or nickel blende, NiS ; *nickel glance*, NiAsS ; and *garnierite*, a silicate of magnesium and nickel, $(NiMg)H_2SiO_4$, found in New Caledonia.

Preparation.—The cobalt ores are usually worked to get cobalt salts, and not the metal. The ores are first roasted to remove arsenic and sulphur. The resulting oxides are digested with hydrochloric acid, and the solution treated with hydrogen sulphide to remove the copper, lead, antimony, etc. Bleaching powder is then added in just sufficient quantity to oxidize the iron, which is then precipitated by the addition of chalk. The clear solution is treated with more bleaching powder to precipitate the cobalt oxide ; any nickel which might be present is precipitated by the addition of milk of lime. Cobalt metal is obtained by reducing the oxide in a current of hydrogen, or by reducing the oxide with aluminium powder as in Goldschmidt's process for chromium, Fig. 182.

Nickel and cobalt ores are treated by different methods depending upon the nature of the ore under treatment. Many ores are treated by a process similar to that described for the extraction of copper. The ore is " Bessemerized " in a converter, Fig. 178, so as to oxidize the iron, and furnish a matte rich in copper and nickel. This is roasted, and the resulting oxides are reduced with coke. An alloy of copper and nickel

is thus obtained. The two metals are separated by an electrolytic process.

A nearly pure nickel is made by Mond's process, which is based upon the formation of a readily volatile compound of nickel—nickel carbonyl, $Ni(CO)_4$—when the roasted ore (oxides) is heated to about 300° so as to transform the oxides to metal. The resulting mixture is heated with carbon monoxide under a pressure of about 15 atmospheres at a temperature of about 100°. The vapours of the escaping nickel carbonyl can be decomposed by heating the gas to 200° under atmospheric pressure. The escaping carbon monoxide is used again.

Properties.—Cobalt and nickel are hard white metals, cobalt is slightly bluer than nickel. Both metals are malleable and ductile. Iron is strongly magnetic, cobalt and nickel are but feebly magnetic ; iron forms Fe_3O_4 when heated with steam ; nickel and cobalt form the monoxides. Iron rusts in moist air, cobalt and nickel only oxidize very slightly unless heated in air. Dilute hydrochloric acid and sulphuric acid dissolve cobalt and nickel slowly, whereas iron is rapidly dissolved by these acids. Cobalt and nickel are both attacked by nitric acid, forming the corresponding nitrates—$Co(NO_3)_2$ and $Ni(NO_3)_2$.

Alloys and Uses.—Nickel is much used for "nickel plating" other metals on account of its silvery appearance, and the fact that it does not readily tarnish in air. The nickel is deposited from a double sulphate of ammonium and nickel by a process similar to that used for "silver and gold plating." Nickel is used in making several important alloys : *e.g. German silver* has 25 per cent. of nickel and the rest copper and zinc ; *nickel steel* is hard and tough, and is used for parts of machinery designed to withstand continuous wear and shocks, and in the manufacture of armour plates, burglar-proof safes, etc. Nickel coins contain about 25 per cent. nickel, and 75 per cent. of copper.

Cobalt oxides and silicates are used for colouring glass, and pottery glazes, etc. *Smalt* is a glass made by fusing cobalt oxide and silica, and when ground it is used as a pigment. *Thénard's blue* is a blue pigment made by calcining cobalt oxide with alumina.

Distinction and separation of cobalt and nickel.—The general colour of aqueous solutions of nickel salts is green and of cobalt pale red. Ammonium sulphide with both gives a black precipitate of the sulphide ; alkali hydroxide solutions precipitate an apple-green hydroxide, $Ni(OH)_2$, from nickel salts ; and a blue basic salt from solutions containing cobalt salts, the latter becomes olive-green on exposure to the air, and when heated it forms a rose-red precipitate of cobalt hydroxide. A saturated solution of nitroso-β-naphthol in acetic acid gives a brick-red precipitate with cobalt salts alone ; and the addition of a saturated solution of potassium thiocyanate followed by agitation with ether furnishes with cobalt salts a blue ethereal layer said to be perceptible if one part of cobalt is present in 50,000 parts of solution. The two latter reactions are not produced by nickel. With nickel salts the addition of an ammoniacal solution of dimethylglyoxime gives a rose-red coloration or a scarlet precipitate. This test is said to indicate 1 part of nickel in 200,000 parts of a solution when but 1 c.c. of solution is used ; the reaction is not produced by cobalt.

To separate cobalt from nickel analytically, the nitro-β-naphthol processes can be used ; or cobalt may be precipitated in the presence of nickel as a yellow potassium cobaltinitrite by treating a solution of the mixed salts with potassium nitrite and acetic acid. *To separate nickel from cobalt,* the dimethylglyoxime process may be used ; or the alkaline solution may be treated by an excess of potassium cyanide and bromine whereby nickel hydroxide is alone precipitated.

§ 10. The Relationship of the Members of the Iron Family.

The atomic weights of the iron, cobalt, and nickel group are not very different numerically. It is not at all uncommon to find that elements with but small differences in their atomic weights show marked differences in their physical and chemical properties. For example, boron, 11, and carbon, 12 ; potassium, 39·1 ; argon, 40 ; calcium, 40·1 ; selenium, 79·2 ; and bromine,

79·96; iodine, 126·97; tellurium, 127·6. The physical properties of the iron, cobalt, and nickel family are summarized in the table:

TABLE XXIV.—PHYSICAL PROPERTIES OF THE IRON FAMILY.

	Iron.	Cobalt.	Nickel.
Atomic weight . .	55·85	58·97	58·7
Specific gravity . .	7·8	8·5	8·8
Atomic volume . .	7·16	6·94	6·68
Melting-point . .	1600°	1500°	1450°

The elements are usually associated together in nature; they are all magnetic, nearly white, hard metals with a high melting-point. Their chemical properties exhibit a gradual transition from iron to nickel. Iron forms two well-defined basic oxides, so does cobalt, but the basicity of the cobalt sesquioxide is so feeble that the corresponding salts are only known in solution—the double salts, however, are stable. Nickel gives only one basic oxide—nickel monoxide—the sesquioxide does not appear to form salts. Although the atomic weight of nickel is less than that of cobalt, the physical and chemical properties of the members of the family show a transition from iron to cobalt to nickel. This is not a common phenomenon with the other family groups. The three elements are related to aluminium, manganese, and chromium through iron (ferrates, chromates, manganates, and the alums); and to copper through nickel.

Questions.

1. What compounds are formed in the rusting of iron and in the action of steam on red-hot iron? Explain the difference between the action of hydrochloric acid on iron, and on iron rust.—*Science and Art Dept.*

2. When five grains of oxide of iron are heated in hydrogen, 3·5 grains of iron are left. What is the formula of the oxide?—*Oxford Junr. Locals.*

3. One gram of iron is converted into ferric chloride, and the

product is dissolved in water. What volume, at normal temperature and pressure, of hydrogen sulphide is theoretically required to completely reduce the ferric chloride to ferrous chloride ?—*Science and Art Dept.*

4. What is the action of dilute sulphuric acid on metallic iron ? Describe as many experiments as you can which prove that both products of the action are reducing agents.—*London Univ.*

5. What are the names and formulæ of the chief natural compounds from which iron is extracted in this country ? State briefly the chief reactions which take place in a blast furnace. What impurities occur in crude iron so obtained ?—*London Univ.*

6. Give examples of ferrous and ferric salts ; point out their distinctive characters, as well as tests for them ; describe and explain the methods by which they can be changed the one into the other.—*Science and Art Dept.*

7. How can you prepare the following bodies, directly or indirectly, from iron pyrites : the allotropic forms of sulphur ; sulphur dioxide ; sulphurous acid ; hydrogen sulphide ?—*Science and Art Dept.*

8. How do nickel and cobalt resemble each other ? How would you identify them if both were present in the same solution ?—*Sydney Univ.*

9. Two tons of magnetic oxide of iron (to be considered as pure) are smelted in a furnace with coke for the production of iron. If the coke contains ten per cent. of ash, calculate approximately the theoretical quantity of coke necessary for the reduction. (C=12, O=16, Fe=56.)—*Sydney Univ.*

10. Describe the mode of extracting iron from its ore.—*Cape Univ.*

11. Describe the preparation of cast iron from iron ore. How does cast iron differ from chemically pure iron ?—*Sydney Univ.*

12. What is the composition of the two principal ores of iron ? By what process is the metal extracted from these ores ? How and from what substances is the material known as slag produced ? —*Science and Art Dept.*

13. What is the composition of cast iron, and what are the chief differences in chemical composition and physical properties between cast iron, wrought iron, and steel ? Give an outline of the processes by which the second and third are made from the first.—*Sydney Univ.*

14. Give an outline of the physical properties of wrought iron, cast iron, and steel. In what respects do these substances differ in their chemical composition ?—*London Univ.*

15. How would you prepare metallic iron from ferric oxide ? What happens when a solution of sulphuretted hydrogen is passed through a solution of ferric chloride ?—*London Univ.*

16. By what chemical tests would you ascertain whether a sample of iron is cast or wrought iron ?—*London Univ.*

17. Mention some of the ores of metal and cobalt, and state the method of obtaining the respective metals usually employed. State a reaction which would enable you to distinguish the salts of these metals.—*London Univ.*

18. Point out the distinguishing characteristics of iron and steel, and describe the various modes by which iron is converted into steel.—*London Univ.*

19. Describe the Bessemer process of manufacturing steel.—*London Univ.*

20. How would you prepare the following compounds from metallic iron : ferrous iodide, chloride, sulphate, and carbonate ; *Ferric* chloride, hydrate, and oxide ? Explain the changes involved in each process.—*London Univ.*

21. How would you prepare the following substances : (*a*) ferric oxide from metallic iron, (*b*) chromium sesquioxide from potassium dichromate, (*c*) mercuric oxide from mercury, (*d*) sodium nitrite from sodium nitrate ?—*London Univ.*

22. How would you prepare (*a*) a ferrous and a ferric salt, (*b*) a cuprous and a cupric salt ; (*c*) a mercurous and a mercuric salt ? Describe the difference in appearance and in properties in each case.—*London Univ.*

23. What volume of hydrogen chloride at 0° and 760 mm. is required to convert 89 grms. of iron into ferrous chloride, and what volume of chlorine at 0° and 760 mm. would convert the latter into ferric chloride ? How much zinc and sulphuric acid would be required to convert the ferric chloride back once more into ferrous chloride ?—*Bombay Univ.*

24. Describe exactly how you have prepared, in a crystalline form, a salt of either copper or iron. What weight of zinc carbonate ($ZnCO_3$) must be used to produce 41 grms. of crystallized zinc sulphate ($ZnSO_4.7H_2O$) ?—*Delegacy Local Exams.*

25. Describe in detail the preparation from a metal of (1) a soluble crystallized salt, (2) an insoluble salt that you have made, stating the precautions taken to ensure purity. How would you prepare crystallized sodium carbonate from sodium bicarbonate ?—*Cape Univ.*

26. Explain (giving equations) the reactions involved in (*a*) the oxidation of ferrous salts by potassium permanganate, potassium dichromate, nitric acid, (*b*) the reduction of ferric salts by sulphurous and hydrogen sulphide, stannous chloride.—*Sydney Univ.*

27. Dilute sulphuric acid is poured on to iron filings ; when the action has ceased, the liquid is poured off, concentrated, and allowed to cool. Describe the appearance and properties of all the substances formed.—*Staffs. County Schol.*

28. What do you understand to be the difference between "equivalent" and "atomic weight"? How would you determine the equivalents of iron and copper?—*Science and Art Dept.*

29. Describe the most direct method you know for transforming (*a*) NaCl into Na_2CO_3; (*b*) cast iron into steel; (*c*) Cr_2O_3 into CrO_3.—*Owen's Coll.*

30. How is steel prepared (*a*) by the cementation process, (*b*) by the Bessemer process?—*Science and Art Dept.*

31. Name the more important soluble compounds of cobalt and state how each is prepared.—*Science and Art Dept.*

32. State how you would prepare from metallic nickel a specimen of nickel oxide.—*Science and Art Dept.*

33. Give an account of the manufacture from its ore *either* of (i.) cast iron *or* (ii.) copper.—*Owen's Coll.*

34. $FeSO_4$ reduces gold from its compounds, it also decomposes manganate and permanganate of potash and the chromate and bichromate of potash. Explain the reactions, and give the equations of two of them.—*New Zealand Univ.*

35. What is the nature of the process called rusting of iron? How would you carry out an experiment to prove the truth of your explanation? Mention any other examples of a similar process. What is the general name of the substances formed when this process occurs?

CHAPTER XXVII

Boron, Aluminium, and Related Elements

§ 1. Boric Acids and the Borates.

Extraction.—Volcanic jets of steam (soffioni) at a temperature between 90° and 120°, issuing from the fumaroles on the so-called Maremme di Toscana—or Tuscany Marshes—carry small quantities of boric acid. The steam condenses in lagoons (lagoni) of water which often surround the jets. The water of the lagoons becomes highly charged with the acid, and the boric acid can be obtained in a crystalline condition by evaporating the water of the lagoons. Artificial lagoons for arresting the jets of steam were established in Tuscany in 1818; and artificial soffioni were bored in 1854. The natural heat of the steam is utilized in concentrating the water. The crude acid—called *Tuscany acid*—is contaminated with ammoniacal salts, etc., and it is coloured yellowish brown. The crude acid contains about 82·5 per cent. of boric acid, and it can be refined by dissolving it in hot water, and mixing the solution with freshly ignited powdered charcoal. This removes the colouring matters. The clear solution is then allowed to crystallize, and this is placed on the market as "refined boric acid" or "refined boracic acid." The water of the hot springs at Sulphur Bank and other places in Nevada and California is rich in borates.

Action of solvents.—Boric acid crystallizes during the cooling of its hot aqueous solutions in white shining plates. When the aqueous solution is boiled, the acid volatilizes with the steam; 100 grams of water at 100° dissolve 27·5 grams of H_3BO_3; at 50°, 8·8 grams; and at 0°, 1·95 grams. Boric acid

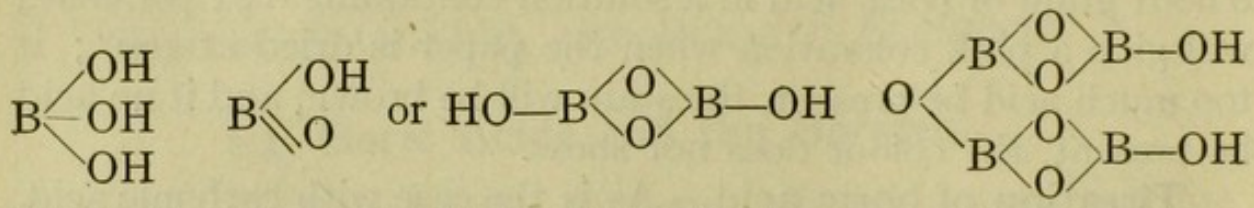
is more soluble in alcohol than in water. The alcoholic solution burns with a characteristic flame tinged with green, and in this way, 0·001 gram of boric acid can be detected in a solution containing 0·1 per cent. of the acid. The aqueous solution turns blue litmus claret-red; and moist yellow turmeric paper is coloured brown. Unlike the brown colour produced by alkalies with turmeric paper, the boric acid stain is not destroyed by acids. In a solution acidified with hydrochloric acid, 0·0001 gram of boric acid in a solution containing 0·01 per cent., will give a pink coloration when the paper is dried at 100°; if too much acid be present, the stain will be brown, and if no acid be present, the colour does not show.

Titration of boric acid.—As is the case with carbonic acid, boric acid is not affected by methyl orange. If phenolphthalein be used as indicator, and the boric acid be titrated with sodium hydroxide, the pink colour of the phenolphthalein appears before all the boric acid is neutralized. This is due to the hydrolysis of the alkaline borate: $NaOH+H_3BO_3 \rightleftharpoons NaBO_2+2H_2O$. If mannite or glycerol (free from acid) is added to the solution, the hydrolysis is hindered, hence the end point of the titration is reached when the red colour of the phenolphthalein persists after the addition of more mannite is added.

If heated to 140°, boric acid forms **tetraboric acid**; or the so-called "pyroboric acid," $H_2B_4O_7$, owing to the loss of water: $4H_3BO_3=5H_2O+H_2B_4O_7$. When boric acid is heated to a still higher temperature—"red heat"—it forms anhydrous **boron trioxide,** or boric oxide. The fused mass solidifies to a colourless transparent glass which absorbs moisture from the atmosphere, and becomes opaque, finally passing into boric acid. Anhydrous silica does not combine directly with water: anhydrous boric oxide does. Boric oxide volatilizes extremely slowly at a red heat. Sulphuric acid is not so strong an acid as hydrochloric acid at ordinary temperatures, but, owing to the more volatile nature of hydrochloric acid, the less volatile and weaker sulphuric acid is able to convert the chlorides into sulphates, as indicated previously. Similarly, in consequence of the non-volatility of boric acid at a red heat, it is able to decompose the compounds of the stronger acids with the bases

and form borates: $B_2O_3+3K_2SO_4=2B(OK)_3+3SO_3$. Sulphuric and hydrochloric acids are much stronger than boric acid when competing for the bases in aqueous solutions, but at a red heat, the more volatile acids are driven off.

Constitution.—The three boric acids are related by the empirical formulæ: orthoboric acid, $B_2O_3.3H_2O$; metaboric acid, $B_2O_3.H_2O$; and tetraboric acid, $2B_2O_3.H_2O$. The relationship is perhaps best shown by the graphic formulæ:



Orthoboric acid, $B(OH)_3$. Metaboric acid, BO(OH) or $H_2B_2O_4$. Tetraboric acid, $H_2B_4O_7$.

The meta- and pyro- boric acids immediately pass to orthoboric acid in aqueous solution.

Orthoborates.—The salts of orthoboric acid are unstable, and few well-defined orthoborates have been prepared. **Magnesium orthoborate,** $Mg_3(BO_3)_2$, is one of the best known orthoborates.

Metaborates.—The metaborates appear to be the most stable salts of boric acid. Potassium forms a metaborate, KBO_2; and a series of potassium acid borates—$KBO_2.HBO_2$, or KHB_2O_4, etc.

Tetraborates or **pyroborates.**—These also are stable compounds. The best known is *borax*, $Na_2B_4O_7.10H_2O$. A series of complex calcium and magnesium borates occur in nature: *borocalcite*, $CaB_4O_7.6H_2O$, from Iquique; *boronatrocalcite* (ulexite), $Na_2B_4O_6.2CaB_4O_7.18H_2O$, from Chili; *boracite*, $2Mg_3B_8O_5.MgCl_2$, from the Stassfurt deposits; *pandermite*, $Ca_2B_6O_{11}.4H_2O$, from Panderma in Asia Minor; *colemanite*; etc.

The borates nearly always contain water of crystallization, and, excepting the alkaline borates, they are but slightly soluble in water. The borates are easily decomposed by water, and acidulated solutions of the borates give the flame and other reactions characteristic of boric acid. In some places boric acid is made directly from the native calcium borates by

dissolving the mineral in hot hydrochloric acid and collecting the crystals of boric acid which separate on cooling. The acid can also be made by the action of sulphuric or hydrochloric acid on borax.

Boric oxide, like alumina, is an intermediate or amphoteric oxide, for it has feeble acidic and feeble basic properties. As a weak acid it forms a series of salts—borates. Boric oxide also forms complex salts—**boro-silicates**—with the metallic oxides and silica, *e.g.* tourmaline. Corresponding with the basic properties of the oxide, unstable compounds like the acid sulphide, $B(HSO_4)_3$; phosphate, BPO_4, etc., have been formed. Most of the salts are hydrolyzed by water, dilute acids, and dilute alkaline solutions.

§ 2. Borax.

Manufacture.—Borax occurs as a natural deposit—*tincal*—in the dried-up inland lakes in some parts of India, Tibet, and California—*e.g.* the "borax marsh" in the Saline Valley. Native tincal contains about 55 per cent. of borax proper : $Na_2B_4O_7.10H_2O$. This is extracted by lixiviating the mass with water, and evaporating the clear solution until the crystals separate. Before 1870, most of the borax used in Europe was made by digesting a solution of boric acid with the proper amount of soda ash, whereas the borax now in commerce is usually made from native calcium borates. The powdered mineral is boiled with a slight excess of an aqueous solution of sodium carbonate. Calcium carbonate is precipitated as a "mud" : $Ca_2B_6O_{11}+2Na_2CO_3 \rightleftharpoons 2CaCO_3+Na_2B_4O_7+2NaBO_2$. On crystallizing the clear solution, crystals of borax are obtained. Carbon dioxide is blown through the mother liquid to convert the sodium metaborate into borax : $4NaBO_2+CO_2 \rightleftharpoons Na_2CO_3+Na_2B_4O_7$. The borax separates in fine crystals, leaving sodium carbonate in the solution. The residual "mud" is compressed in a filter press to remove the soluble matters it contains.

The action of water.—100 grams of water at 10° dissolve 1·6 grams of borax, $Na_2B_4O_7$; at 50°, 10·5 grams ; and at 100°,

52·5 grams. The aqueous solution has a feebly alkaline reaction owing to hydrolysis. In concentrated aqueous solutions : $Na_2B_4O_7+3H_2O \rightleftharpoons 2NaBO_2+2H_3BO_3$; and on further dilution, hydrolysis may be practically completed : $NaBO_2+2H_2O \rightleftharpoons NaOH+H_3BO_3$.

Titration of borax.—A dilute solution of borax may be titrated with a standard hydrochloric acid until all the soda is neutralized and the boric acid is all free, provided methyl orange be used as indicator. The reaction is : $Na_2B_4O_7+2HCl+5H_2O = 2NaCl+4H_3BO_3$. The boric acid has no effect on the methyl orange. If the same amount of the standard acid be added to the same amount of the borax solution, and phenolphthalein is then used as indicator, the freed boric acid can be titrated as indicated previously. In this manner, the amount of alkali and the amount of boric acid in a sample of borax can be determined.

The action of heat.—When heated, borax fuses, loses water, and swells up into a white porous mass, owing to the expulsion of the water. Finally the borax melts to a clear glass—borax glass—which is anhydrous borax. Like boric acid, fused borax dissolves many colouring oxides, giving glasses with a characteristic colour. The borax " beads " used in flame testing are based on this fact. Thus :

TABLE XXV.—COLOURS OF BORAX BEADS WITH SOME METALLIC OXIDES.

Metallic oxide.	Oxidizing flame.	Reducing flame.
Copper . .	Green (hot) ; blue (cold)	Colourless or red.
Cobalt . .	Blue	Blue.
Chromium .	Green	Green.
Iron . . .	Yellow (cold) ; brown (hot)	Dirty green or olive.
Nickel . .	Violet (hot) ; yellowish-brown (cold).	Grey and opaque.
Manganese .	Amethyst.	Grey and opaque.

The dissolution of metallic oxides in fused borax is supposed

to be connected with the fact that borax contains an excess of acid anhydride: $2NaBO_2.B_2O_3$. The union of the metallic oxide with the B_2O_3 forms a metaborate. Thus, with copper, $Na_2B_4O_7+CuO=Cu(BO_2)_2+2NaBO_2$.

Uses.—Large quantities of borax are used in the manufacture of enamels, glazes, and of optical glass; in preserving articles of food if its use is not restricted by law; as a mild antiseptic for making lotions and ointments; in the manufacture of soap; as a cleansing and stiffening agent in laundry work; for stiffening candle wicks; in making varnishes for metals; manufacture of drying oils; with casein as a substitute for gum arabic; as a flux; and in soldering and brazing. Solder only adheres to clean metal surfaces, and molten borax will often dissolve the contaminating oxides which prevent solder adhering

History.—Although mentioned in the early Latin writings on chemistry, it is probable that the term "borax" did not always refer to the substance now called "borax"; for instance, the Arabians applied a similar term to both borax and nitre. In 1702, W. Homberg made boric acid from borax by treating borax with sulphuric acid, and called the acid *sal sedativum*. J. H. Pott (1741) showed that Glauber's salt was produced at the same time. Hence, sulphuric acid with borax furnishes boric acid and Glauber's salt. Baron (1748) proved that borax is a compound of Homberg's *sal sedativum* and soda. After Lavoisier's work on acids, the term boracic acid was substituted for *sal sedativum*, and "boracic acid" was later abbreviated to "boric acid." J. L. Gay-Lussac and J. Thénard isolated the element in a more or less impure condition in 1808.

Boron.—The element is made by reducing boric oxide with sodium, magnesium, or aluminium in a covered crucible at a high temperature. The element occurs in several different forms—crystalline and non-crystalline. It is rather inactive chemically. It forms **borides** with metals like magnesium and calcium, and with silicon and carbon. Boron combines with nitrogen, forming a **boron nitride,** BN; with sulphur forming **boron sulphide,** B_2S_3; etc.

Other compounds of boron.—**Boron chloride** and **boron**

fluoride can be made by the action of hydrochloric or hydrofluoric acid respectively upon boron or on boric oxide; say, by heating a mixture of concentrated sulphuric acid, calcium fluoride, and boric oxide: $B_2O_3+6HF=2BF_3+3H_2O$. An excess of water is needed for the complete hydrolysis of the trichloride. If but a small quantity of water be used, a solid hydrate is produced. The boron trihalides are all hydrolyzed by water, thus: $BF_3+3H_2O=B(OH)_3+3HF$. The hydrogen fluoride, so produced, unites with some of the unchanged boron trifluoride, BF_3, producing a complex monobasic acid—**hydrofluoboric acid,** HBF_4, thus: $BF_3+HF=HBF_4$. A series of corresponding salts called borofluorides or fluoborates have been obtained.

§ 3. Aluminium—Occurrence and Preparation.

History.—The word "alumen," or its Greek equivalent, was formerly applied as a grouping term for substances with an astringent taste. Geber and some others classed alum with the "vitriols," but Paracelsus considered it to be radically different, for he pointed out that its *corpus* is not metallic but an intimate mixture of earths. The earthy *corpus* was confused with lime until J. H. Pott (1746) showed that the base is really an *argillaceous earth;* and in 1854, A. S. Marggraf proved clearly that the base is entirely different from lime, and that clay contains the *alum earth* united with silica.

Occurrence.—Aluminium, or aluminum, does not occur free in nature, but its compounds are numerous and widely distributed. It comes third, after oxygen and silicon, on Clarke's list. *Corundum, ruby,* and *sapphire* are more or less impure forms of the oxide, Al_2O_3; *emery* is a mixture of iron oxide and corundum. There are three recognized hydrates occurring in nature—*gibbsite* or *hydrargillite,* $Al_2O_3.3H_2O$; *bauxite,* $Al_2O_3.2H_2O$, or $Al_2O(OH)$; and *diaspore,* $Al_2O_3.H_2O$, or $AlO(OH)$, or $Al(OH)_3$. The word **bauxite** is used in rather a general way for native aluminium hydroxides containing the equivalent of, say, 50 to 70 per cent. of Al_2O_3, about 25 to 30 per cent. of water, with more or less ferric oxide, titanic oxide,

and silica. Some bauxites approximate to the trihydrate, others appear to be mixtures of the trihydrate and lower hydrates. The bauxites are often classed as ferruginous and non-ferruginous. The double fluoride—*cryolite*, $AlF_3.3NaF$—occurs in Greenland; *turquoise* is a hydrated phosphate. The *felspars* and *clays*, as well as a great number of common minerals, are complex silicates of aluminium with other bases. Bauxite and cryolite are the chief compounds used in the preparation of the metal aluminium.

Isolation of the metal.—After Davy's work on potassium, calcium, etc., many attempts were made to isolate the unknown element in alumina, and F. Wöhler succeeded in reducing anhydrous aluminium chloride, $AlCl_3$, to the metal by warming the chloride with potassium: $AlCl_3+3Na=3NaCl+Al$. Wöhler's first experiments furnished a light grey metallic powder, and it was not until 1845 that the compact metal was obtained. The metal was at that time a "chemical curiosity." In 1855, aluminium sold at the rate of about £120 per kilogram, and in 1913 about 1*s.* 4*d.* per kilogram. H. St. C. Deville, in 1854, reduced aluminium chloride in quantity by means of sodium in place of Wöhler's potassium; H. Rose (1855) recommended the reduction of cryolite by sodium; and N. Beketoff the reduction of cryolite by magnesium These chemical processes are not now used on an industrial scale.

Although clays usually contain the equivalent of 20 to 36 per cent. of alumina, no method is known for separating silica from the alumina cheaply enough for use on a manufacturing scale. It is necessary to use a fairly pure bauxite for the process, otherwise the metallic aluminium will be seriously contaminated with impurities. Apart from the cost of the electrical energy, the purification of the raw bauxite is the most costly item in the process. Native bauxite is usually too impure to be used without a preliminary purification to remove the iron, titanium, and silicon oxides.

R. Bunsen isolated aluminium by the electrolysis of the fused chloride in 1854, and the result was confirmed by Deville in the same year. A. and E. H. Cowles Bros. (1884) reduced alumina by heating it with carbon in an electric arc furnace.

The formation of aluminium carbide, Al_4C_3, introduced some practical difficulties. The method was for a time more or less successfully employed in making alloys of aluminium with copper. The electric furnace was charged with corundum, carbon, and metallic copper. After the charge had been heated about five hours, a copper-aluminium alloy was obtained. The cheap production of aluminium was made possible by the discovery, by C. M. Hall, in 1886, that a solution of alumina in a molten mixture of cryolite and some other fusible fluoride, say, potassium fluoride, is an electrolyte, for, when electrolyzed, aluminium collects at the cathode, oxygen at the anode. Patents by C. S. Bradley (1883–1891), P. Héroult (1887 *et seq.*), and many others embodied ideas more or less valuable, and, as a result, aluminium can now be made cheaply on a large scale, Electrolytic processes are practically the only methods used for the preparation of aluminium.

Héroult's electrolytic process for aluminium.—In this process the electrolyte is a solution of bauxite in fused cryolite. The " electrolytic cell " is a rectangular iron box (about 8 feet long and 6 feet wide). This cell, Fig. 186, is connected with the electric generator so that the iron box itself serves as cathode. The anode, or rather anodes, is a set of about 48 carbon rods (3 inches diameter and 15 inches long) arranged in three or four rows and suspended from copper rods connected with the other pole of the generator. The resistance of the electrolyte to the current gives enough heat to keep the mass fluid. The liquid metal sinks to the bottom of the cell, whence it is " tapped " from time to time. The oxygen evolved at the cathode either escapes as a gas or unites with the carbon to form carbon monoxide, which either burns or escapes. The process is continuous, for fresh supplies of bauxite are added when needed. The resistance of the bath increases when the alumina wants replenishing ; and this causes a lamp, shunted off the main

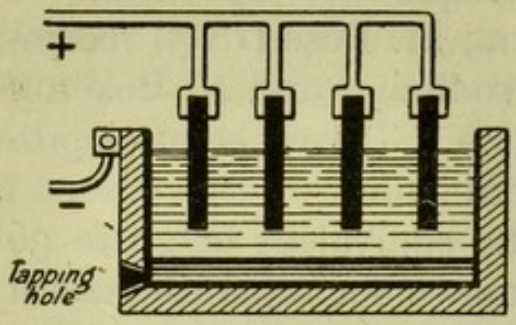


FIG. 186.—Héroult's Aluminium Furnace (Diagrammatic).

circuit, to glow. This tells the workmen that a fresh charge of bauxite is needed.

§ 4. The Properties of Aluminium.

Aluminium is a bluish-white metal capable of taking a high polish. The dull surface usually seen on the metal is an effect of a superficial film of oxide. Aluminium is lighter than most metals, its specific gravity is 2·6, and therefore it has nearly the same specific gravity as glass, and one-third the specific gravity of iron. With frequent annealing aluminium can be rolled into sheets, wire, and foil. It is a good conductor of heat and electricity.

Aluminium remains practically unaltered in dry air, while in moist air and in boiling water, a superficial film of oxide seems to protect the metal from further action. Even at 700° to 800° it oxidizes but slowly; at higher temperatures it burns brilliantly with the evolution of much heat. In virtue of its intense electropositive character, aluminium is a powerful reducing agent. Aluminium powder when intimately mixed with many metallic sulphides or oxides—manganese, chromium, tungsten, uranium, iron, etc.—along with some flux, say fluorspar, when ignited, reduces the oxides or sulphides to the metal. *E.g.* with pyrites, it forms aluminium sulphide and metallic iron. The mixture becomes very hot during the reaction and a temperature of 3000°–3500° is sometimes attained. The heat of this reaction can be utilized for softening and welding iron rails, steel castings, etc., where an intense local heat is needed. The rails to be welded are packed in a mixture of iron oxide and aluminium powder together with a special cement to make the mass compact. When the mass is ignited, it burns and heats the rails to a temperature high enough to weld the metals together. The mixture of aluminium powder with various metallic oxides is sold as *thermite*, and the process is called H. Goldschmidt's or the aluminothermic process.

Aluminium, when heated with the halogens and with nitrogen forms **halides**, and **nitride** respectively. Aluminium dissolves slowly in cold dilute hydrochloric acid, and rapidly in hot, the

concentrated acid giving an aqueous solution of **aluminium chloride,** and the hydrogen gas. Nitric acid, dilute or concentrated, acts so slowly that nitric acid is usually said to have "no action on aluminium." Sulphuric acid has very little action in the cold, but the hot concentrated acid converts it into **aluminium sulphate** with the evolution of sulphur dioxide. Aluminium is rapidly dissolved by sodium and potassium hydroxides with the evolution of hydrogen and the formation of **sodium or potassium aluminate**: $2Al + 6KOH = 2Al(OK)_3 + 3H_2$. Organic acids (*e.g.* acetic acid) are almost without action on the metal at ordinary temperatures, but they are said to have an appreciable solvent action in the presence of sodium chloride. Salt solutions, *e.g.* sea-water, rapidly corrode the metal.

Alloys.—See aluminium bronze discussed in connection with the alloys of copper. *Magnalium* is the trade name of an alloy containing about 90 per cent. of aluminium with less than 2 per cent. of magnesium and small quantities of other metals. The tensile strength of magnalium is greater than aluminium, and the alloy can be turned in a lathe. Magnalium is also less corroded than aluminium, zinc, copper, or brass. Hence, it is replacing aluminium for many purposes.

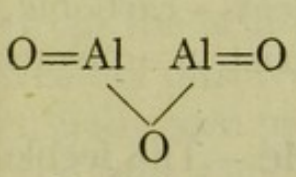
Aluminium amalgam is made by adding aluminium filings to a $\frac{1}{2}$ per cent. solution of mercuric chloride for a couple of minutes, and washing the product with alcohol and ether. The amalgam decomposes water at the ordinary temperature, liberating hydrogen and forming aluminium hydroxide. The mercury seems to retard the formation of a thin coating of oxide on the surface of the metal which would prevent further oxidation. Aluminium amalgam is a valuable neutral reducing agent because neither acid nor alkali is needed for the reaction.

Uses.—Large quantities of aluminium powder mixed with oil are used as paint for steam-pipes, and other metal objects exposed to heat or the weather. Aluminium is used for cooking utensils, the metallic parts of military outfits; certain parts of air ships, etc.; precision instruments; surgical instruments; and as an ornamental metal for interior decoration; and artistic objects, etc. The wire is used as a conductor of electricity,

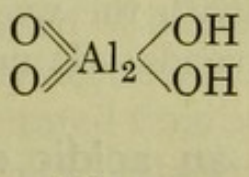
because aluminium wire though thicker than copper for a given conductivity is not so heavy and does not strain the supports so much. Aluminium is used as a reducing agent in the production of certain metals—chromium, etc.—and in the manufacture of "thermite." The formation of oxides during the melting of many metals is prevented if a little aluminium be present, hence aluminium—0·16 to 0·05 per cent. is commonly added to molten steel as it comes from the Siemens-Martin's, or Bessemer's furnace. This enables castings to be made more free from "blow holes." Aluminium is difficult to solder, and therefore the parts of large articles are commonly welded together by autogeneous soldering.

§ 5. Aluminium Oxide and Hydroxide.

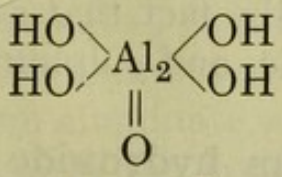
Three hydroxides of aluminium occur in nature, and they can be represented graphically, though empirically, by assuming that aluminium is a triad, and that alumina, or corundum, is approximately Al_2O_3, or,



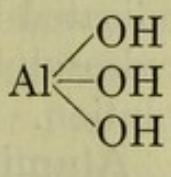
Corundum, Al_2O_3.



Diaspore, $Al_2O_2(OH)_2$.



Bauxite, $Al_2O(OH)_4$.



Gibbsite, $Al(OH)_3$.

The gelatinous precipitate which is obtained when ammonia or an alkaline carbonate is added to a solution of an aluminium salt, is a **colloidal aluminium hydroxide**—$Al(OH)_3$—and it contains more or less absorbed water, $AlCl_3+3NH_4OH=Al(OH)_3+3NH_4Cl$. The curve obtained by measuring the rate at which the gelatinous hydrate loses water on a rising temperature does not show, in a convincing manner, the transition from one hydrate to the other. Aluminium hydroxide can be obtained in the sol (hydrosol) condition by dialyzing an aqueous solution of aluminium chloride, or a solution of freshly precipitated aluminium hydroxide in aluminium chloride or aluminium acetate; and in the gel (hydrogel) condition by adding a solution of some electrolyte. Freshly precipitated aluminium

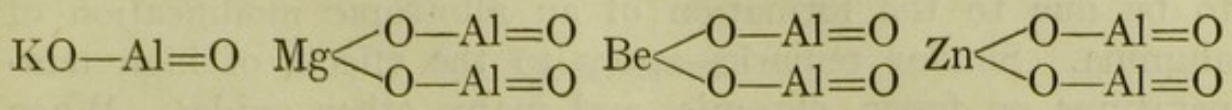
hydroxide dissolves easily in acids and in alkaline hydroxides. If the precipitate has stood a long time under water, or if the precipitate be dried, it dissolves very slowly in these reagents.

When aluminium hydroxide is precipitated in a solution containing a colouring matter, the latter is precipitated with the aluminium hydroxide, and the aluminium hydroxide with the absorbed colouring matter is called a lake. Advantage is taken of this property in dyeing cloth. The aluminium hydroxide is first precipitated in the fibres of the cloth, and the fabric is then immersed in the dye, and some of the dye is fixed by the aluminium hydroxide in the fibres. Hence, aluminium hydroxide is a dye-fixing agent or mordant. Dyes which stain the fibres directly need no mordant.

Aluminium hydroxide as a basic oxide.—Aluminium hydroxide is amphoteric, for it exhibits both feebly acidic and feebly basic properties. The existence of salts like aluminium chloride, aluminium sulphate, etc., is evidence of the basic qualities; and the feeble basic qualities of the hydroxide is indicated by the fact that salts with the weak acids—carbonic, hydrosulphuric, and sulphurous acids—do not exist in aqueous solution.

Aluminium hydroxide as an acidic oxide.—The feeble acidic properties of aluminium hydroxide are evidenced by the solubility of the hydroxide in alkalies and by the formation of salts—**aluminates**—with the strong bases. The hydroxide $Al(OH)_3$, that is, H_3AlO_3, is called **orthoaluminic acid** when it is desired to emphasize its acidic nature. The corresponding salts are orthoaluminates, *e.g.* $Al(ONa)_3$; $Al(OH)(ONa)_2$; and $Al(OH)_2(ONa)$ are supposed to be formed when solutions containing the proper amounts of sodium and aluminium hydroxides are evaporated to dryness. Salts corresponding with $AlO(ONa)$, that is, $NaAlO_2$, are considered to be derived from the acid $HAlO_2$, called **meta-aluminic acid,** which corresponds with the ortho-acid less one molecule of water. The minerals *spinel* —$MgO.Al_2O_3$, or magnesium meta-aluminate, $Mg(AlO_2)_2$— *chrysoberyl*—$BeO.Al_2O_3$, or beryllium meta-aluminate, $Be(AlO_2)_2$; *gahnite*—$ZnO.Al_2O_3$, or zinc meta-aluminate, $Zn(AlO_2)_2$—are

supposed to be meta-aluminates which can be represented by the graphic formulæ :



Potassium meta-aluminate. Spinel. Chrysoberyl. Gahnite.

Aluminates.—The aluminates are not very stable. Their aqueous solutions are strongly alkaline on account of hydrolysis. They are decomposed by carbon dioxide with the precipitation of aluminium hydroxide :

$$2NaAlO_2+CO_2+3H_2O \rightleftharpoons 2Al(OH)_3+Na_2CO_3.$$

Ammonium chloride produces a similar precipitate, owing probably to the formation of an unstable ammonium aluminate : $Al(ONa)_3+3NH_4Cl \rightleftharpoons Al(ONH_4)_3+3NaCl$, which is completely hydrolyzed by water : $Al(ONH_4)_3+3H_2O \rightleftharpoons 3NH_4OH+Al(OH)_3$. The aluminium hydroxide so obtained is a pulverulent powder not gelatinous like that precipitated from the acid solution of aluminium salts ; it is also much less readily dissolved by acetic acid. The alumina of commerce has usually been precipitated from sodium aluminate, and it generally contains some sodium carbonate due to the imperfect washing of the precipitate.

Aluminium oxide, Al_2O_3.—Aluminium oxide, or alumina, occurs in nature as colourless crystalline corundum ; and tinted with various metallic oxides as *ruby*, *sapphire*, *amethyst*, *emery*, etc. Alumina is prepared as a white powder by the ignition of aluminium hydroxide, aluminium nitrate, or ammonia alum. Alumina fuses at about 2000°. Alumina is prepared in a crystalline condition by strongly heating a mixture of aluminium fluoride and boric oxide : $2AlF_3+B_2O_3=Al_2O_3+2BF_3$. Artificial rubies have been made by heating alumina with chromic oxide and boric oxide. The latter acts as a flux and gradually volatilizes, leaving behind the crystalline artificial "gem." When alumina is heated above about 800° an exothermal change takes place. The alumina changes in some way, for it then becomes almost insoluble in acids ; its specific

gravity rises rapidly from 2·8 to 4·0; and other physical properties change at the same time. The change is supposed to be due to the formation of an allotropic modification of alumina. Similar remarks apply to the effects of high temperatures on ferric, chromic, and many other oxides. When heated with reducing agents—potassium, sodium, calcium carbide, etc.—alumina is reduced to the metal. Bauxite is used in the manufacture of the so-called "bauxite bricks," and for lining the bed of basic open hearth furnaces. Fused bauxite is sold as "alundum," "diamantine," etc., and used in the manufacture of abrasive materials.

§ 6. The Relationships of Boron-Aluminium Family.

The variations in the physical properties of the five elements, boron, aluminium, gallium, indium, and thallium, with increasing atomic weight is indicated in the following table:

TABLE XXVI.—PROPERTIES OF THE BORON-ALUMINIUM FAMILY.

	Boron.	Aluminium.	Gallium.	Indium.	Thallium.
Atomic weight .	11·0	27·1	69·9	114·8	204·0
Specific gravity.	2·45	2·7	5·9	7·4	11·8
Atomic volume .	4·5	10·0	11·8	15·5	17·3
Melting-point .	over 2000°	657°	30°	176°	285°

With the exception of boron and aluminium, the elements of this series are scarce and rare. The non-metallic characters predominate in boron, and boron least resembles the other members of the family, but it resembles silicon, a member of another family. Boric oxide exhibits very feeble basic properties. The basic properties of the elements increase, and the acidic properties decrease with increasing atomic weights until thallium is reached. Thallium trichloride, $TlCl_3$, for instance, is partially hydrolyzed by water. The trivalent thallium compounds resemble the other members of the group; but the univalent thallium compounds behave like silver and the

alkali metals. Thallium metal resembles lead. Aluminium in some respects resembles magnesium, zinc, and cadmium.

Questions.

1. Enumerate the metals which are capable of producing "alums." Write the formula of common alum, describe its usual crystalline form; and, being supplied with a sufficient quantity of the salt, state how you would proceed to make a specimen consisting of distinct crystals.—*Science and Art Dept.*

2. Describe the chief physical and chemical properties of aluminium. From what sources and by what processes is the commercial metal best obtained? Describe any useful alloys of this metal.—*Science and Art Dept.*

3. 0·3697 grm. of aluminium liberated 0·04106 grm. of hydrogen on being dissolved in a strong solution of sodium hydrate. On the assumption that alumina is a sesquioxide, Al_2O_3, find from these data the atomic weight of aluminium.—*Science and Art Dept.*

4. Give some account of the metal aluminium, and the composition, preparation, and properties of alumina, aluminium chloride, aluminium sulphate, and common alum.—*Science and Art Dept.*

5. Describe exactly how you would proceed to carry out the following conversions: (1) Potassium sulphate into potassium chloride; (2) potassium chloride into potassium carbonate; (3) sodium nitrate into sodium chloride; (4) aluminium carbonate into aluminium sulphate; (5) magnesium carbonate into magnesium chloride; and (6) zinc chloride into zinc nitrate.—*Sydney Univ.*

6. Give a full account of the uses of borax and sulphuretted hydrogen in analytical chemistry.—*Cape Univ.*

7. What are the following, and how are they prepared: (*a*) borax, (*b*) alum, (*c*) bronze, (*d*) corrosive sublimate, (*c*) Glauber's salt?—*Panjab Univ.*

8. Given metallic aluminium, potassium carbonate, and any other necessary chemicals, how would you prepare a sample of potash alum? Give the general characteristics of the alums, and mention their uses. How is anhydrous aluminium chloride prepared? What are its main physical properties?—*Adelaide Public Exam. Board.*

9. How would you ascertain whether a white crystalline substance is boric acid?—*London Univ.*

10. Name the substances formed when the following substances are heated: (*a*) chalk, (*b*) black oxide of manganese, (*c*) alum, (*d*) borax.

11. Express by equations the reactions which occur when a solution of caustic soda (sodium hydroxide) is added to solutions

of the following : alum, copper sulphate, ferric chloride, and sulphuric acid.—*London Univ.*

12. How would you prepare alumina from alum, and aluminium from alumina ? Explain the reactions by means of symbols.—*London Univ.*

13. Give some account of boron, boric acid, and the principal borates.—*London Univ.*

14. How is common borax manufactured ? Specify facts which appear to throw light on the constitution of the salt. How is the element boron prepared and distinguished ?—*London Univ.*

15. What is the composition of borax, and to what class of salts does it belong ? Mention some examples of other salts of similar composition. What is the action of a solution of borax on litmus ?—*London Univ.*

16. Give three general methods of preparing chlorides ; illustrate your answer by describing very briefly the preparation of anhydrous chlorides of iron, mercury, silver, aluminium, calcium, and magnesium.—*London Univ.*

17. Describe a method for the preparation of boron trifluoride. Give a short account of the occurrence, preparation, properties, and uses of boracic acid. What happens when a mixture of boracic acid and sodium sulphate is very strongly heated ?—*Adelaide Public Exam. Board.*

18. Give an account of the occurrence of aluminium in nature and the method by which the free metal is manufactured. Describe the uses of aluminium and its compounds in the arts and industries, and the chemical and physical properties upon which these uses depend. With what elements is aluminium most closely related ?—*Bombay Univ.*

19. How is boric acid made from borax ? How much boron trioxide is contained in 3·82 grms. of borax ?—*Science and Art Dept.*

20. How would you prepare boron, metaboric acid, and boron trioxide ?—*Science and Art Dept.*

21. Describe the appearance and write the formulæ of the following substances : potassium permanganate, potassium dichromate, alum, potassium iodide, ferrous sulphate, borax,—stating in each case the amount of water, if any, contained in the crystals.—*Science and Art Dept.*

CHAPTER XXVIII

Nitrogen Oxides

§ 1. Nitrous Oxide, or Nitrogen Monoxide.

When dry ammonium nitrate, NH_4NO_3, is heated in a flask fitted with a delivery tube, Fig. 57, the salt melts at about 165°, and it begins to decompose at about 185°. The decomposition proceeds quite rapidly between 200° and 240°. Nitrous oxide and water are formed: $NH_4NO_3 = 2H_2O + N_2O$. At 240° the decomposition is very vigorous, and the mixture may even explode. With ammonium nitrite, NH_4NO_2, under the same conditions, nitrogen gas is obtained: $NH_4NO_2 = 2H_2O + N_2$.

Properties.—Nitrous oxide is a colourless gas with a faint smell. 100 c.c. of water, at 760 mm. pressure, dissolve 67 c.c. of the gas at 20°. Hence, the gas is usually collected over hot water in order to lessen the loss due to its solubility in that liquid. The aqueous solution has a sweetish taste. The gas is about four times as soluble in alcohol as in water. Nitrous oxide condenses to a colourless limpid liquid at −89·3° under atmospheric pressure, and freezes to a white solid at −102·7°.

Nitrous oxide resembles oxygen in its behaviour towards combustibles. A glowing splinter bursts into flame when plunged into the gas. Ignited phosphorus, sulphur, etc., burn vividly in nitrous oxide gas. When J. Priestley discovered oxygen in 1774, he was already familiar with nitrous oxide, which he had discovered a couple of years previously. Hence, in describing the brilliancy of the flame of a burning candle in oxygen, he said: "I got nothing like this remarkable appearance from any kind of air besides this particular modification of nitrous air." The burning body decomposes the nitrous oxide, unites with the oxygen, and leaves the nitrogen as a

residue. If sulphur be but feebly burning, its flame may be extinguished when plunged into nitrous oxide, probably because the temperature is not high enough to decompose the gas: $S+2N_2O=SO_2+2N_2$. It is therefore easy to mistake nitrous oxide for oxygen. One distinguishing test is to add a bubble of the suspected gas to nitric oxide; if red fumes are produced the gas is oxygen. Nitrous oxide does not give red fumes with nitric oxide. Another test depends on the far greater solubility of nitrous oxide in alcohol than oxygen.

When inhaled, nitrous oxide produces unconsciousness, and insensibility to pain. Hence, it has long been used as an anæsthetic for small surgical operations, dentistry, etc. But owing to the unpleasant after effects sometimes produced, it is not used so much as formerly. If the inhalation be long continued, it may produce death; while if but small quantities are inhaled, it may produce a kind of hysteria, or intoxication. Hence, the gas is sometimes called "laughing gas." As L. Edgworth remarked (1799), after breathing the gas, "I burst into a violent fit of laughter, and capered about the room without having the power of restraining myself": and H. Davy wrote (1794), after breathing sixteen quarts of the gas, "I danced about the laboratory as a madman." The effects of the gas are not quite the same on different people.

§ 2. Nitric Oxide, or Nitrogen Dioxide.

Preparation.—Nitric oxide is prepared by the action of nitric acid, specific gravity 1·2 upon metallic copper or mercury. The copper turnings are placed in a two-necked Woulfe's bottle, Fig. 42, or a Kipp's apparatus, Fig. 62. The bottle is about one-fourth filled with water, and about the same volume of concentrated nitric acid is added. A rapid evolution of gas occurs. The gas should be collected as soon as possible because when the reaction has been in progress some time, particularly if the temperature rises during the reaction, nitrous oxide and nitrogen may appear with the nitric oxide. The results are said to be better if a little sodium nitrite, say, two per cent., be added to the mixture in the Woulfe's bottle.

Properties.—Nitric oxide is a colourless gas a little heavier

than air. When brought in contact with air, it immediately combines with the oxygen, forming brownish-red fumes of nitrogen peroxide. No other gas gives red fumes when exposed to the atmosphere or to oxygen gas. Hence, it is not possible to describe the smell, and the physiological action of this gas. If the two gases—nitric oxide and oxygen—be thoroughly dried, no combination occurs. If dry nitric oxide be passed into liquid oxygen or liquid air, greenish flecks of **nitrogen hexoxide** are formed Analyses give results corresponding with the empirical formula NO_3. Hence the reaction is represented $NO+O_2=NO_3$. Nitrogen hexoxide decomposes at temperatures a little above the boiling-point of oxygen.

At 0° and 760 mm. pressure, 100 volumes of water dissolve 7·3 volumes of the gas ; and at 20°, 4·6 volumes. Nitric oxide dissolves in a solution of ferrous sulphate. A " compound " of nitric oxide and ferrous sulphate appears to be formed. This imparts a dark brown colour to the solution.

Nitric oxide is difficult to liquefy. The liquid boils at −150°, and the white solid melts at −167°. The liquid is colourless if air be excluded, otherwise the liquid may be tinted green or blue.

Nitric oxide is not combustible, and it only supports combustion under special conditions, that is when the temperature is raised sufficiently to decompose the gas. The flame of feebly burning phosphorus is extinguished, but if the phosphorus be burning vigorously, combustion is continued in the gas: $10NO+4P=2P_2O_5+5N_2$. Burning sulphur is extinguished, but if the sulphur be boiling when it is plunged in the gas combustion sometimes continues. Potassium also burns in the gas forming a mixture of nitrites and nitrates. Sodium can be heated in the gas without burning.

§ 3. Nitrogen Peroxide, or Nitrogen Tetroxide.

Preparation.—As indicated above, this gas is formed when one volume of oxygen is mixed with two volumes of nitric oxide : $2NO+O_2=2NO_2$. If the gas be led through a freezing mixture, the peroxide condenses either as a liquid or as a solid. Perhaps the best way of making nitrogen peroxide

is to put, say, 200 grams of coarse lumps of arsenic trioxide, As_2O_3, into a flask, and add 250 grams of nitric acid (specific gravity 1·4). Heat the mixture on a sand-bath, and lead the gases through a tower packed with glass wool, Fig. 187, and finally into a U-tube surrounded by a freezing mixture of ice and salt. A dark blue liquid is condensed. This is a mixture of nitrogen peroxide with other nitrogen oxides. When the evolution of gas has ceased, pass a current of air or oxygen through the condensed liquid while still in the freezing mixture until the liquid becomes yellowish brown. Decant the nitrogen peroxide from the syrupy liquid, and redistil the mixture by warming in hot water, and passing the gases through tower and condensing tube as in Fig. 187.

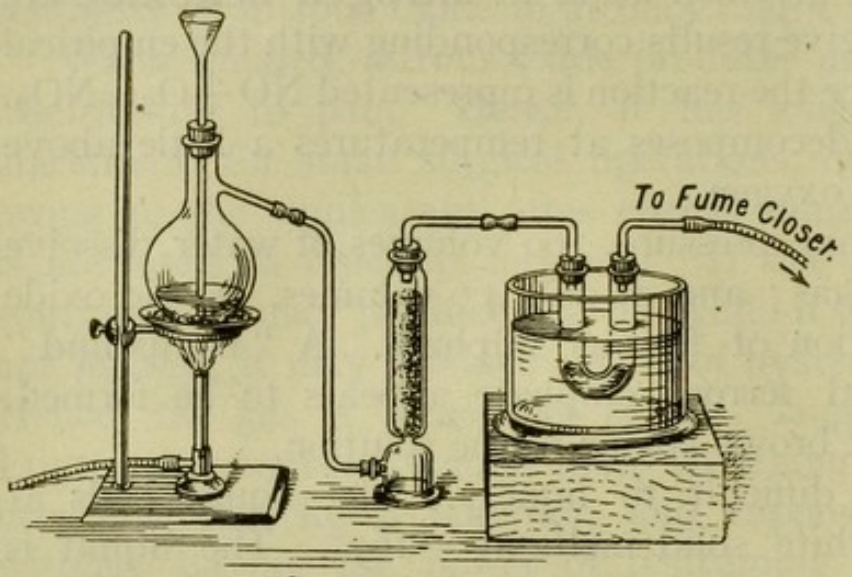


Fig. 187.—The Preparation of Nitrogen Peroxide.

Action of heat on nitrogen peroxide.—At low temperatures nitrogen peroxide forms colourless prismatic crystals. The crystals melt at −9°. As the temperature of the liquid rises, it begins to acquire a pale greenish-yellow tint, which becomes deeper and deeper, until, at 10°, the liquid is distinctly yellow; at 15°, orange; and at 26°, the liquid boils and forms a reddish-brown vapour. The colour of the vapour becomes deeper and deeper until, at 40°, it is dark chocolate brown, and almost opaque; at 140°, the vapour is almost black. On cooling the vapour, the same changes occur in the reverse order. The effect seems to be connected with a change in the vapour density of the compound. The vapour density for N_2O_4 is 92·02; and for NO_2, 46·01. The actual value of this constant passes from 84·7 at −72·6° and 115·4 mm. pressure, to 46·0 at 140° and 760 mm. pressure; showing that in all probability the molecules

of the gas are N_2O_4 at low temperatures, and NO_2 at the higher temperatures. At about 500°, an appreciable number of the dark brown molecules of NO_2 begin to dissociate into a colourless mixture of nitric oxide and oxygen : $2NO_2=2NO+O_2$. The action of heat on nitrogen peroxide may therefore be represented by the equations :

$$\underbrace{N_2O_4}_{\text{About 20°}} \rightleftharpoons \underbrace{2NO_2}_{\text{Between 140° and 300°}} \rightleftharpoons \underbrace{2NO+O_2}_{\text{Above 500°}}$$

Colourless. Dark brown. Colourless.

Properties.—Nitrogen peroxide is a poisonous gas, and soon produces headache and sickness if but a little is present in the atmosphere.

Nitrogen peroxide is not combustible, and it extinguishes the flame of a taper. Phosphorus, sulphur, and carbon, if burning vigorously, may continue burning in the gas, but only when the temperature of combustion is sufficiently high to decompose the gas. Nitrogen peroxide is an energetic oxidizing agent. Phosphorus, carbon, potassium, mercury, copper, etc., when heated in the gas, are oxidized, while the gas is decomposed. The gas liberates iodine from potassium iodide ; and it reduces permanganates.

Action of water.—Nitrogen peroxide is decomposed by water. At low temperatures, a mixture of nitric and nitrous acid are formed : $N_2O_4+H_2O=HNO_3+HNO_2$, and with aqueous solutions of the alkalies, the corresponding salts are obtained. When nitrogen peroxide is dissolved in water, the solution passes through a series of colour changes—blue, green, orange. This is due to the gradual solution of the nitrogen peroxide in the nitric acid. If sufficient water be present, the solution finally becomes colourless.

J. Priestley (1772) analyzed air by taking advantage of the fact that when nitric oxide is added to air, nitrogen peroxide is formed, and the red fumes are dissolved by potassium hydroxide. Hence, if nitric oxide be gradually added to a known volume of air, in presence of this alkali, the nitrogen peroxide is absorbed. The residual gas is nitrogen, all the oxygen is removed by the nitric oxide. This method is not often used, because other

processes are less troublesome. The formation of acid when nitrogen peroxide dissolves in water; and the formation of nitrogen peroxide by the action of oxygen on nitric oxide may be illustrated by an apparatus fitted up as shown in Fig. 188. A little water is placed in the globe. The globe is then filled with nitric oxide. The lower vessel is filled with water tinted with blue litmus. Oxygen is led slowly into the globe through the side tube. Red fumes of nitrogen peroxide are formed; this gas is absorbed by the water and the pressure is reduced. The coloured water rises from the dish into the globe to restore equilibrium. The blue litmus is coloured red by the acid formed in the globe. If everything is properly regulated, the globe will be nearly filled with water, and the first rush of water will appear as a miniature fountain inside the globe.

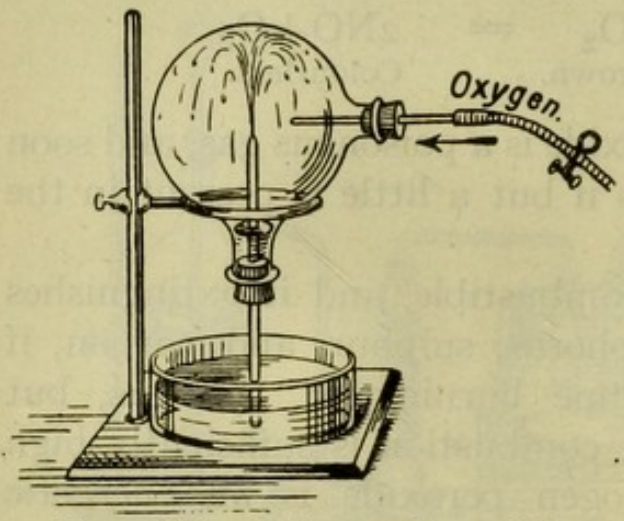


FIG. 188.—Nitrogen Peroxide Fountain.

When a mixture of nitric oxide and nitrogen peroxide is passed through a tube cooled to about −30°, a more or less impure form of **nitrogen trioxide**—N_2O_3—condenses to a bluish liquid. As soon as the temperature rises, the liquid dissociates: $N_2O_3 = NO + NO_2$, nitric oxide escapes, and leaves a residual yellow liquid of nitrogen peroxide. Nitrogen trioxide appears to be **nitrous anhydride,** because of the possible reaction: $N_2O_3 + H_2O = 2HNO_2$.

TABLE XXVII.—THE DISTINCTION OF NITROGEN PEROXIDE, CHLORINE, HYDROGEN PEROXIDE, AND OZONE.

Reagent.	Ozone.	Hydrogen peroxide.	Chlorine.	Nitrogen oxide.
KI and starch	Blue	Blue	Blue	Blue
Indigo solution	Bleached	Bleached	Bleached	Bleached
Litmus solution	,,	,,	,,	,,
Clean silver foil	Blackened	Nil	White film	No change

TABLE XXVII.—(*Continued*).

Reagent.	Ozone.	Hydrogen peroxide.	Chlorine.	Nitrogen oxide.
Mercury globule	"Tail" on glass	Nil	White mess	Not attacked
Chromic acid and ether	Nil	Blue	Nil	Nil
Titanic acid .	Nil	Yellow	Nil	Nil
"Tetra base"	Violet	Nil	Blue	Yellow to brown
Potassium permanganate solution	Unchanged	Decolorized	Decolorized	Decolorized

Recapitulation.—Before dismissing the nitrogen oxides it will be found instructive to draw up a table of their comparable properties—omitting the little known hexoxide :

TABLE XXVIII.—PROPERTIES OF THE NITROGEN OXIDES.

	Nitrogen monoxide.	Nitric oxide.	Nitrogen trioxide.	Nitrogen peroxide.	Nitrogen pentoxide.
Formula . . .	N_2O	NO	N_2O_3	N_2O_4	N_2O_5
Atomic ratio N : O	2 : 1	2 : 2	2 : 3	2 : 4	2 : 5
State of aggregation	Gas	Gas	Gas	Liquid	Solid
Colour	Colourless	Colourless	Reddish brown	Colourless	White
Combustible . .	No	No	No	No	No
Supporter of combustion	Yes	Feeble	—	—	—
Action of litmus solution	Nil	Nil. The red fumes in air redden blue litmus	Reddened	Reddened	Reddened
100 vols. water at 20° dissolve	67 vols.	4·6 vols.	Forms nitrous acid	Forms a mixture of nitrous and nitric acids	Forms nitric acid
Unites with metal forming	—	Forms *nitrosyls*	—	Nitro metals and *nitroxyls*	—
Melting-point . .	−102·7°	−167°	−111°	−9°	30°
Boiling-point . .	−89·8°	−150°	—	+26°	47°
Vapour density (H_2 =2)	44	29·88	Decomposes	Varies with temperature	—

§ 4. Dalton's Law of Multiple Proportions.

The formation of chemical compounds is not a capricious and fortuitous process, but it proceeds in an orderly fashion. Chemical combination is restricted to certain fixed proportions of matter. These limitations appear to have been prescribed by Nature as part of her scheme in building the material universe. This fact arrested the attention of J. Rey in 1630. Rey's conclusion that in the calcination of the metals "Nature has set limits which she does not overstep," agrees with many facts; but we must now amplify the position we adopted in reference to the law of constant composition because there are certain limitations. If one gram of lead be calcined for a long time at 500°, never more than 1·078 gram of a red powder—red lead—is obtained. Here, 64 grams of oxygen correspond with 621 grams of lead. If the lead be calcined at about 750°, one gram of lead will not take up more than 0·007 gram of oxygen to form a yellow powder—litharge; otherwise expressed, 64 grams of oxygen correspond with 828 grams of lead. Here then Nature has set *two* limits; lead forms at least two definite oxides—a red oxide stable at a dull red heat, and a yellow oxide stable at a bright red heat. The relative proportions of lead and oxygen in the two oxides are as follows:

	Oxygen.	Lead.
Red oxide (red lead)	64	$621 = 207 \times 3$
Yellow oxide (litharge)	64	$828 = 207 \times 4$

This means that for a given weight of oxygen, the yellow oxide has four-thirds as much lead as the red oxide. Similarly, hydrogen forms two oxides—water and hydrogen peroxide; barium forms two oxides — barium monoxide and barium peroxide; and carbon forms two well-defined oxides called respectively carbon monoxide and carbon dioxide. In these we have:

	Oxygen	Carbon.
Carbon dioxide	8	$3 = 1 \times 3$
Carbon monoxide	8	$6 = 2 \times 3$

At least six oxides of nitrogen are known. In these, the relative proportions of nitrogen and oxygen are as follows:

	Nitrogen.	Oxygen.
Nitrogen monoxide	14	$8 = 1 \times 8$
Nitrogen dioxide	14	$16 = 2 \times 8$
Nitrogen trioxide	14	$24 = 3 \times 8$
Nitrogen tetroxide	14	$32 = 4 \times 8$
Nitrogen pentoxide	14	$40 = 5 \times 8$
Nitrogen hexoxide	14	$48 = 6 \times 8$

These six compounds of the same elements united in different proportions from a series of substances so well marked and contradistinguished that it is questionable if the most acute human intellect would ever have guessed that they contained the same constituents. Starting from the compound with the least oxygen, we see that for every 14 grams of nitrogen, the amount of oxygen increases by steps of 8 grams. Accordingly, in all six compounds of nitrogen and oxygen, the masses of nitrogen and oxygen are to one another as $m \times 14 : n \times 8$, where m and n are whole numbers. Hundreds of cases equally simple might be cited. Similar facts helped to establish an idea deduced by J. Dalton (1802–4) from the atomic theory, and now called **the law of multiple proportions: when one substance unites with another in more than one proportion, these different proportions bear a simple ratio to one another.**

The idea embodied in this law can be neatly illustrated by means of squared paper. Let the abscissæ, Fig. 189, represent weights of oxygen, and the ordinates weights of nitrogen which enter into combination with the oxygen. The known compounds of these two elements are represented by symbols "o" in the diagram. If the law of multiple proportions perfectly describes nature's *modus operandi*, and no other disturbing influence be at work, we can represent possible, but yet undiscovered, compounds of nitrogen and oxygen by points "•"; and compounds representable by the intermediate positions are impossible. The law is considered to be so well founded that it can be applied to predict the composition of compounds which have never been prepared. Thus, if an oxide of nitrogen containing rather more oxygen than nitrogen hexoxide be made, we may predict that it will contain $7 \times 8 = 56$ parts of oxygen for every 14 parts of nitrogen by weight. Again, if a substance be found to contain oxygen and nitrogen,

not in the proportion 14 : 8 or a multiple of 8, it is in all probability a mixture, not a true compound. Thus, air contains oxygen and nitrogen, but the proportions of nitrogen to oxygen is as 14 : 4·29, and this is represented by the cross " × " in Fig. 189. This fact is usually given along with other circumstantial evidence to show the probability that air is a mixture and not a chemical compound.

Are solutions chemical compounds ?—Our definitions say, No ! We might easily be led to **reason in a circle** (*in circulo probando*) by a rigid application of the so-called constant and multiple - proportion laws. A salt dissolves in water in all proportions up to a certain limiting value. The process of solution, in some cases, seems to be otherwise indistinguishable from chemical combination. It is sometimes said that the process of solution cannot be a case of chemical combination, because there are no signs of abrupt *per saltum* changes characteristic of combination in multiple proportions. **The composition of homogeneous solutions can vary continuously within certain limits, while a compound has one fixed and definite composition.** Accordingly we refuse to call all substances compounds which do not conform with the definition. Hence, in virtue of this arbitrary definition, solutions are said to be mixtures and not chemical compounds. More bluntly expressed : a prejudice in favour of the definition in question may warp the judgment to such an extent as to lead to a denial of the possibility of contradictory phenomena. Such a perversion of the judgment must be detrimental to the progress of science. Hence the danger of cherishing a blind faith in our so-called " laws of nature." A writer has said, " Efforts have been made to find compounds which do not conform to the laws of chemical combination, but all such attempts have resulted in failure." From what has just been said, **if exceptions to the laws of**

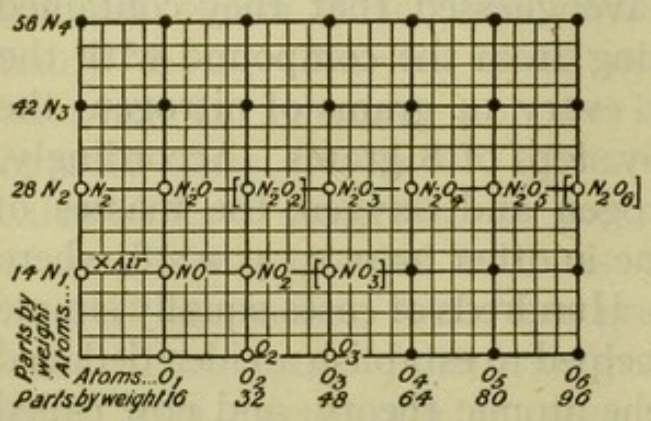


FIG. 189.—Law of Multiple Proportions.

chemical combination were discovered we should refuse to call them compounds, and the quest for exceptions must of necessity fail.

Questions.

1. Summarize a few important methods for preparing the ordinary basic oxides. Note: (1) Roasting the metal in air; (2) calcining the hydroxide; (3) the carbonate; (4) the nitrate, and (4) the sulphates. Note also the sulphates usually require a much higher temperature than the nitrates for decomposition.

2. Two oxides of nitrogen have the following composition:

Nitrogen	63·64	46·67
Oxygen	36·36	53·33

Show that these numbers are in agreement with the law of multiple proportions.—*Malvern College.*

3. Given sulphur, how could you obtain a small quantity of sulphuric acid? Explain how you would test a sample of sulphuric acid for nitric acid and hydrochloric acid.—*Malvern College.*

4. State Gay-Lussac's law of combination of gases by volume. What volume changes occur when (*a*) sulphur is heated in nitrous oxide; (*b*) carbon is heated in carbon dioxide; (*c*) sodium is heated in hydrogen chloride; (*d*) phosphorus is heated in nitric oxide?—*Victoria Univ.*

5. Give a detailed description of what is observed when saltpetre is heated in a retort with concentrated sulphuric acid. What are the properties of the distillate? State what happens when a strong aqueous solution of the distillate is poured on copper filings.—*Victoria Univ.*

6. How is pure nitrous oxide made? By what characters or tests can it be distinguished from oxygen and from nitric oxide respectively?—*Science and Art Dept.*

7. Describe tests for distinguishing between (*a*) oxygen and nitrous oxide; (*b*) carbon dioxide and nitrogen; (*c*) chlorine and nitrogen peroxide. Point out which of the tests described may be regarded as physical and which as chemical.—*Trinity Coll.*

8. Two bottles are given; one contains the vapour of bromine and the other vapour of nitrogen peroxide (N_2O_4); how would you ascertain which of the two contains bromine? Give a brief description of the characteristic properties of each substance.—*London Univ.*

9. Describe how you would ascertain by experiments whether a gas composed of one volume of nitrogen and one volume of

oxygen is a mechanical mixture or a chemical compound of the two elements.—*London Univ.*

10. Explain how nitrogen peroxide can be produced giving the chemical equations which take place in its formation. At low temperatures nitrogen peroxide forms an almost colourless liquid ; it becomes yellow on heating, and eventually brown. The vapour, when first formed, is reddish-brown, but at temperatures above the boiling point of water it is almost black. How can these changes be accounted for ?—*London Univ.*

11. 100 grms. of saltpetre are heated with an excess of sulphuric acid in a retort. Name the acid and calculate the quantity of it produced. The acid formed is neutralized with ammonia, and the salt so obtained is heated until it is completely decomposed. A gas is thus produced. What is its name, what are its chief characters, and what volume of it at the standard temperature and pressure should be obtained ?—*London Univ.*

12. Two bottles are placed before you, each containing a colourless gas. On removing the stoppers, (*a*) colourless, steamy fumes escape from the one, and (*b*) orange-red vapour from the other. What might each of these gases be, and how would you further test it in order to identify it with certainty ?—*London Univ.*

13. One lb. of sulphur may combine with 1 lb. of oxygen or with $1\frac{1}{2}$ lbs. of oxygen. What compound is formed in each case ? If no other compounds of sulphur and oxygen are known, how does the existence of these two only illustrate the law of multiple proportions ?—*Science and Art Dept.*

14. Give at least one example of each of the following actions, indicating what takes place, and if possible writing the equations for the changes : (*a*) a metal on hydrochloric acid ; (*b*) a metal on dilute sulphuric acid ; (*c*) a metal on strong sulphuric acid ; (*d*) a metal on nitric acid ; (*e*) a non-metal on strong sulphuric acid.—*Staffs. County Schol.*

15. What gas is obtained by heating ammonium nitrate ? Mention its characteristic properties. What weight in grammes of ammonium nitrate would yield, on complete decomposition, a volume of this gas which would just fill a gas holder of capacity 85 litres, the gas being at a temperature of 25° C. and under a pressure equal to that of 748 mm. of mercury ? (H=1, O=16, N=14.)—*Cape Univ.*

16. Formulate and explain the reactions which occur in the experiments : (*a*) nitrous oxide passed over glowing charcoal ; (*b*) sulphur fused with potassium nitrate ; (*c*) caustic potash solution added gradually to dilute sulphuric acid ; (*d*) potassium permanganate solution added gradually to a mixture of dilute sulphuric acid and hydrogen peroxide.—*Cape Univ.*

17. What relation exists between the molecular weight and the

density of a gas ? What density has each of the following gases : ammonia, nitrous oxide, nitrogen, ozone ? (H = 1, N = 14, O = 16.) —*Sydney Univ.*

18. Contrast the properties of nitrous oxide and nitric oxide. You are given three jars, each containing a different gas ; the three gases are oxygen, nitric oxide, and nitrous oxide. How would you find out which jar contained which gas ?—*Staffs. County Schol.*

19. How is nitrous oxide (laughing gas) prepared ? What are its properties ? When passed over red-hot iron the iron takes the oxygen and forms oxide of iron, whilst the nitrogen passes on : what volume of nitrogen could be obtained from 25 c.c. of nitrous oxide ?—*London Univ. Matric.*

20. Explain the chemical reactions which occur when (*a*) potassium chlorate is heated, (*b*) iodine is warmed with caustic potash, (*c*) chlorine is mixed with hydrogen iodide, (*d*) nitric acid is poured on copper, (*e*) nitrogen is passed over heated magnesium. Give equations.—*Owens Coll.*

21. What reactions occur when the following pairs of substances dissolved in water are mixed together : (*a*) HCl and HNO_3 ; (*b*) HCl and $KClO_3$; (*c*) $NaHCO_3$ and $MgSO_4$; (*d*) SO_2 and I_2 ?—*Science and Art Dept.*

22. State precisely what happens when the following gases are passed over red-hot copper turnings : (*a*) oxygen ; (*b*) hydrogen ; (*c*) chlorine ; (*d*) nitric oxide.—*Science and Art Dept.*

23. How would you proceed to make a specimen of nitric acid ? What do you understand by the statement that nitric acid is an oxidizing agent ? Give an instance of its action as such.—*Oxford Prelim. Locals.*

24. An oxide of nitrogen is found to have a vapour density 15, what does this tell us concerning its formula ? A metallic oxide is found to contain $21\frac{1}{3}$ per cent. of oxygen. The specific heat of the metal is found to be 0·055. What is the exact equivalent of the metal, and what is its probable atomic weight ?—*Owen's Coll.*

25. Three cylinders are given to you full of colourless invisible gases which may be either oxygen, or nitric oxide, or nitrous oxide. How would you identify them ?—*Calcutta Univ.*

26. What is the difference in composition between a sulphite and a sulphate, between a nitrite and a nitrate, and between nitrous oxide and nitric oxide ?—*London Univ.*

CHAPTER XXIX

Ammonia and Air

§ 1. Ammonia—Occurrence and Preparation.

History.—Ammonia was known to the early chemists, and Geber describes the preparation of ammonium chloride by heating urine and common salt. Hence the alchemists' term—*spiritus salis urinæ*. Ammonium chloride was first brought to Europe from Egypt, where it was prepared from the "soot" obtained by burning camel's dung. The name ammonia seems to be connected somehow with the Egyptian sun-god—Ra Ammon; ammonium salts must have been known to the early Egyptian priests. The term *sal ammoniac* was one of the early names for ammonium chloride; the equivalent term *sal armoniacum*, which appears in the translations of Geber's writings, and which was used for some time afterwards, was probably a misspelling, since the term "salt of Armenia"—*sal armoniacum*—was applied to common salt and to native sodium carbonate. S. Hales (1727) noticed that when lime was heated with sal ammoniac in a retort arranged to collect the gas over water, no gas appeared to be given off; on the contrary, water was sucked into the retort; when J. Priestley (1774) tried the experiment with a mercury gas trough, he obtained ammonia gas which he called "alkaline air."

Occurrence.—Small quantities of ammonia occur in atmospheric air and in natural waters. It is produced by the action of putrefying bacteria (p. 337) on organic matter in the soil, etc. The odour of ammonia can often be detected near stables. Ammonium salts are also deposited on the sides of craters and

fissures of the lava streams of active volcanoes; and with boric acid in the fumaroles of Tuscany.

Preparation.—Ammonia gas is given off when an intimate mixture of commercial ammonium chloride or ammonium sulphate is heated with twice its weight of quicklime, CaO, or slaked lime, $Ca(OH)_2$. The reaction is represented: $2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$. Ammonia reacts with the ordinary drying agents—calcium chloride, sulphuric acid, phosphorus pentoxide—and accordingly these agents must not be used with the idea of drying the gas. A tower of quicklime, indicated in Fig. 190, is generally employed when dry gas is wanted. If a mixture of ammonium chloride and quicklime is to be heated, a copper flask, without the tube funnel, Fig. 190, is preferable to glass since steam is liable to condense on the walls of the flask, trickle down, and crack the hot glass. Otherwise the disposition of the apparatus is similar. When ammonia gas is required for the laboratory, it may be obtained from a cylinder of liquid ammonia, by boiling commercial aqua ammonia in a flask, Fig. 190. For routine experiments the drying tower is not needed, and jars of the gas can be collected by the downward displacement of air as was the case with hydrogen.

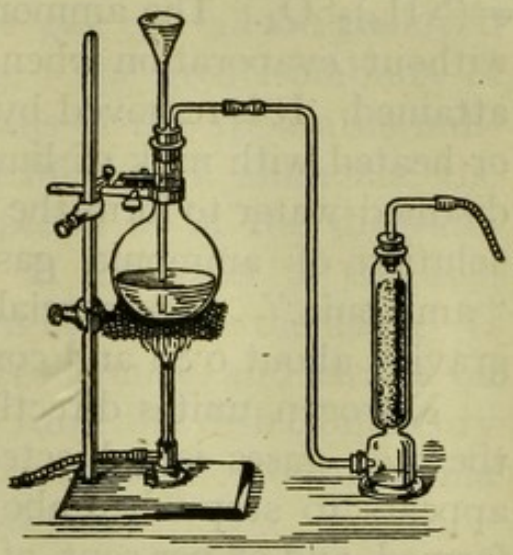


FIG. 190.—Preparation of Ammonia.

Ammonia is formed during the action of water on some of the metallic nitrides. The action of superheated steam on calcium cyanamide (*q.v.*) also furnishes ammonia: $CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$. The yield is 99 per cent. of that indicated by this equation. The process appears likely to have a commercial future.

Ammonia is formed when nitrogenous compounds—coal, leather, bones, etc.—are heated in closed vessels. The old term for ammonia—*spirits of hartshorn*—refers to an old custom of preparing ammonia by heating hoofs and horns in closed vessels.

The formation of ammonia by heating nitrogenous compounds in closed vessels is particularly noticeable if the organic matter be heated with soda lime—that is, quicklime slaked with a concentrated solution of sodium hydroxide is used as a test for nitrogen inorganic compounds. Most of the ammonia of commerce is derived from the ammoniacal liquid obtained as a by-product in the manufacture of coal gas, and in furnace gases. This liquid is boiled with milk of lime, and the ammonia which is evolved is absorbed by dilute sulphuric acid—$2NH_3 + H_2SO_4 \rightleftharpoons (NH_4)_2SO_4$. The ammonium sulphate so obtained crystallizes without evaporation when a sufficient concentration has been attained. It is removed by perforated ladles and recrystallized, or heated with milk of lime, and the resulting gas absorbed in distilled water to form the **aqua ammonia** of commerce. The solution of ammonia gas in water is conventionally styled "ammonia." Commercial aqueous ammonia has a specific gravity about 0·88 and contains about 35 per cent. NH_3.

Nitrogen unites directly with hydrogen when a mixture of the two gases is subjected to electric sparks. The reaction appears to stop when about 2 per cent. of ammonia has been formed, and 98 per cent. of gas remains uncombined. The same result is obtained if ammonia gas be exposed to the electric sparks, 98 per cent. decomposes. The reaction is therefore reversible: $2NH_3 \rightleftharpoons N_2 + 3H_2$. If water or acid be present, the ammonia is absorbed as fast as it is formed, and the reaction proceeds to an end. All the nitrogen and hydrogen combine. The two gases nitrogen and hydrogen also combine if heated in the presence of finely divided metals, *e.g.* iron. The amount of ammonia formed is considerably increased if the pressure be raised. The gases are kept in circulation so that the ammonia can be removed as fast as it is formed. The reaction promises to be useful for the commercial synthesis of ammonia. The process has recently been taken up by the Badische Anilin und Sodafabrik for exploiting commercially.

Uses.—Ammonia is used in refrigerating machines; as a cleansing agent, on account of its property of dissolving greases; in the manufacture of soda by the Solvay process; in chemical operations where a volatile alkali is needed; etc.

§ 2. The Properties of Ammonia.

Ammonia is a colourless gas with a pungent odour. If inhaled suddenly, it will bring tears to the eyes; if large quantities be inhaled, suffocation may ensue. Ammonia is a little more than half as heavy as air, and consequently, the gas is collected, like hydrogen, by the downward displacement of air.

Action of water.—The gas is extremely soluble in water: one volume of water at 0° and 760 mm. dissolves 1298 volumes of gas, and at 20°, 710 volumes. The gas can all be removed from its aqueous solution by boiling. The great solubility of ammonia in water is illustrated by means of the apparatus indicated in Fig. 190. The flask is first filled with ammonia, the stopper inserted, and the stopcock opened as in the diagram. The rush of water produces a spray. If the water in the dish be coloured with red litmus, it will turn blue inside the flask. If a jar of dry ammonia be collected over mercury, and carried on a dish of mercury into a tray of water, and the dish of mercury removed below the surface of water, the absorption of ammonia is so rapid that the cylinder is often broken.

Considerable heat is evolved during the solution of the gas: $NH_3 + Aq = NH_3Aq + 8{\cdot}4$ Cals. If a rapid current of air be driven through a cold solution of ammonia in water, the heat absorbed as the ammonia is expelled from the solution will reduce the temperature so as to freeze a small globule of mercury. The production of cold is best demonstrated by blowing air through a solution of ammonia standing on a few drops of water on a block of wood. The beaker will soon be frozen to the block of wood.

Refrigeration.—The heat of evaporation of liquid ammonia is 5·7 Cals. at −33°. This means that 17 grams of liquid ammonia at −33° requires 5·7 Cals. of heat before it can pass into a gas at −33°. Otherwise expressed, when the gas is liquefied, heat is liberated; and conversely, heat is absorbed when the liquid is vaporized. If, therefore, liquid ammonia be evaporated, a relatively large amount of heat is absorbed from its surroundings. Advantage is taken of this fact in the preparation of artificial ice, cold storage, etc. Ammonia gas is liquefied by compression

in the "condensing coils" by means of a pump; the heat generated as the gas liquefies is conducted away by the cold water flowing over the condensing pipes, Fig. 191. The liquid ammonia runs into coils of pipes, "expansion coils," dipping in brine. The pressure is removed from the liquid ammonia in the expansion coils, and the heat absorbed by the rapidly evaporating liquid cools the brine below zero. The gas from the evaporating liquid is pumped back into the condensing coils; and so the process is continuous. Cans of water placed in the brine are frozen into cakes. In cold storage rooms, the cold

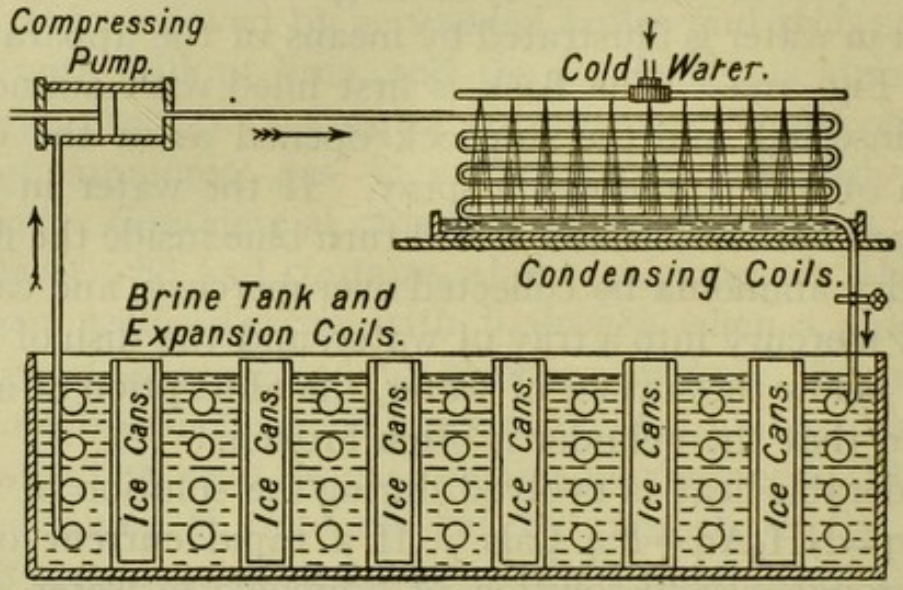


FIG. 191.—Refrigeration Plant (Diagrammatic).

brine circulates in coils near the ceiling of the room to be cooled, and returns to the cooling tank. Sulphur dioxide and carbon dioxide are also employed for refrigeration; but ammonia is more generally used.

Liquid and solid ammonia.—Ammonia unites with silver chloride to form a compound which is decomposed by heat. If the compound of silver chloride with ammonia be heated in one leg of a V-shaped hermetically closed tube immersed in water, p. 141, and the other leg immersed in a freezing mixture —say calcium chloride and ice—the ammonia gas condenses in the cold leg of the V-tube to a colourless limpid liquid. The liquid boils at $-33{\cdot}5°$, and solidifies to white transparent crystals at $-78°$.

Oxidation of ammonia.—Ammonia is a non-supporter of ordinary combustion and it is incombustible in air. It burns in oxygen, forming nitrogen, water, and small quantities of ammonium nitrate, and nitrogen peroxide. If ammonia be mixed with oxygen, say, by bubbling a stream of oxygen through a small quantity of concentrated ammonia warmed in a flask, the gas issuing from the flask can be ignited; it burns with a yellow flame. In a few moments the solution in the flask will be too dilute to show the flame. By sending a jet of ammonia into the air holes of a Bunsen's burner, the flame will be found to expand, and acquire a yellow tinge. The effect is shown better by delivering a jet of ammonia into the centre of the tube of a Bunsen's burner. If a stream of oxygen be sent into a cylinder fitted as shown in Fig. 192, and a stream of ammonia be sent into the same cylinder through a wide glass tube, the ammonia can be ignited, and it will burn with a yellowish flame.

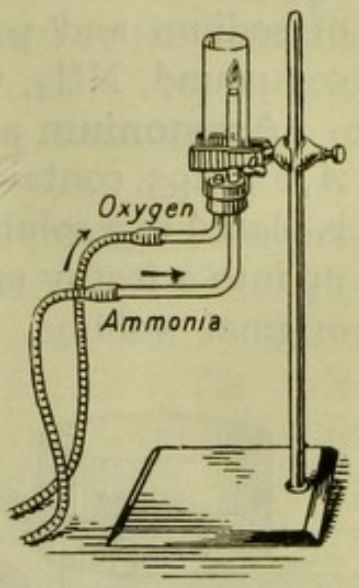


FIG. 192.—Combustion of Ammonia in Oxygen.

§ 3. Ammonium Salts.

Ammonia as a base.—One of the most striking properties of ammonia chemically speaking is the basic character of its aqueous solution. The aqueous solution turns red litmus blue, yellow turmeric paper brown, conducts electricity, and in general reacts like a base. Indeed it is supposed that a molecule of water combines with a molecule of ammonia to form a solution of ammonium hydroxide: $NH_3+H_2O=NH_4OH$. Hence, aqueous ammonia is sometimes called **ammonium hydroxide.** If the aqueous solution of ammonia be neutralized with an acid —nitric, sulphuric, or hydrochloric acid—the corresponding ammonium salt is formed—ammonium nitrate, NH_4NO_3; ammonium sulphate, NH_4HSO_4, or $(NH_4)_2SO_4$; ammonium chloride, NH_4Cl. It will be observed that we are here dealing

with a valent radicle NH_4 which is called **ammonium.** The assigning of the name does not make this radicle any less hypothetical than if it were nameless. The fact that ammonium appears to form a series of salts closely analogous with the salt of sodium and potassium has instigated many to seek for a compound, NH_4, with a corporeal existence.

Ammonium amalgam.—When a little mercury amalgam, *A*, Fig. 193, containing about one per cent. of sodium or potassium is placed in a solution of ammonium chloride, the mercury swells up into a frothy mass, illustrated in *B*, Fig. 193, thirty times its original volume. The inflated mass can be compressed or expanded by raising or lowering the pressure. If mercury be brought into a concentrated aqueous solution of ammonium, and a current of electricity be passed through the solution in such a way that the cathode dips into mercury, the mercury swells up in a similar manner. If the temperature be kept below 0°, the amalgam shows little tendency to inflation. It is supposed that a true solution of ammonium NH_4 in mercury is formed, which rapidly decomposes into mercury, hydrogen, and ammonia when warmed above 0°. These gases, entangled with the mercury, are said to cause the frothing. Others consider that the amalgam is a mere solution of ammonia and hydrogen in mercury.

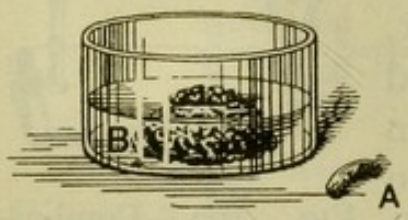


FIG. 193.—Ammonium Amalgam.

The ammonium salts are usually very soluble in water, and when the solutions are boiled, partial decomposition occurs. The solution, originally neutral, may become acid owing to the volatilization of more ammonia than acid. When the ammonium salts are heated with the fixed alkalies—potassium or sodium or calcium hydroxides, or calcium oxide—the ammonia is volatilized. Hence, the old term *volatile alkali* for ammonia.

Identification of ammonia and ammonium salts.—(1) When the salts are heated with an alkali or lime, the characteristic smell of ammonia is obtained; (2) With hydrochloroplatinic acid, they give a yellow precipitate of ammonium chloroplatinate; (3) Nessler's reagent gives a

yellow coloration. The intensity of the tint with a given concentration is nearly proportional to the amount of ammonia present.

Ammonium sulphate.—This salt is usually made from "gas liquor" as indicated on p. 561. It is also formed by the neutralization of ammonia with dilute sulphuric acid. It is used principally as a fertilizer, and also in the manufacture of ammonium compounds.

Ammonium nitrate.—This salt is used chiefly in the preparation of nitrous oxide; and in the manufacture of fireworks and explosives. For instance, the explosive "ammonite" is said to contain between 80 and 90 per cent. of this salt. The ordinary crystals of this salt are rhombic, and isomorphous with potassium nitrate. The heat of solution is: $2NH_4NO_3 + 400Aq = -12{\cdot}6$ Cals. If 60 parts of the salt be dissolved in 100 parts of water at 13°, the temperature of the liquid falls to about −13°; and if the water be at 0°, the temperature of the liquid falls to about −16°. Hence, a mixture of ice and ammonium nitrate is a valuable mixture for reducing the temperature below the freezing-point of water. Ice and common salt are often used for the purpose. Such mixtures are called **freezing mixtures.**

Ammonium nitrite.—This salt is made by saturating an aqueous solution of ammonia with nitrous acid, or by adding silver nitrite to a solution of ammonium chloride. When heated the solution decomposes into nitrogen and water, so that the crystals cannot be prepared by evaporation in the ordinary manner. The solid can be obtained by evaporating a clear aqueous solution of the salt over sulphuric acid *in vacuo* at ordinary temperatures; or better, by adding ether to an alcoholic solution of the salt when crystals of ammonium nitrite separate. Very little gas is evolved if the salt be heated *in vacuo* below 40°; on cooling most of the salt crystallizes; at 70°, the salt slowly decomposes and a large part sublimes.

Ammonium chloride.—If ammonia gas be brought in contact with hydrogen chloride, dense white fumes of ammonium chloride are formed: $NH_3 + HCl = NH_4Cl$. This can be

illustrated by placing a bottle of aqueous ammonia alongside a bottle of hydrochloric acid, and blowing across the mouth of the one bottle to the other, Fig. 194. Ammonium chloride is made by mixing an aqueous solution of ammonia and hydrochloric acid, and by passing ammonia gas into dilute hydrochloric acid. The last-named process is usually employed on a manufacturing scale. The crude product is purified by heating the solid in a large iron or earthenware pot with a dome-shaped cover, Fig. 195. The ammonium chloride volatilizes and the solid condenses as a white crystalline fibrous mass inside the cover. Most of the impurities remain in the vessel. The

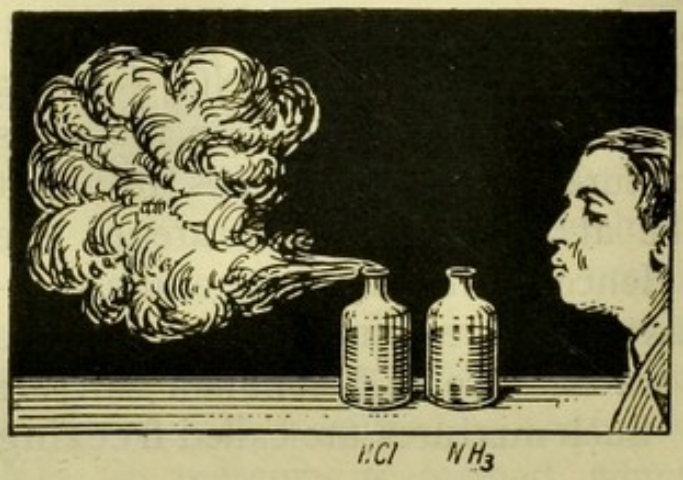


FIG. 194.—Formation of Ammonium Chloride.

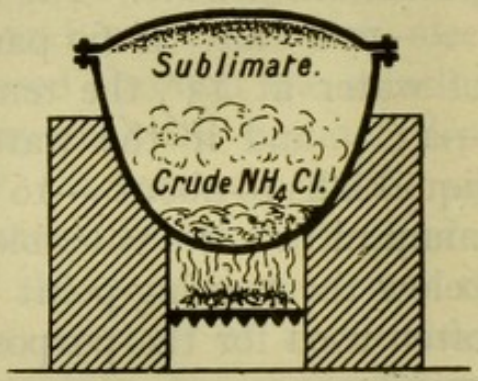


FIG. 195.—Sublimination of Ammonium Chloride.

process of vaporizing a solid and condensing the vapour back to the solid condition is called sublimation. Ammonium chloride is a white granular, fibrous, crystalline solid, with a sharp saline taste. It dissolves in water and at the same time lowers the temperature. The heat of solution is $-3{\cdot}7$ Cals. Ammonium chloride is used for charging Leclanché cells; as a constituent of soldering fluids to protect metals from oxidation during the soldering it is also used in galvanizing iron, and in the textile industries.

The dissociation of ammonium chloride.—The vapour density ($H_2=2$) of ammonium chloride at 350° is 29·04; and at 1040°, 28·75. The theoretical value for the molecule NH_4Cl is 53·5. Hence, we cannot be dealing with that molecule at the temperatures named. Suppose the vapour of ammonium

chloride be dissociated so that a mixture of equal volumes of ammonia and hydrogen chloride is formed corresponding with $NH_4Cl = NH_3 + HCl$. The vapour density for complete dissociation would then be 26·75, that is, half the value for NH_4Cl—that is, $\frac{1}{2}$ of (17 + 36·5). The experimental result thus shows that dissociation is nearly complete. A simple calculation shows that the vapour contains about 17 per cent. of ammonium chloride, and 83 per cent. of a mixture of equal volumes of ammonia and hydrogen chloride. According to H. B. Baker (1894), if the vapour density be determined in a vessel of hard glass with a thoroughly dried sample of ammonium chloride, the number is quite normal, namely, 53·4.

The dissociation of ammonium chloride under ordinary conditions is easily illustrated by taking advantage of the difference in the speeds of diffusion of the two gases, ammonia and hydrogen chloride. The process of atmolysis (p. 225) can be used. Place a little ammonium chloride near the middle of a piece of hard tube, Fig. 196, and a little lower down the tube place a piece of blue litmus paper. Place a loose plug of asbestos a little above the salt, and then a piece of red litmus paper. Heat the ammonium chloride. The ammonia being the lighter gas, diffuses more quickly than the hydrogen chloride. Consequently, when the ammonium chloride is heated, the blue litmus will be reddened by the excess of slow diffusing hydrogen chloride in the lower part of the tube ; and the red litmus will be blued by the ammonia which passes to the upper part of the tube before the hydrogen chloride.

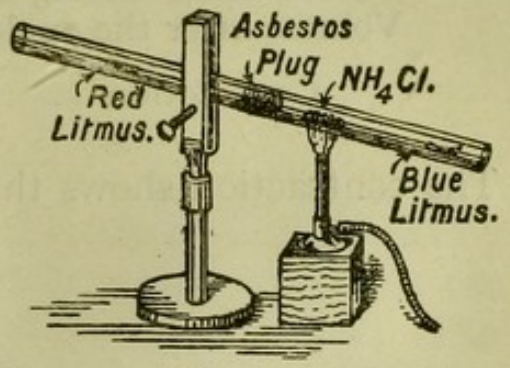


FIG. 196.—Dissociation of Ammonium Chloride (H. J. H. Fenton's experiment).

§ 4. The Composition of Ammonia.

1. By explosion with oxygen.—Repeating an old experiment of C. L. Berthollet (1785), if a definite volume ammonia

gas be sparked in the eudiometer on the right, Fig. 197, the volume of the gas will be nearly doubled in a short time owing to the dissociation :

$$\underbrace{2NH_3}_{2 \text{ volumes}} \rightleftharpoons \underbrace{N_2 + 3H_2}_{4 \text{ volumes}}$$

As indicated above, about 98 per cent. of the gas dissociates in this manner. Mix the dissociated gas with sufficient oxygen to give an explosive mixture with the hydrogen, and spark the mixture. The contraction will indicate the amount of water in the gas, since the volume of liquid water is negligibly small in comparison with the volume of the component gases. *E.g.*

Volume of ammonia	10·0 c.c.
Volume after sparking	19·9 c.c.
Volume after adding oxygen	72·3 c.c.
Volume after the explosion	49·9 c.c.
Contraction	22·4 c.c.

The contraction shows that 22·4 c.c. of water has been formed, two-thirds of this, 14·9 c.c., represents the hydrogen obtained from the 10 c.c. of ammonia used for the experiment. Hence, 10 c.c. of ammonia furnish very nearly 14·9 c.c. of hydrogen and 5 c.c. of nitrogen, that is, three volumes of hydrogen per volume of nitrogen within the limits of the experimental error.

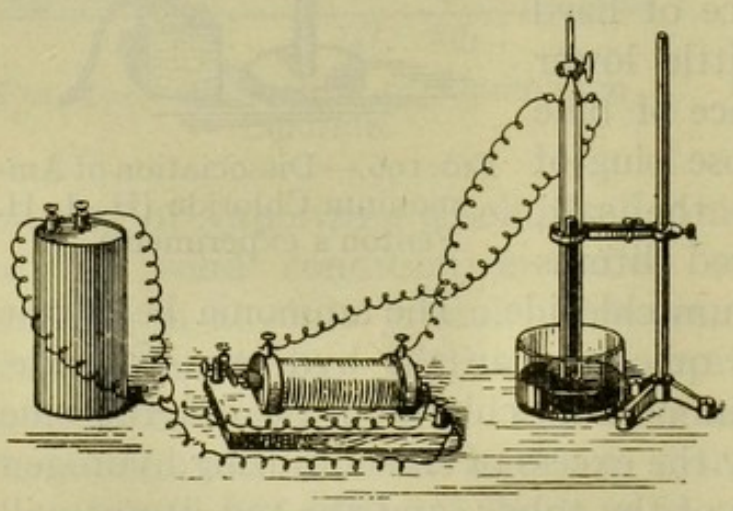
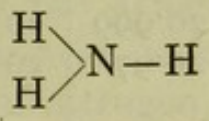


FIG. 197.—The Decomposition of Ammonia by Electric Sparks.

2. By electrolysis.—If a concentrated aqueous solution of ammonia be electrolyzed, Fig. 125, nitrogen and hydrogen are evolved at the two electrodes very nearly in the proportion one volume of nitrogen for three volumes of hydrogen. The aqueous ammonia does not conduct very well unless a little

ammonium sulphate or other ammonium salt be dissolved in the solution.

3. The vapour density of ammonia and Avogadro's hypothesis.—The two proofs just considered show that three volumes of hydrogen combine with one volume of nitrogen to form ammonia. By Avogadro's hypothesis, the number of molecules which combine are in the same ratio ; and since the two gases hydrogen and nitrogen have diatomic molecules, it follows that ammonia contains three atoms of hydrogen for one atom of nitrogen. Hence, the formula of ammonia must be NH_3, or N_2H_6, etc. The vapour density of ammonia ($H_2=2$) is nearly 17. If the atomic weight of hydrogen be 1 and nitrogen 14, the molecular weight of ammonia is 17. This agrees with the number obtained for the vapour density. Hence, the formula of ammonia is NH_3. Here the nitrogen atom is trivalent, and accordingly the graphic formula for ammonia is :



4. Gravimetric analysis.—The composition of ammonia by weight can be verified by gravimetric analysis. Ammonia gas is passed over a tube containing heated copper oxide. The resulting water is weighed, Fig. 64, and the volume of nitrogen passing along is determined, and the corresponding weight computed (p. 162). The numbers so obtained give the combining proportions of hydrogen and nitrogen in ammonia. The result shows that 14·01 parts of nitrogen are combined with 3·024 parts of hydrogen. The molecular formula is then to be established by Avogadro's hypothesis.

§ 5. The Composition of the Atmosphere.

In 1661, R. Boyle wrote : "The air is a confused aggregate of effluviums from such differing bodies, that, though they all agree in constituting by their minuteness and various motions one great mass of matter, yet perhaps there is scarcely a more heterogeneous body in the world." These words, true as they

are, forcibly impress the fact that air is a mixture of several different gases. Air contains oxygen and nitrogen along with much smaller quantities of ammonia and other nitrogen compounds: hydrogen, hydrocarbons, hydrogen peroxide, carbon dioxide, sulphur compounds, organic matter, suspended solids, chlorides, ozone, water vapour, argon, helium, krypton, neon, xenon. The last five are sometimes called the "noble gases" or the "inert gases" of the atmosphere because their chemistry is summed up in the words: "They do not react with any known substance, and they are generally included with the atmospheric nitrogen."

Oxygen and nitrogen.—The following analyses are quoted to illustrate the variability of oxygen in air :—

Locality	Minimum.	Maximum.	Mean.	Number of analyses.	Analyst.
Paris . . .	20·913	20·999	20·96	100	V. Regnault
Cape Horn . .	20·72	20·97	20·86	20	A. Muntz and E. Aubin
Cleveland, Ohio	20·90	20·95	20·93	45	E. W. Morley

The amount of atmospheric nitrogen varies reciprocally with the oxygen. If oxygen be high, the nitrogen will be low, and conversely. Hence, after making due allowance for differences in the methods of analysis by different men, it is clear that **the relative proportions of nitrogen and oxygen in the air are almost, but not quite, constant.**

Carbon dioxide.—Similar remarks apply to the amount of carbon dioxide. This is rather higher in towns than in the open country; but diffusion of air by winds, etc., prevents an excessive accumulation in any part—excluding, of course, badly ventilated rooms. Thus, 3·027 volumes of carbon dioxide has been reported per 10,000 volumes of air in Paris; and near Dieppe, 2·942 volumes. These numbers may be regarded as normal. In towns, during a fog, seven or eight volumes may accumulate; and in badly ventilated rooms, ten times the normal amount of carbon dioxide may be present. The other

constituents—excluding moisture—are usually regarded as impurities. The essential constituents of normal or average air occur in the following proportions :—

TABLE XXIX.—AVERAGE COMPOSITION OF ATMOSPHERIC AIR.

Per cent. of	By weight.	By volume.
Nitrogen	75·51	78·03
Oxygen	23·15	20·99
Inert gases	1·30	0·95
Carbon dioxide	0·04	0·03

Ozone, hydrogen peroxide, and nitrogen oxide.—The ozone and hydrogen peroxide are probably formed by electrical discharges in the atmosphere as indicated previously. The same remark applies to the oxides of nitrogen. Free nitric acid has been reported in the atmosphere of tropical regions, but generally, the nitric acid is combined with ammonia. About 3 lbs. of ammoniacal nitrogen, and 1 lb. of nitric acid are said to be returned to the earth per acre per annum with the rain. In rural districts the soil is said to receive between 4 and 6 lbs. of combined nitrogen per acre per annum from the rain.

Ammonia.—The ammonia in the atmosphere is largely a product of organic decomposition, and it is returned to the earth by rain in the form of ammonium nitrate, and sometimes as ammonium sulphate or chloride.

Hydrogen and hydrocarbons.—A. Gautier (1901) found that the air of Paris contains per 100 litres—19·4 c.c. of free hydrogen, 12·1 c.c. of methane, 1·7 c.c. of other hydrocarbons, and 0·2 carbon monoxide. Gautier's estimate is probably rather high. The presence of hydrocarbons in air explains the oleaginous character of the deposits which form on roofs, leaves of trees, etc., in towns.

Sulphur compounds.—Sulphur compounds are present in small quantities as hydrogen sulphide, sulphur dioxide, and sulphuric acid in the air of towns. It has been estimated that

about 17¼ lbs. of sulphur trioxide is annually "poured" upon each acre of land at Rothamsted.

Chlorine compounds.—Rain near the sea brings down a certain amount of chlorine derived from the sea water. The proportion of salt in the air is greatest near the sea, and diminishes rapidly further away from the coast. As an average of twenty-six years' observations at Cirencester, 36·1 lbs. of sodium chloride per acre are said to be brought per annum to the earth with the rain. The amount of "wind-borne" sea salt is greatest when the wind blows from the sea. Free hydrochloric acid derived from manufacturing operations is sometimes found in the air of towns.

Moisture.—The average amount of moisture, aqueous vapour, in air is rather less than one per cent. by volume; it may reach 4 per cent. in humid climes. The actual amount of aqueous vapour air can carry before it is saturated depends upon the temperature. The higher the temperature, the greater the amount of moisture air can carry (p. 44). Air seldom if ever contains less than one-tenth the possible amount. A method for the determination of moisture in air was indicated on p. 48. For the methods used by meteorologists, see any text-books on physics—Hygrometry.

§ 6. Is Air a Mixture or a Compound of Oxygen and Nitrogen?

Let us assume the function of a judge in a law court and sum up the evidence for the jury:

1. The proportions of the constituents of air vary a little, but even this small variation is not found with pure chemical compounds—law of constant proportions. Hence, not all the nitrogen and oxygen are combined.

2. The atomic proportion of nitrogen and oxygen in air is as 3·77 : 1; this is approximately as 15 : 4. Hence, if all the nitrogen and oxygen are combined, the formula of the compound is $N_{15}O_4$, which does not fit very well with the facts summarized by the law of multiple proportions, p. 507. A

similar result is obtained by considering the volume relations of nitrogen and oxygen in air—Gay-Lussac's law, p. 148.

3. The characteristic physical properties of nitrogen and oxygen are modified in air only so far as obtains when nitrogen and oxygen are *mixed* in the same proportions. The properties of the two gases are not changed so much as would be expected if a chemical compound were formed. No heat, no change of volume, or any other sign of chemical change is observed when air is made artificially by mixing the gases together in the right proportions. "If a measurable physical property were different in air and in an equivalent mixture of the constituents of air, the conclusion would follow that air is a compound" (H. St. C. Deville).

The constituents of air can be separated by mechanical means: *e.g.* solution in water (p. 207); by atmolysis (p. 225), and by allowing liquid air to vaporize, when the nitrogen distils off before the oxygen.

Not one of these reasons is in itself conclusive, but all, taken together, form a long chain of circumstantial evidence which would lead any jury to return the verdict: Air is a mechanical mixture of nitrogen, oxygen, etc.

§ 7. The Analysis of Air.

The absorption of oxygen by phosphorus.—The oxygen can be absorbed from air by using a gas pipette like that shown in Fig. 90, charged with sticks of phosphorus. The air is measured in the gas burette in the usual manner, transferred to the pipette, and returned to the burette for measurement. The decrease in volume represents the volume of oxygen absorbed by the phosphorus.

The absorption of oxygen by hot copper.—The oxygen can also be withdrawn from air in the following manner: A hard glass or quartz tube about 3 mm. bore, and 10—12 cm. long is filled with metallic copper made by reducing the granulated oxide in a current of hydrogen. The copper is held in place by plugs of asbestos at each end. This tube is mounted

between Hempel's burette, Fig. 198, and a two-bulbed gas pipette. Both the burette and pipette are charged with mercury. The upper bulb of the pipette is empty when the lower bulb is full of mercury; the mercury extends to a mark on the gauge tube of the pipette. The burette contains a measured volume of nitrous oxide. By opening the stopcock, and raising the levelling tube a slow current of the gas is led over the red-hot metallic copper into the pipette. When the lower bulb of the pipette is nearly full of gas, return the gas to the burette, by lowering the levelling tube. When the gas is cold, read its volume when the mercury in the measuring and levelling tubes is at the same level.

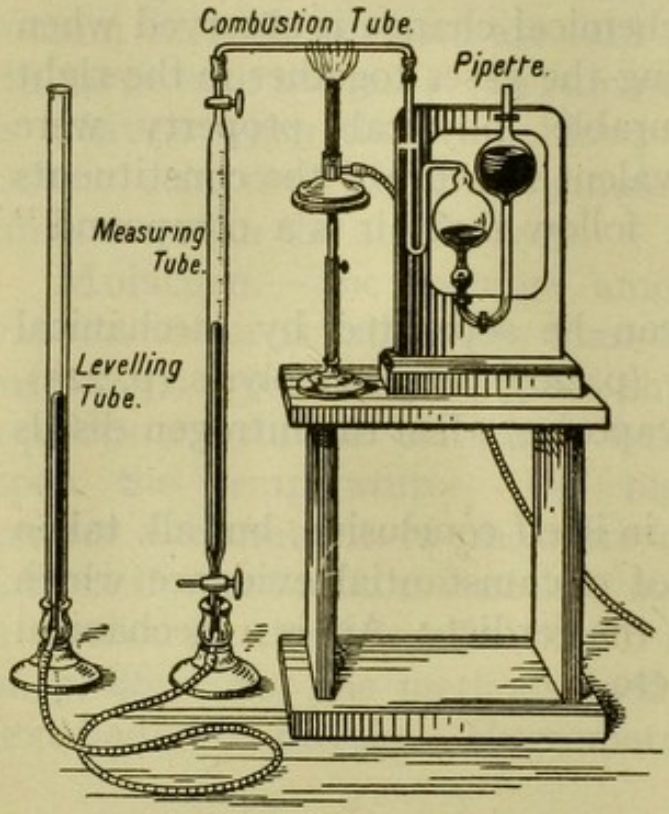


FIG. 198.—Composition of Nitrogen Oxides.

The same apparatus can be used for the gaseous oxides of nitrogen. These are decomposed; the oxygen is retained by the copper; and the volume of the residual nitrogen measured. The combustion tube can be weighed before and after the combustion to get the amount of oxygen retained by the copper. In this way, it will be found that—

2 volumes of nitrous oxide furnish two volumes of nitrogen.
2 volumes of nitric oxide furnish one volume of nitrogen.
2 volumes of nitrogen peroxide (N_2O_2) furnish two volumes of nitrogen.

Of course the oxygen absorbed by the copper can be determined by weighing the combustion tube before and after the passage of the gas. In some classical experiments made by J. B. A. Dumas and J. Boussingault in 1841, the nitrogen was

collected and weighed in a large glass globe instead of being measured volumetrically.

§ 8. Maximum, Active, and Sleeping Valencies.

There are two carbon oxides, carbon monoxide, CO, and carbon dioxide, CO_2. If carbon monoxide could be written O=C=C=O, and there is nothing in the analysis by weight which prevents this, all might be well ; but writing the formula in this manner would involve a contradiction of Avogadro's hypothesis, since the vapour density of carbon monoxide corresponds with the molecule CO, not C_2O_2. We cannot see the way clear to admit carbon monoxide as an exception to Avogadro's hypothesis, for that would introduce confusion into our system, and there would be no immediate prospect of restoring order. Some get over the difficulty by assuming that two of the free valencies in carbon monoxide mutually saturate one another, and write the graphic formula O=C<; others assume that oxygen is quadrivalent, and write C≡O. This latter plan gets over the difficulty with carbon because oxygen is known to act sometimes as if it were quadrivalent. The case of sulphur bivalent in hydrogen sulphide ; quadrivalent in sulphur dioxide ; and sexivalent in sulphur trioxide : fits very well into the suggestion that pairs of valencies can mutually saturate one another.

It has been supposed that valency is a " fundamental property of the atom which is just as constant and invariable as the atomic weight " ; and further that **each element has a maximum valency towards certain other elements.** When an element in a compound appears to have a lower valency than its maximum valency, the compound is said to be an **unsaturated compound,** in contrast with a **saturated compound** in which the atoms are exercising their maximum valency. In many unsaturated compounds, the valencies appear to diminish in pairs. The pairs of " sleeping valencies " or " latent bonds " are supposed to be self-saturated. As a matter of fact, the hypothesis of the self-saturation of the bonds in pairs breaks down completely. The idea probably

arose from the application of an inaccurate hypothesis which is stated in some of the older books on chemistry in words like these: "All chemical evidence shows that a body with unsatisfied bonds cannot exist by itself." All chemical evidence, as we shall see, shows nothing of the kind. Bivalent mercury and many other elements, when vaporized, give gases with one-atom molecules. Again, the relative density of nitric oxide (Avogadro's hypothesis) will not let us write N_2O_2, that is, O=N—N=O. We are therefore confronted with what appears to be an odd unsaturated valency in the molecule —N=O. In view of facts like these, it is difficult to maintain the thesis that the apparent inconstancy of the valency of an element is due to the mutual "saturation" of pairs of valencies. It is better to accept the fact that **the active valency of an element is a variable habit of combination,** and leave the explanation of the meaning of valency open. To distinguish between the greatest valency an element is known to exhibit, and the valency which actually prevails in a particular compound, the terms **maximum valency** and **active valency** may be respectively employed.

Questions.

1. What weight of ammonium chloride is required to produce 30 litres of ammonia measured at 15°, and under a pressure of 730 mm.? (N=14, Cl=35·5.)—*Malvern College.*

2. Explain, giving all necessary equation, how you could obtain qualitatively (1) chlorine from potassium chloride, (2) copper from copper sulphate, (3) nitrogen from ammonia, (4) oxygen from nitric acid.—*Malvern College.*

3. How are gases usually dried? What drying agent would you employ in each case for the following gases: (*a*) oxygen, (*b*) nitric oxide, (*c*) nitrous oxide, (*d*) chlorine, (*e*) ammonia, (*f*) hydrogen chloride, (*g*) carbon dioxide? How would you collect the gases just named?—*Victoria Univ.*

4. When substances are brought into contact, how would you know whether they acted chemically on one another, or simply remained mechanically mixed? Describe minutely in illustration: (1) The combination of any two elements; (2) An example of double decomposition.—*Oxford Junr. Locals.*

5. How could you prepare crystallized sal-ammoniac from a solution of ammonia? Describe the chief properties of the pure

salt and state how you can obtain ammonia gas from it.—*Science and Art Dept.*

6. Describe any experiment which shows that ammonium chloride when vaporized undergoes dissociation.—*Science and Art Dept.*

7. Explain what is generally understood by the terms *acid* and *alkali*. Calculate what weight of sulphuric acid will just neutralize one gram of each of the following substances respectively: caustic potash, ammonia, sodium carbonate.—*Cambridge Junr. Locals.*

8. Describe the preparation of dry ammonia gas, and give a sketch of the necessary apparatus. Why are many of the compounds of ammonia usually represented as containing the group NH_4?—*Cambridge Senr. Locals.*

9. Give examples of "dissociation," and point out methods of demonstrating the fact in each case.—*London Univ.*

10. Calculate the vapour density of ammonium chloride. By experiment it is found to be 26·69 ($H_2=2$). How do you explain the difference between the observed and calculated results? Can you give any experimental evidence in support of your explanation? Do you know of any other similar cases?—*Science and Art Dept.*

11. If you had a jar of gas given you, how could you tell whether it contained chlorine, oxygen, hydrogen, carbon monoxide, carbon dioxide, or ammonia?—*London Univ.*

12. Show what is the action of heat on the following substances: mercuric oxide, sodium nitrate, silver sulphate, lead nitrate, barium peroxide, ammonium chloride.—*Sydney Univ.*

13. Name the principal "impurities" which are usually present in the air of towns. How could you determine the amount of any *two* of these substances present in 100 volumes of air? How does town air differ from country air, and how may these differences be accounted for?—*Board of Educ.*

14. A jar of colourless gas is given you, standing over water, it extinguishes a lighted match without taking fire itself. Name as many gases with these properties as you know. How would you decide which of these the gas in question is?—*Staffs. County Schol.*

15. What is the ultimate source of ammonia? How is the gas prepared? What is the action of a solution of it upon (*a*) hydrochloric acid, (*b*) chlorine, (*c*) a solution of ferric chloride, $FeCl_3$? Give equations.—*Staffs. County Schol.*

16. What chemical elements do sodium nitrate and ammonium sulphate respectively contain? Why are these substances valued in agriculture?—*Staffs. County Schol.*

17. Explain what is meant by the statement that air is a mixture of nitrogen and oxygen, and water a compound of hydrogen

and oxygen. How could you show that both air and water contain oxygen ?—*Staffs. County Schol.*

18. Classify the following substances under the headings acids, bases, salts : washing soda, vinegar, marble, ammonia, lime, alum, water, saltpetre, oil of vitriol, aqua fortis. What do you understand by the terms acid, base, salt ?—*Staffs. County Schol.*

19. Give the modes of formation and chief properties of nitrous oxide and nitric oxide. How would you distinguish between air and a mixture in equal volumes of nitrous oxide and nitrogen ?—*Owens Coll.*

20. Explain what takes place on passing air over red-hot copper, and steam over red-hot iron. Describe experiments to show that ammonia will furnish half its volume of nitrogen, and that nitrous oxide will furnish its own volume of nitrogen.—*Owens Coll.*

21. What is meant by the vapour density of a substance ? Why is it important to determine the vapour density of substances ? What are the formulæ and the vapour densities of the following : ammonia, nitric oxide, hypochlorous acid, ozone ? (N=14, Cl=35·5.)—*Owens Coll.*

22. How is the percentage of oxygen in the air accurately ascertained by the eudiometer ? From the known density of air (14·4 if that of hydrogen is 1) and the densities of oxygen (16) and nitrogen (14), calculate the percentage composition of air by volume. —*Owens Coll.*

23. Describe and explain the methods by which the quantities of the following constituents of the air of a room might be determined : the oxygen, the aqueous vapour, the carbon dioxide. How could you demonstrate that each constituent of the atmosphere exerts its own pressure independently of the other constituents ?—*Owens College.*

24. Describe the preparation of the following gases, and state in each case how you would collect them, and ascertain whether the vessel was full : Ammonia, chlorine, nitrous oxide, hydrogen sulphide, hydrogen bromide.—*Owens Coll.*

25. What agencies are always at work polluting the atmosphere ? How is its purity maintained ?—*Oxford Junr. Locals.*

26. What are the commercial sources of ammonia and ammonium compounds, and how is ammonia obtained from them ? How would you prepare chemically pure liquor ammoniæ from the commercial product ?—*Calcutta Univ.*

27. Our atmosphere is said to take part in the process of combustion, of respiration, and of the growth and decay of plants. Explain how and by means of which of its constituents the air acts in each of these processes.—*London Univ.*

28. The ancients used to consider air as one of the elements.

Describe properties of air which cause it no longer to be regarded as an element.—*London Univ.*

29. Why do you call oxygen, hydrogen, and carbon chemical elements? Describe the properties by which you would distinguish nitrous oxide from a mechanical mixture of two volumes of nitrogen to one volume of oxygen.—*London Univ.*

30. How can pure nitrogen be prepared? What are its properties? In what manner is it possible to make it combine (*a*) with oxygen; (*b*) with hydrogen?—*London Univ.*

31. Ammonium carbonate and nitric acid are given to you; how would you prepare nitrous oxide from these? Draw a sketch of the apparatus you would use, and give an equation showing the decomposition which takes place in making the gas.—*Science and Art Dept.*

32. A gaseous substance was found to contain only the elements nitrogen and oxygen and had the composition by weight: oxygen 63·16 per cent., nitrogen 36·84 per cent. What experiments would you make to find out whether it was a definite compound or a mixture?—*Oxford Senr. Locals.*

33. What do you know of the preparation and properties of nitric oxide? What happens if nitric oxide and oxygen are brought together in presence of water, and how would you arrange an experiment to prove what you say?—*Oxford Junr. Locals.*

CHAPTER XXX

Phosphorus, Arsenic, Antimony, and Bismuth

§ 1. Phosphorus—Preparation and Properties

The animal skeleton is mainly composed of bone. Bones contain non-combustible mineral matters, and combustible organic matters. If bones be heated in air, the organic matters burn, and **bone-ash** remains.

The manufacture of phosphorus—retort process.—If powdered bone-ash be intimately mixed with sulphuric acid, white insoluble calcium sulphate is formed. This can be separated by filtration and washed. The clear filtrate is evaporated to a syrupy liquid; mixed with about one-fourth its weight of coke or charcoal, and dried by heating in cast-iron pots. The dried mixture is then heated to redness in a fireclay retort with its neck dipping under the surface of water. A mixture of hydrogen and carbon monoxide gases escapes, and crude phosphorus condenses as a dark brown solid. From this experiment it is inferred that bone-ash is a compound of phosphorus and lime.

The manufacture of phosphorus—electrical process.—If bone-ash or some of the native mineral phosphates be intimately mixed with very finely divided silica and coke, and heated in fireclay retorts to a high temperature, a similar product is obtained. The yield, however, is not so good unless the temperature is inconveniently high. If the mixture be heated in an electrical furnace fitted with carbon rods for conducting the electric current as illustrated in Fig. 199, the production of the high temperature presents no difficulty, and phosphorus distils over. Liquid slag is periodically tapped and run from

the bottom of the furnace *D*, and a new charge introduced so that the process is continuous. The charge is fed into the hopper *A*, and thence passes into the chamber *B*, and to the conveyer *C*, which works something like an Archimedean screw, and carries the charge to the furnace. The furnace is heated by an electric current sent through the electrodes *E*. The phosphorus vapours and gases escape through a tube *G*. To prevent misunderstanding, it may be necessary to point out that the electric current does its work by raising the temperature of the mass, not by electrolysis.

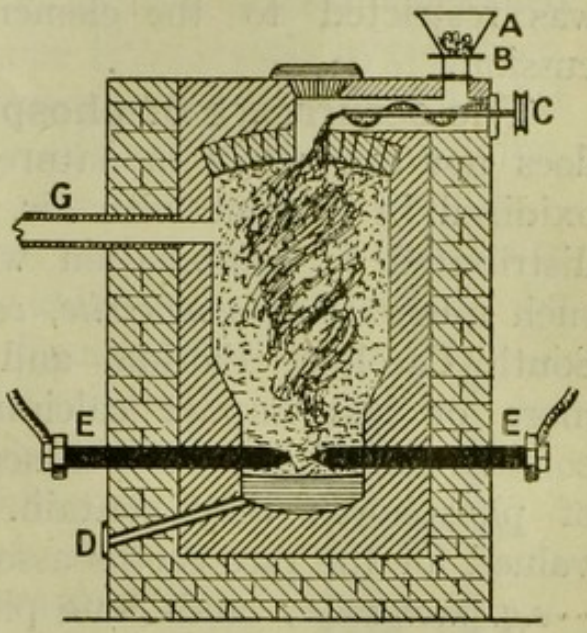


FIG. 199.—Electrical Furnace for the Manufacture of Phosphorus.

The chemistry of the process is somewhat as follows: When calcium phosphate is heated with finely divided silica, SiO_2, calcium silicate, $CaSiO_3$, and phosphoric acid are produced: $Ca_3(PO_4)_2+3SiO_2=3CaSiO_3+P_2O_5$. The latter is reduced by the carbon: $P_2O_5+5C=5CO+2P$. The addition of a flux keeps the calcium silicate in a fluid condition and enables it to be tapped from the furnace as a molten slag. The carbon probably accelerates the rate of decomposition of the phosphate by the silica because the reaction progresses more quickly at a lower temperature in the presence of carbon than when carbon is absent.

History.—It is generally supposed that phosphorus was accidentally discovered by Brand, an alchemist in Hamburg, between 1668 and 1669, while distilling a mixture of sand and concentrated urine, during his quest for a substance which would turn the base metals into gold. In the eighteenth century, the term "phosphorus" was applied to substances like commercial barium and calcium sulphides which, after exposure to a bright light, glow with a "phosphorescent" light while in the dark. The word "phosphorus" is derived

from Greek words meaning " light bearer," and it was naturally applied to the substance discovered by Brand, because it too glowed in the dark. Terms like " phosphorus miribalis," and " phosphorus igneous," etc., were used for phosphorus by the early writers on chemistry. Later the term " phosphorus " was restricted to the element phosphorus now under discussion.

The occurrence of phosphorus.—Phosphorus, of course, does not occur free in nature, because it is so very readily oxidized in contact with air. It is, however, rather widely distributed in combination with oxygen—as phosphates—in such minerals as *sombrerite*, *coprolites*, and *phosphate rock* (of South Carolina, Florida, and Tennessee), all of which are more or less impure calcium phosphates—$Ca_3(PO_4)_2$. The commercial value of these minerals is determined by the amount of phosphorus they contain. Some native phosphates are valued for the rare earths associated with the phosphoric acid —*e.g. monazite ;* and some phosphates are present in certain gems—*turquoise*, etc.

Properties.—The purified phosphorus is a pale yellowish translucent solid almost as hard as beeswax. Hence it can easily be cut with a knife. It melts at 44° and boils at 290°. The vapour density of phosphorus shows that its molecule has four atoms, symbolized P_4. It ignites in air at about 30°, so that the heat of the hand with a little friction suffices to inflame the mass. Phosphorus therefore is never handled in air, but it is kept and manipulated under water. Phosphorus is an extremely dangerous substance manipulated carelessly. Burns from phosphorus are very painful and heal slowly. Phosphorus slowly oxidizes in air, and at the same time appears phosphorescent if viewed in a dark room. Water can dissolve sufficient phosphorus to show phosphorescence in the dark, but it is generally considered to be insoluble in water. It readily dissolves in carbon disulphide. Carbon disulphide is a very volatile liquid, and in consequence when it evaporates the phosphorus is left behind, and the residue will probably ignite spontaneously in air owing to the heat developed by the rapid oxidation of the finely divided phosphorus. This is

illustrated by writing on paper with a rod dipped in a solution of phosphorus in carbon disulphide.

Phosphorus burns with a brilliant flame in air or oxygen, and produces dense white clouds which condense to a voluminous white powder—*flowers of phosphorus*—which has a composition corresponding with the formula P_2O_5, and is accordingly called **phosphorus pentoxide.** This oxide is extremely hygroscopic, and it is used in special cases for drying gases which do not react with it. Phosphorus also combines readily with sulphur, chlorine, iodine, etc. Phosphorus sulphide is used in making matches.

If a piece of yellow phosphorus and a piece of iodine are allowed to touch one another, they enter into combination. So much heat is evolved during the formation of the **phosphorus iodide** that the mixture bursts into flame. A piece of phosphorus ignites spontaneously on a deflagrating spoon when plunged in a jar of chlorine and burns with formation of **phosphorus chloride.** Phosphorus unites with the metals forming phosphides, thus **calcium phosphide** is formed when metallic calcium is heated with phosphorus under naphtha, or when the vapour of phosphorus is led over red hot lime.

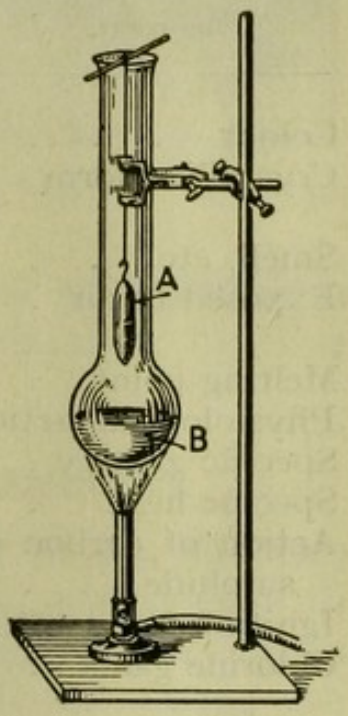


FIG. 200.—The Preparation of Red Phosphorus.

Red phosphorus.—If yellow phosphorus be kept for a lengthened period it gradually passes into a red powder which, unlike yellow phosphorus, is insoluble in carbon disulphide. The speed of transmutation is accelerated by raising the temperature, and it is prepared on a large scale by heating yellow phosphorus to about 250° just below its boiling-point. This change is easily shown by sealing a piece of yellow phosphorus in a test tube, *A*, Fig. 200, and hanging the tube above the surface of, say, diphenylamine, as indicated in the diagram. The diphenylamine is heated to its boiling-point (310°), and the phosphorus can be easily maintained at that temperature until it is all changed into the red variety. The diphenylamine

condenses in the upper part of the tube and returns to the main body of liquid. The tube of red phosphorus is then opened. The reverse change—red to yellow phosphorus—can be effected by distilling the red variety. The vapour condenses in the yellow form. The red variety is denser, more stable, non-poisonous, and far less active chemically than the yellow form. A comparison of the properties of the two varieties is indicated in the following table, which gives a summary of the leading differences in the two varieties of phosphorus :—

TABLE XXX.—COMPARISON OF THE PROPERTIES OF RED AND YELLOW PHOSPHORUS.

Property.	Red phosphorus.	Yellow phosphorus.
Colour	Dark red	Almost colourless
Crystalline form .	Rhombohedral crystals	Cubic crystals
Smell, etc. . . .	Tasteless, odourless	Garlic-like smell
Exposed to air . .	No phosphorescence no oxidation	Phosphorescence and oxidation
Melting-point . .	500° to 600°	44°
Physiological action	Non-poisonous	Poisonous
Specific gravity . .	2·106 to 2·14	1·83 to 1·85
Specific heat . .	0·170	0·189
Action of carbon disulphide . . .	Insoluble	Soluble
Ignition temperature	260°	30°
Chlorine gas . .	Fires if heated	Fires spontaneously

Phosphine, PH_3.—When phosphorus is heated with caustic alkaline solutions—for instance, milk of lime or a solution of potassium hydroxide—an unpleasant smelling gas is evolved which ignites spontaneously in air. The experiment is made by means of the apparatus illustrated in Fig. 201. A mixture of potassium hydroxide solution and yellow phosphorus is placed in the flask fitted with delivery tube, etc., as illustrated in the diagram. A current of an inert gas—coal gas, hydrogen, or carbon dioxide—is first led through the apparatus to drive out the air. The mixture in the flask is then heated. The

phosphorus reacts with the alkali, forming gaseous phosphine, PH_3, associated with some impurities. The mixture of gases so prepared is sometimes called *phosphuretted hydrogen*. Each bubble of gas rises to the surface of the water, and, when it comes in contact with the air, ignites with a slight explosion and burns with a brilliant flash of light, forming a vortex ring of phosphorus pentoxide, P_2O_5. The property of spontaneous combustion is due to the presence of traces of another hydride. The interesting property about phosphine is the analogy it bears with ammonia, and it forms a series of **phosphonium compounds** analogous with those of ammonia, thus, PH_4Cl is related with NH_4Cl, etc.

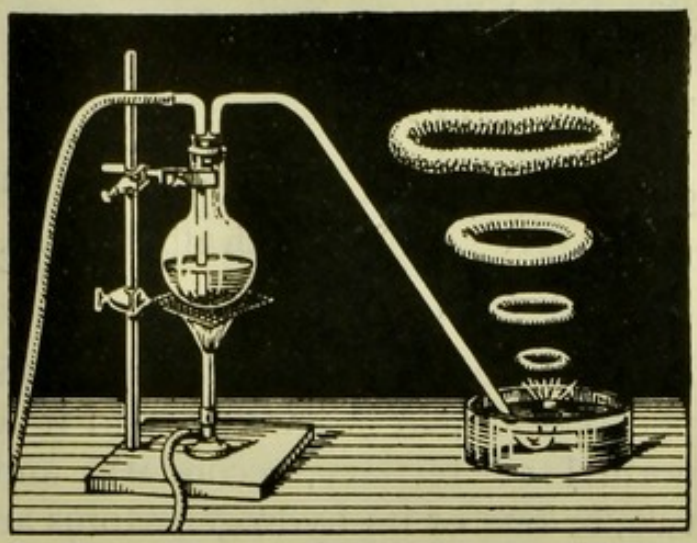


FIG. 201.—The Preparation of Phosphine.

§ 2. The Oxides and Acids of Phosphorus.

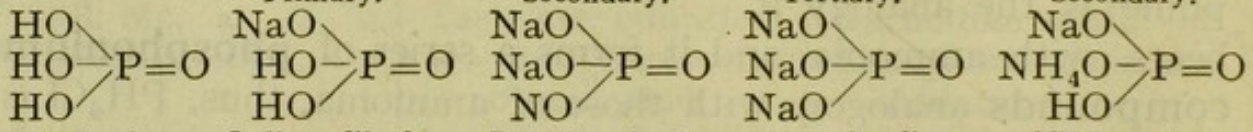
Oxides.—Phosphorus forms a number of oxides, the more important are **phosphorus trioxide,** P_2O_3, analogous with nitrogen trioxide; and **phosphorus pentoxide,** P_2O_5, analogous with nitrogen pentoxide. The trioxide is found among the products of combustion of phosphorus in a limited supply of air; and the latter is formed when phosphorus burns in oxygen or in an excess of air.

Phosphoric acids.—The pentoxide reacts with water forming phosphoric acid. If the solution is well boiled, or if red phosphorus be digested with nitric acid, a phosphoric acid is formed which gives a canary-yellow precipitate with silver nitrate. The acid is called **orthophosphoric acid,** and its composition corresponds with the formula H_3PO_4; if this acid be heated to 250°, it forms a tetrabasic acid called **pyrophosphoric acid,** $H_4P_2O_7$. This acid gives a white precipitate with silver

nitrate. If pyrophosphoric acid be heated to redness, it passes into monobasic **metaphosphoric acid,** HPO_3, which also gives a white precipitate with silver nitrate, but unlike the other two phosphoric acids, it coagulates a clear aqueous solution of albumen (white of egg). Summarizing the distinctive reactions of the three phosphoric acids or their salts :—

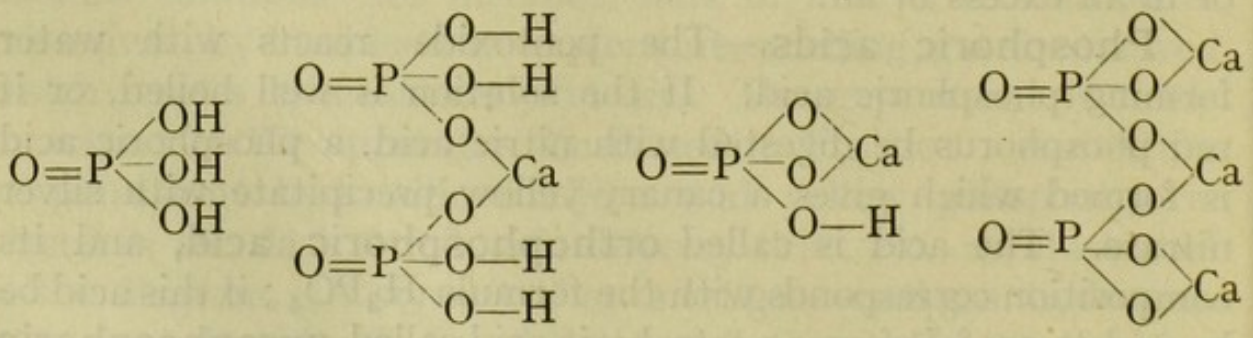
Silver nitrate { yellow . . . . . ORTHOPHOSPHORIC ACID.
white ; with albumen { nil . . PYROPHOSPHORIC ACID.
Coagulates METAPHOSPHORIC ACID.

Each of the phosphoric acids forms a series of salts. Orthophosphoric acid is tribasic, and it forms three series of salts—normal or tertiary, secondary, and primary according as all two, or one of its hydrogen atoms are replaced by an equivalent radicle. Thus, there are three **sodium orthophosphates** :



Orthophosphoric acid. | Sodium dihydrogen phosphate. | Disodium hydrogen phosphate. | Normal sodium phosphate. | Microcosmic salt.

The normal salt is alkaline to litmus ; the secondary salt is neutral, and the primary salt is acid. The disodium phosphate with water of crystallization : $Na_2HPO_4 . 12H_2O$, is the ordinary sodium phosphate of commerce. The hydrogen atom may be replaced by different radicles. Thus the secondary acid salt —ammonium sodium hydrogen phosphate, also called **microcosmic salt**—is illustrated by the graphic formula above. The corresponding **calcium orthophosphates** are :



Orthophosphoric acid, H_3PO_4. | Monocalcium phosphate, $Ca(H_2PO_4)_2$. | Dicalcium phosphate, $CaHPO_4$, or $Ca_2H_2(PO_4)_2$. | Tricalcium or normal phosphate, $Ca_3(PO_4)_2$.

Calcined bones contain the equivalent of from 60 to about 80 per cent. of the normal phosphate. Vegetable life is mainly dependent upon the solubility of calcium phosphate in the soil solution for the phosphorus required for proper nutrition. When crops are produced year after year on the same soil, the soil becomes unproductive and impoverished owing to the removal of certain constituents necessary for their healthy growth. To maintain the fertility of the land, those constituents must be restored. The application of mineral phosphates and bone-ash will restore the phosphorus to exhausted soils. The normal calcium phosphates, however, are not very soluble, and to insure a quick distribution of the phosphate in soils, and a more concentrated solution of phosphoric acid in the water about the roots of plants for agricultural purposes a more soluble phosphate than normal calcium phosphate is considered necessary. To convert the normal salt into a more soluble acid salt, normal calcium phosphate is treated with sulphuric acid—usually chamber acid—in order to transform most of it into the **monocalcium phosphate**: $Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$. The monocalcium phosphate so formed becomes $CaH_4(PO_4).H_2O$, and the calcium sulphate $CaSO_4.2H_2O$. This mixture contains a little undecomposed normal phosphate. The mixture is generally called **superphosphate,** and sometimes "acid phosphate." The superphosphate is used as a fertilizer. On exposure to the air, moisture is absorbed, and the undecomposed normal phosphate reacts with the *soluble* monocalcium phosphate, forming a *sparingly soluble* **dicalcium phosphate**: $Ca_3(PO_4)_2 + H_2O + CaH_4(PO_4)_2H_2O = 4CaHPO_4.2H_2O$. The superphosphate is then said to have "reverted" or "precipitated." The chief sources of the phosphatic fertilizers of commercial importance are (1) phosphatic rock; (2) bones and bone preparations; (3) guanos; and (4) basic or Thomas slag. The latter is the discarded lining of basic process steel furnaces which absorbed phosphorus from pig iron in the process of manufacturing steel.

Phosphorous acid.—If ordinary phosphorus be turned in a limited supply of air some phosphorus trioxide or

phosphorus anhydride is formed as well as phosphorus pentoxide. Some red phosphorus is formed at the same time. The vapour of phosphorus anhydride has a density corresponding with the molecular weight P_4O_6. When dissolved in water, this oxide forms an acid phosphorous acid: $P_4O_6 + 6H_2O = 4H_3PO_3$. The same acid is formed when water reacts with phosphorus trichloride, PCl_3, the product obtained when phosphorus burns in chlorine. Phosphorous acid forms a series of salts, the **phosphites,** which are generally dibasic—*e.g.* **sodium phosphite** is Na_2HPO_3.

Hypophosphorous acid.—When phosphorus is boiled with potassium, sodium, or barium hydroxide, not only is a gaseous phosphine formed, but the solution contains the corresponding salt of a monobasic acid, H_3PO_2. For instance, **sodium hypophosphite,** NaH_2PO_2. The action of the alkali hydroxide is thus represented by the equation:

$$3H_2O + 3KOH + 4P = PH_3 + 3KH_2PO_2.$$

The phosphorus cycle in nature.—Small quantities of phosphates are found in granitic rocks. By the weathering and decay of these rocks, the combined phosphorus ultimately finds its way into the soil, spring water, and the sea. All fertile soils contain phosphorus, since phosphorus is needed to build up certain essential parts of vegetable tissue. Plants require phosphorus from their earliest life, and seeds contain a plentiful supply for the germination of the embryo. The equivalent of one pound of phosphorus is said to be present in about 100 lbs. of corn, and in about 1200 lbs. of fodder. Animals, too, like plants, must have phosphorus, and they are dependent for their supply upon the plants or upon the herbivorous animals upon which they feed. Animals concentrate the phosphorus in their bones and tissue. The bones of an adult man contain the equivalent of 1900 to 2400 grms. of normal calcium phosphate. The waste of muscular and nervous tissue involves a decomposition of the phosphorus compounds. The products of decomposition are carried by the blood to the kidneys, and there excreted with the urine—chiefly as sodium ammonium phosphate. There seems to be a relation between the amount of

phosphorus compounds discharged from the system, and the activity of the brain, and this idea has crystallized in the well-known phrase *Ohne Phosphor kein Gedanke* (without phosphorus, no thought). A normal adult excretes the equivalent of from 3 to 4 grms. of phosphoric acid per day. Part of this is derived from the vegetable food, and part from muscular waste. In this way phosphorus can find its way back to the soil. Hence too the origin of the phosphorus in the large deposits of *guano*—the excrement of seabirds—on the islands off the Peruvian coast, and a number of islands in the South and the Caribbean Seas. *En passant* it may be added that many islands have been " stripped " from the guano they once contained. Nitrogenous matters and potash, all valuable manures, are also associated with guano. The guanos have undergone more or less decomposition by the action of rain, etc., and they are sold on the " per cent. of nitrogen " they contain. Some guanos are enriched by the addition of dried blood, ammonium phosphate, etc., and sold as special fertilizers.

§ 3. Matches.

Common friction matches.—These are made by cutting soft wood into the required shape by machinery. One end of the strip is dipped into some inflammable substance—paraffin or sulphur, and then into a paste made from yellow phosphorus, manganese dioxide, glue, and colouring matter. The manganese dioxide may be replaced by other oxidizing agents—potassium chlorate, nitre, etc. The matches are then dried. The glue protects the phosphorus from oxidation, but by rubbing the head of the match on a rough surface, sufficient heat is generated to ignite the phosphorus in contact with the oxidizing agent. The burning phosphorus ignites the sulphur or paraffin, and this in turn fires the wood. Cotton threads dipped in paraffin are used in place of wood to form the so-called *wax vestas*.

Safety matches.—In spite of the greatest care, the phosphorus disease prevails in match factories using yellow phosphorus. The substitution of red for yellow phosphorus is far

less dangerous to the health of the worker. The head of the match is then made from a coloured mixture of antimony sulphide, potassium chlorate, and glue. Other oxidizing agents are used—red lead, potassium bichromate, etc. The surface on which the match is to be rubbed for ignition is covered with a mixture of red phosphorus, powdered glass, and glue. These matches—called safety matches—have the disadvantage that they can only be ignited by friction on a prepared surface or if quickly rubbed on a smooth non-conducting surface like glass or slate ; but they are not liable to ignite by accidental friction.

§ 4. Arsenic, Antimony, and Bismuth.

Occurrence.—Arsenic, antimony, and bismuth occur free in nature, but compounds of these elements occur most frequently as sulphides and arsenides. The sulphides are mostly of the type R_2S_3, where R is used for arsenic, antimony, or bismuth. Thus, *realgar* and *orpiment* are sulphides, As_2S_3 ; *mispickel* or *arsenical pyrites* has a composition corresponding with FeAsS ; *stibnite* or *grey antimony ore* is an antimony sulphide, Sb_2S_3 ; and *bismuth glance*, Bi_2S_3.

Extraction of the elements.—When the sulphides are roasted in air, oxides of the type R_2O_3 are formed ; and when the oxides are mixed with powdered charcoal and heated in a clay crucible, the oxides are reduced, and, in the case of antimony or bismuth, the molten element collects as a " button " at the bottom of the crucible. Arsenic, however, wants special treatment because it sublimes or passes away as vapour without melting to a liquid. Accordingly, with arsenic, the crucible is provided with an iron cone in which the vapour condenses as a sublimate. The sulphides can be reduced to the elements by heating them with scrap iron. Mispickel, if heated alone in an iron tube out of contact with the air, decomposes with the evolution of arsenic vapour : FeAsS=FeS+As, and the arsenic is collected in condensing chambers.

Properties of arsenic.—Arsenic is a steel-grey metallic-looking substance, brittle, and with a high specific gravity —5·73. When heated, it sublimes without melting. Its vapour density

corresponds with a four-atom molecule—As_4. In its physical properties, arsenic resembles the metals, but chemically it has many analogies with the non-metal phosphorus. At about 180°, arsenic burns with a blue flame forming **arsenic trioxide,** usually written As_2O_3, although the vapour density corresponds with the molecule As_4O_6; it is oxidized by boiling nitric and sulphuric acids; it burns in chlorine gas forming **arsenic trichloride,** $AsCl_3$. Several allotropic forms are known.

Arsenic, like phosphorus, forms two oxides: **Arsenic trioxide,** As_2O_3; and **arsenic pentoxide,** As_2O_5. With phosphorus, the pentoxide is formed by the combustion of the element, while the trioxide is formed with arsenic, antimony, and bismuth. Arsenic trioxide also called *white arsenic* unites with bases to form salts, *e.g.* **sodium arsenite,** Na_3AsO_3, **silver arsenite,** Ag_3AsO_3. **Arsenic pentoxide** forms salts analogous with the phosphates, and they can be referred to similar acids: **orthoarsenic acid,** H_3AsO_4; **pyroarsenic acid,** $H_4As_2O_7$; and **metarsenic acid,** $HAsO_3$. A **copper arsenite** was once used for colouring wall paper green; another copper salt—*Paris green*—is used as an insecticide. The soluble arsenic compounds are poisonous, ferric hydroxide is the best antidote. With hydrogen sulphide, soluble salts of arsenious acid give a yellow precipitate of **arsenic trisulphide,** As_2S_3; and soluble arsenates, a yellow precipitate of **arsenic pentasulphide,** As_2S_5, mixed with the trisulphide, As_2S_3. Artificial and natural arsenic sulphides are used as pigments.

Properties of antimony.—Antimony is a silvery-white metallic-looking substance. It is brittle, and has a high specific gravity—6·75. It melts at about 630°. Its vapour density corresponds with a four-atom molecule—Sb_4. Its metallic character is rather more pronounced than arsenic, but otherwise it resembles arsenic somewhat closely. It too burns with a blue flame to **antimony trioxide,** Sb_2O_3, and it combines with chlorine forming **antimony trichloride,** $SbCl_3$. It too forms a number of allotropes. Antimony forms oxides and salts corresponding with arsenious and arsenic acids. It also forms analogous orange-yellow sulphides. It is interesting

to note that antimony hydroxide—$Sb(OH)_3$—acts as a weak acid, forming **antimonites**; and as a *weak base* forming salts, thus with hydrochloric acid it gives **antimony trichloride,** $SbCl_3$.

Properties of bismuth.—Bismuth closely resembles antimony in general appearance, but it has a reddish tint. It is brittle and has a specific gravity 9·8. It melts at about 269°. Its vapour density corresponds with a two-atom molecule. The metallic character of bismuth is far more pronounced than antimony, but chemically it bears a close resemblance to that element. When heated, it forms **bismuth trioxide,** Bi_2O_3; and it burns in chlorine, forming **bismuth trichloride,** $BiCl_3$. Bismuth, unlike antimony and arsenic, gives an oxide Bi_2O_3, which does not act as a weak acid, but it does act as a weak base, forming salts with strong acids—*e.g.* **bismuth nitrate,** $Bi(NO_3)_2$, **bismuth chloride,** $BiCl_3$.

Uses.—Arsenic is used in the manufacture of arsenic compounds—arsenic trioxide, etc., and in certain alloys. The presence of a trace in lead—1 : 1000—makes lead harder. "Chilled shot" is hardened with arsenic. The addition of arsenic lowers the melting-point of the lead and makes it more fluid so that when the shot is made by allowing the molten lead to drop from a height into water, the shot becomes spherical before it is cooled by the water.

Antimony and bismuth are used in the manufacture of alloys. The antimony alloys melt at a rather low temperature and expand on solidification, and it is used in the manufacture of certain alloys—*e.g. type metal*—where fine lines have to be cast. Type metal and stereotype metal contain antimony, lead, and tin. The bismuth alloys are usually somewhat hard, and fusible. Many of the **fusible alloys** melt in warm water. For instance, *Rose's fusible metal* (tin, 1; lead, 1; bismuth, 2) melts at 93·75°; and *Wood's fusible metal* (tin, 1; lead, 2; cadmium, 1; bismuth, 4) melts at 60·5°. Fusible alloys, which melt at a low temperature, are used for making safety plugs in steam boilers; fuses in electrical connections; in fire alarms; and in automatic sprinklers for buildings, so that if a fire breaks out, the heat fuses a plug of the metal which chokes

the water pipe, and this is followed by a rush of water from the main. The gas pipe which enters a building can also be fitted with a piece of fusible alloy so that if a fire breaks out, the alloy will melt, choke the gas pipe, and stop the flow of gas. Fireproof doors can also be kept open by fusible plugs which allow the doors to automatically close in the event of fire.

§ 5. Arsenic and Antimony Hydrides.

Bismuth does not form a hydride. The hydrides of arsenic —**arsine,** AsH_3—and of antimony—**stibine,** SbH_3—resemble phosphine and ammonia in composition and many properties. Neither arsenic nor antimony unite directly with hydrogen. Both hydrides are produced by the action of nascent hydrogen from metallic zinc or magnesium and sulphuric acid, upon solutions containing compounds of these two elements. Arsine is, and stibine is not, produced by the action of hydrogen generated when potassium hydroxide acts upon zinc. **Fleitmann's test** (1850) for distinguishing between arsenic and antimony is based upon this fact. The action of arsine on *concentrated* aqueous solutions of silver nitrate furnishes a double compound of silver arsenide and silver nitrate—namely, $Ag_3As.3AgNO_3$, and this compound is decomposed on dilution forming metallic silver and arsenious acid :

$$AsAg_3.3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3AsO_3.$$

This is the principle of **H. Gutzeit's test** for arsenic (1879). With *dilute* solutions of silver nitrate, metallic silver is at once precipitated. Stibine under similar conditions gives a precipitate of **silver antimonide,** Ag_3Sb.

Marsh's test.—This famous test for arsenic was devised by J. Marsh in 1836. Place about 3 grams of metallic zinc in a small flask, *A*, Fig. 202, and add 20 c.c. of sulphuric acid (1 volume of acid, 8 volumes of water). The exit tube is fitted with a calcium chloride drying tube, *E*. When all the air has been expelled from the apparatus by the hydrogen, light the jet of gas issuing from the exit tube *B*. Light the gas burner so that the exit tube is heated at *C*. If no mirror is formed

in the tube near *C*, the reagents are free from arsenic and antimony. Recharge the apparatus, and add the solution to be tested *viâ* the tap funnel *D*. If arsenic or antimony be present, a mirror will be deposited in the tube in 15 or 20 minutes. The gas is then extinguished and the exit tube disconnected. The mirror can be tested for arsenic by heating the mirror with a small flame while the tube is held in an inclined position. A garlic-like odour can be detected if 0·02 milligram of arsenic is present. When the tube is cold, arsenic trioxide will be found at a little distance from the flame in octahedral crystals which can be seen with the naked eye. These three results—mirror, garlic-like odour, and octahedral crystals, prove the presence of arsenic. Cumulative evidence is furnished by the application of other tests. If antimony be present, the mirror will be found nearer the hot flame *C* than is the case with arsenic, indeed, some antimony may be deposited in the tube before the gas reaches the hottest portion of the tube because stibine is more readily decomposed than arsine. If the exit tube be not heated at *C*, and the gases be burned with hydrogen at the end of the tube, a piece of glazed porcelain held in the flame will receive a steel grey or black deposit of arsenic or a velvety brown or black deposit of antimony. If the deposit be treated with sodium hypochlorite solution, arsenic dissolves, while antimony remains insoluble. This illustrates the more ready oxidizability of arsenic than antimony.

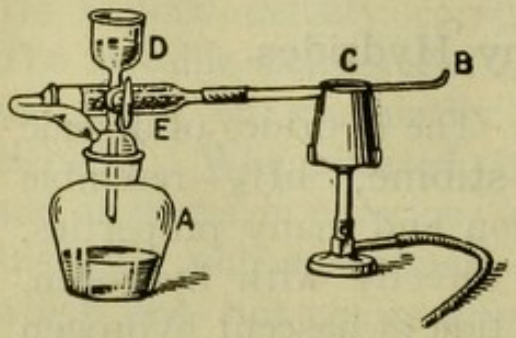


FIG. 202.—Modified Marsh's Apparatus.

§ 6. The Nitrogen Family of Elements.

The properties of the group of elements—nitrogen, phosphorus, arsenic, antimony, and bismuth—just considered shows a gradual transition from non-metallic nitrogen to metallic bismuth. The relationship of the properties of the elements is best shown by arranging them in the order of their atomic

weights, when the gradual and regular difference between the properties of successive elements is made clear :—

TABLE XXXI.—PROPERTIES OF THE NITROGEN-PHOSPHORUS FAMILY.

	Nitrogen.	Phosphorus.	Arsenic.	Antimony.	Bismuth.
Atomic weight	14·01	31·0	5077	120·2	208
Specific gravity	1·026	1·82–2·31	4·69–5·73	6·62	9·78
Atomic weight ÷ sp. gr.	13·7	about 15	13 to 16	18	21·3
Melting-point	−214°	44°	[480°]	629·2°	270°
Boiling-point	−193°	287°	[450°]	1440°	1420°
Metallic characters	None	None	Metallic as element; non-metallic in compounds	Metallic as element; slightly metallic in compounds	Metallic
Hydride . .	Strongly basic	Slightly basic	Indifferent	Indifferent	None
Nitric acid produces	—	H_3PO_4	H_3AsO_4	H_3SbO_4	$Bi(NO_3)_3$
Trioxide . .	Acidic	Acidic	Acidic	Weakly acidic and basic	Basic
Pentoxide . .	Strongly acidic	Strongly acidic	Acidic	Moderately acidic	Weakly acidic

The changes in the melting and boiling points are not so regular as the other properties, but this may be related to the fact that phosphorus, arsenic, and antimony have four-atom molecules whereas bismuth has probably a two-atom molecule. The heat of combination of the different elements with hydrogen shows a somewhat similar gradation : NH_3+12 Cals. ; PH_3+111·6 Cals. ; AsH_3−36·7 Cals. ; SbH_3−81·8 Cals. Ammonia is a relatively strong base, phosphine a feeble base, while arsine and stibine do not show basic qualities. The oxy-acids diminish in strength during the passage from nitric to phosphoric, to arsenic, to antimonic, to bismuthic acid. The acidic properties of the oxides likewise diminish from the strongly acid nitrogen and phosphorus acids, to the feebly acidic oxides of arsenic, antimony, and bismuth. The basic property first appears with

arsenic and becomes stronger during the passage to antimony and to bismuth. The trichloride of nitrogen is very unstable, while with bismuth the trichloride is quite stable. The boiling-points of the trichlorides increase with increasing atomic weights of the elements, thus: NCl_3 boils at 71°; PCl_3, 78°; $AsCl_3$, 130·2°; $SbCl_3$, 200°; and $BiCl_3$, at 447°. The halogen compounds of nitrogen and phosphorus are completely hydrolyzed by water; arsenic trichloride is also hydrolyzed by water, but it can exist in solution in the presence of hydrochloric acid. Antimony and bismuth halides are incompletely hydrolyzed by water. The study of the progressive changes in the properties of these elements could be developed much further, but sufficient has been indicated in what precedes to emphasize the family resemblances.

Questions.

1. How is caustic potash manufactured? What products are formed by the action of chlorine, sulphur, and phosphorus, respectively, on a strong solution of caustic potash?—*London Univ.*

2. Give the formula of a body whose percentage composition is as follows: Sodium, 42·07; phosphorus, 18·9; oxygen, 39·03. Give details of work.—*College Preceptors.*

3. Explain the terms *atom* and *molecule*. Why is the atomic weight of phosphorus taken as 31, and the molecular weight as 124?—*Oxford Senr. Locals.*

4. Describe the preparation of yellow phosphorus from bone ash. How is yellow phosphorus converted into red phosphorus? Compare the properties of the two forms of the element.—*Cape Univ.*

5. Explain the preparation of phosphorus from bones, and point out any other chemical uses to which bones are applied.—*Owens Coll.*

6. By what general characters are the metals distinguished from the non-metallic elements? On what grounds are arsenic and antimony sometimes described as semi-metals?—*Delegacy of Local Exams.*

7. State what happens when phosphorus is heated with a solution of potassium hydrate. Describe the properties of the substances produced.—*Sydney Univ.*

8. Explain what happens when the following substances are heated in a current of chlorine: (1) metallic iron, (2) metallic bismuth, (3) iodine, (4) quicklime, (5) cuprous chloride.—*London Univ.*

9. Mention the principal source from which phosphorus is obtained. Describe the preparation of white phosphorus. In what respects does this suffer from red phosphorus? Describe the preparation and use of the latter.—*Cape Univ.*

10. What is meant by the term *salt?* In which of the following five sets can salts be formed by union of all the elements in the same set? Give the names and chemical formulæ of the salts you have in mind (not more than three in each set) and in each case name the corresponding acid: (1) hydrogen, nitrogen, and oxygen; (2) sodium, sulphur, and oxygen; (3) sodium, hydrogen, carbon, and oxygen; (4) hydrogen, phosphorus, and oxygen; (5) hydrogen, potassium, and sulphur.—*Cape Univ.*

CHAPTER XXXI

Carbon

§ 1. The Properties of Amorphous Carbon.

It remains to discuss the properties of the allotropic forms of carbon.

1. Amorphous carbon includes sugar charcoal, charcoal, lampblack, coal, coke, and gas carbon.

2. Graphite includes amorphous and crystalline graphite.

3. Diamond includes boart and carbonado.

That these are different forms of the one element is proved by the experiment like that indicated on p. 309. Pure varieties of each form—charcoal from sugar, graphite, and diamond—furnish on combustion the same amount of carbon dioxide per gram of material, although the heat energy evolved during the combustion of twelve kilograms of each form is different. Thus :

Diamond	93·24 Cals.
Graphite	93·36 Cals.
Charcoal	96·98 Cals.

These three substances may therefore be regarded as different forms of one element associated with different amounts of available energy.

The term amorphous carbon is used to include the different varieties of vegetable and animal charcoals—lampblack, soot, gas carbon (p. 560), and coal. These are non-crystalline more or less impure forms of carbon. The term "amorphous," however, is rather carelessly used. Strictly speaking, the word is synonymous with "non-crystalline," but it is sometimes used

in reference to the mere external irregular shape of the granules rather than to the internal crystalline structure.

The specific gravity of carbon is greatly influenced by the temperature to which it has been heated, amorphous carbon varying from a specific gravity 1·45 to 1·70. Although charcoal *per se* has a greater specific gravity than water, ordinary charcoal will float on water because it is buoyed up by the air in its pores. If charcoal be weighted with a bit of lead and boiled in water for a few minutes, the air will be displaced by water, and the wet charcoal will sink when placed in cold water. A stick of charcoal can also be "anchored" below the surface of water in a tall cylinder by means of a piece of string and a weight at the bottom of the cylinder. The stoppered cylinder is then connected with an air pump, Fig. 203. The bubbles of gas rise through the water. As the air is removed, the charcoal gradually sinks to the bottom of the cylinder.

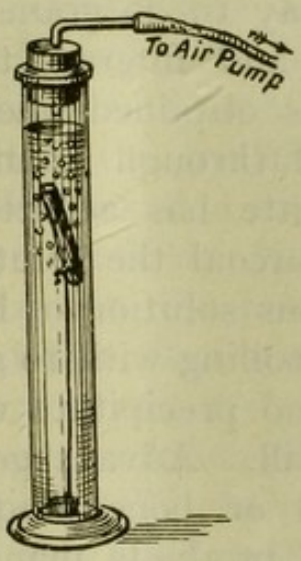


FIG. 203.—Gases absorbed by Charcoal.

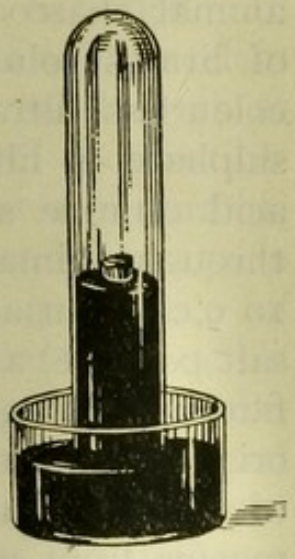


FIG. 204.—Absorption of Ammonia by Charcoal.

Adsorption of gases.—Charcoal has a remarkable power of absorbing gases, etc. A fragment of charcoal, recently heated to expel air from its pores, is placed under a cylinder of ammonia gas, Fig. 204. The ascent of the mercury in the cylinder is a striking demonstration of the absorption of gas by the charcoal. The phenomenon is sometimes styled adsorption, meaning that the gas adheres in some unknown way to the surface of the charcoal. In any case, the "condensed" gas is usually more chemically active than the gas in the ordinary condition. Thus if charcoal be allowed to absorb chlorine, and then be brought in contact with dry hydrogen, the hydrogen and chlorine combine to form hydrogen chloride under conditions where they would not otherwise react. If charcoal

which has been saturated with hydrogen sulphide be brought into oxygen gas, the rapid combination develops so much heat that the charcoal is inflamed. Sewers and foul places are sometimes temporarily purified—"sweetened"—by charcoal; charcoal biscuits have been recommended medicinally for absorbing gases in the alimentary canal in cases of flatulence.

Absorption of liquids and solids.—Charcoal also absorbs solids and liquids in a similar way. A solution of litmus (indigo, tea, vinegar, etc.) passes through filter paper without any noticeable change in the colour of the solution; but if the solution be filtered through charcoal, or if some recently ignited animal charcoal—say 10–20 grams—be shaken up with 50 c.c. of litmus solution and filtered, the filtrate is colourless. A colourless filtrate is obtained when a blue solution of copper sulphate is filtered through animal charcoal; a solution of acid quinine sulphate has a bitter taste, but after filtering through animal charcoal the solution no longer tastes bitter; 10 c.c. of an aqueous solution of lead nitrate (0·5 gram of the salt per litre) after boiling with 10 grams of animal charcoal and filtering, will give no precipitate with hydrogen sulphide—the original solution will. Advantage is taken of this property of animal charcoal or bone black to remove the colouring matter from many products manufactured industrially. *E.g.* coloured solutions of brown sugar are "bleached" on boiling with animal charcoal. The charcoal removes the brown resinous colouring matter, and the evaporated syrup furnishes white sugar; fusel oil can be removed from whisky by filtration through animal charcoal before the whisky is rectified. Charcoal filters are used for removing organic matter, etc., from drinking water.

§ 2. Some Varieties of Amorphous Carbon.

Lampblack is made by burning substances rich in carbon in a limited supply of air so that the maximum amount of smoke is developed—for example, turpentine, petroleum, tar, acetylene, etc. The smoke is passed into large chambers in

which coarse " blankets " are suspended. The " soot " collects on the blankets. Lampblack is used for making printer's ink, stove and shoe polish, paints, and in fact nearly everything in which a black pigment for colouring matter is required. Lampblack is one of the purest varieties of amorphous carbon. The analysis of a sample of acetylene " soot " furnishes 1·4 per cent. of hydrogen, and 98·6 per cent. of carbon. The hydrocarbons can be removed by heating the substance in a current of chlorine.

Wood charcoal.—There are two main varieties of charcoal —wood and bone. Wood charcoal is made by burning wood with a limited supply of air in a charcoal pit or kiln ; or by heating wood in closed vessels so that air is excluded. In illustration, place a few bits of wood at the bottom of a porcelain crucible. Cover the wood with a layer of fine sand so as to cut off the supply of air. Heat the crucible until combustible gases cease to be evolved. When cold, a small piece of charcoal remains in the bottom of the crucible. Note the shrinkage in volume during the carbonization by comparing a piece of charcoal with a bit of wood like that heated in the crucible preserved as duplicate. Charcoal resists the action of moisture, etc., better than wood, and hence wooden piles, fence posts, and telegraph poles are often superficially charred before being put in the ground. Some claim this treatment gives the timber a longer useful life. Charcoal is used as a fuel ; in the manufacture of iron and steel ; in the manufacture of gunpowder ; in metallurgical operations ; as deodorizer ; filtering medium, etc.

The manufacture of charcoal.—One industrial process for making charcoal is to pile logs or billets of wood loosely in vertical heaps, Fig. 205, and cover all with sods and turf to prevent the free access of air. A pile so arranged is called a " charcoal pit " or meiler. The arrangement is not unlike a sulphur calcarone. The wood is lighted by brushwood, and sufficient air is admitted to allow the wood to smoulder, Fig. 206. In about fifteen days the fire dies out, and about 10–20 per cent. of the wood is converted into charcoal, the remaining 80–90 per cent. is lost by combustion. The process is uncertain

and wasteful, and only successful, commercially, where wood is cheap and abundant. In more modern methods the wood is

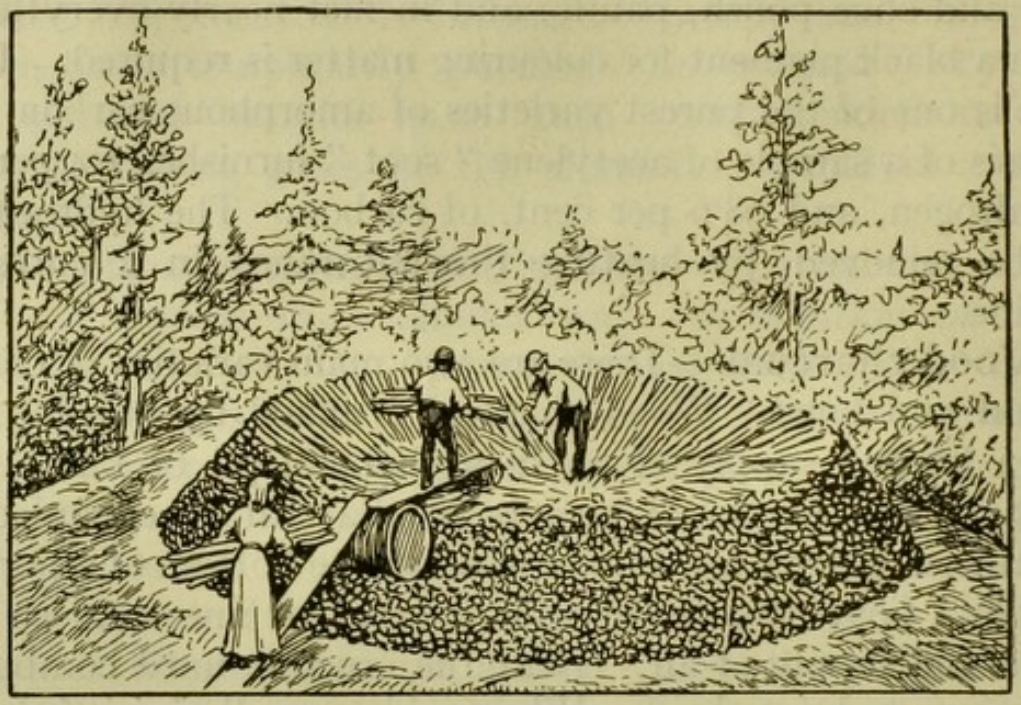


FIG. 205.—Sketch of a Meiler in course of Construction.

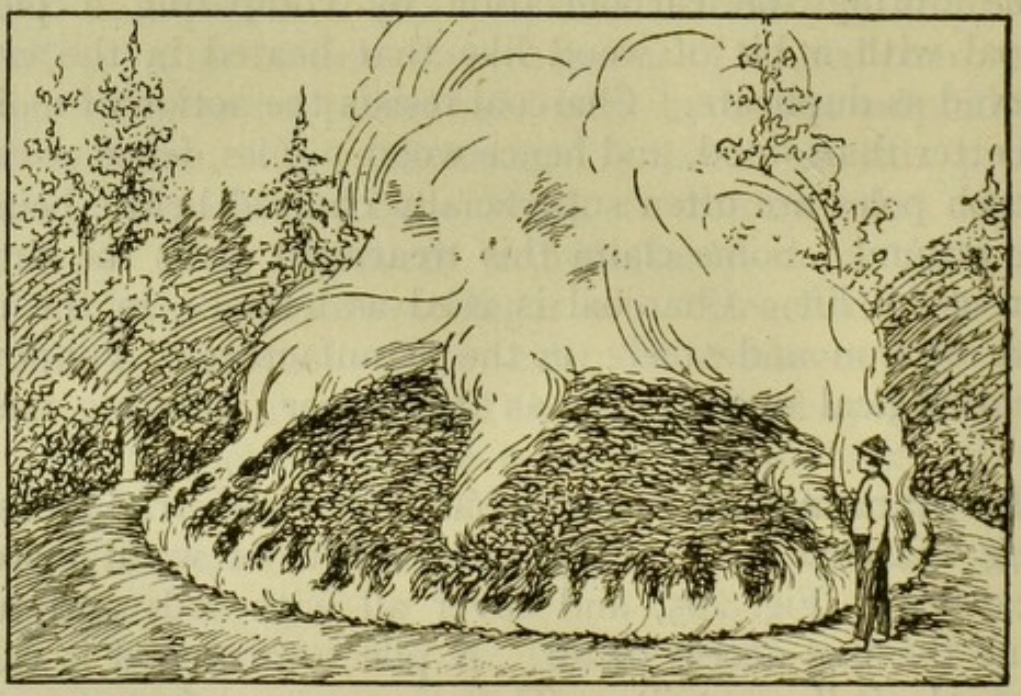


FIG. 206.—Sketch of a Meiler shortly after it has been lighted.

heated in closed vessels and the products of distillation are recovered.

The dry distillation of wood.—This operation can be well

illustrated by placing some pieces of pine wood in a hard glass retort fitted with a receiver, etc., as shown in Fig. 207. The tar—*e.g.* the so-called *Stockholm tar*—and aqueous products condense in the receiver, and the wood gas itself can be lighted. The watery liquid obtained by the dry distillation of wood is redistilled. The first position of the distillate is the so-called "wood-spirit." The wood spirit is purified by distillation from recently ignited quicklime; and by the evaporating of a mixture of the wood spirit with fused calcium chloride to dryness. The resulting compound ($CaCl_2.4CH_3OH$) is decomposed by treatment with water, and the solution is distilled. Finally, the distillate is rectified by repeated distillation over fresh quicklime. The resulting **methyl alcohol,** CH_3OH, boils at 66·78°.

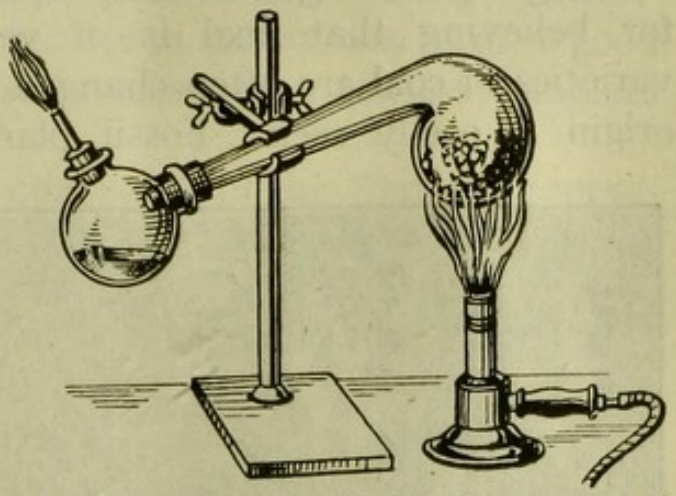


FIG. 207.—Dry Distillation of Wood in the Laboratory.

Bone or animal charcoal.—This is made by heating bones, blood, etc., in closed retorts. The bones may or may not have been subjected to a preliminary extraction with naphtha or benzene to remove the fat—*degreased bones;* or with superheated steam or water to remove gelatine (glue)—*degelatinized bones.* The products of the distillation include: solid—bone charcoal in the retort; liquids—a number of ammonium salts, bone oil, bone pitch, pyridine, etc.; and gases of various kinds. Bone charcoal contains about 10 per cent. of carbon, so that it is questionable if it ought to be included with the varieties of carbon at all. However, the carbon is very finely divided and disseminated through a porous mass of about 80 per cent. of calcium and magnesium phosphates, and it seems to have specially valuable qualities. Bones furnish *bone black*—sometimes called ivory black—the term *ivory black* is usually applied to the product obtained by digesting bone black with hydrochloric acid to remove the calcium phosphates. Blood furnishes

blood charcoal. For the uses of bone black and animal charcoal, see below ; ivory black is used as a pigment ; in the manufacture of blacking, etc.

§ 3. Coal and Coke.

Vegetable origin of coal.—Geologists have potent reasons for believing that coal is of vegetable origin. The softer varieties of coal are often changed so little that their vegetable origin is easily seen. Fossil plants can be recognized, and photographs of thin slices under the microscope show clearly the vegetable character of the coal, as illustrated in Fig. 208. In some of the harder varieties, the vegetable origin can only be demonstrated by analogy and comparison with varieties less modified. There is a closely graded series ranging between peat at one end and the anthracitic coals, or maybe graphite, at the other. It is convenient, however, to pick out certain members of the series as types. We thus obtain peat, lignite, bituminous, and anthracitic coals. There are no hard and fast lines between these different types ; the one merges into the other by insensible gradations.

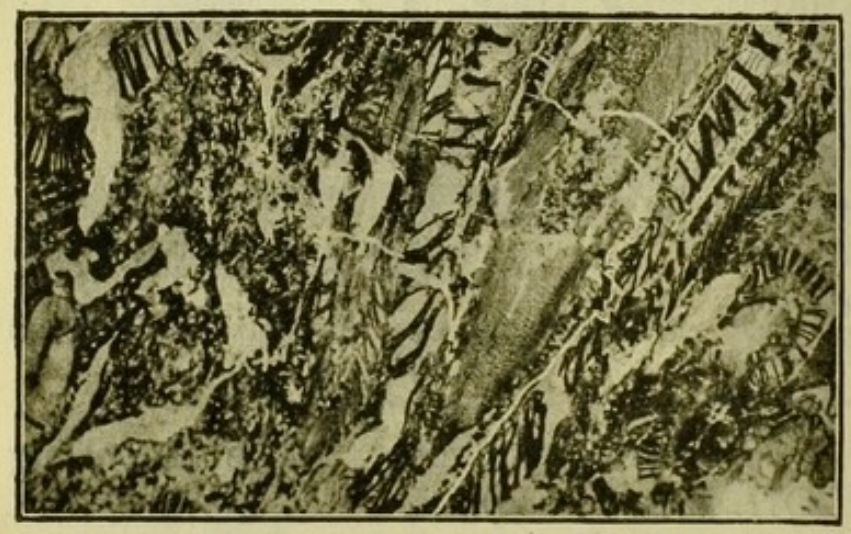


FIG. 208.—Photograph of Thin Slice of Coal from Dalesgate.

The nature of the final product, as now mined, must depend on the character of the original deposits and on the particular conditions which prevailed at the different stages of the process of transformation. The vegetable matter may have been deposited in fresh or salt water, in lakes, lagoons, seas ; in marine swamps ; etc. The original vegetable tissue may have

been algæ deposits in sargossa seas, peat bogs, vegetable accumulations on the soil in luxuriant forests, delta and drift deposits, etc. The pressure may have been comparatively small, extended over a long period of time, and applied comparatively early in the process of transformation ; the pressure may have been very great and applied late in the process of conversion ; etc. An " old " coal geologically, might be " young " chemically, and conversely. Geologists can sometimes form a good idea what has happened, in other cases, they confess complete ignorance.

The different types of coal.—Assuming that **peat** represents the first stage in the metamorphosis of vegetable tissue into coal, it is possible to recognize several different types of peat ranging from bog-moss to heavy black peat which is closely related to **lignite or brown coal**—the second stage in the process of conversion. Analysis shows that lignite contains a large amount of moisture, and although it ignites readily, and burns with a long smoky flame, its calorific power is comparatively low. Lignite generally disintegrates rapidly on exposure to the air. **Bituminous coal**—the third stage in the transformation—is denser than lignite, black, and comparatively brittle. It does not disintegrate on exposure to the air like lignite. Thin sections under the microscope show traces of woody fibre, lycopodium spores, etc. It burns with a yellow flame, and has a greater heating power than lignite. Some bituminous coals when heated, soften and seem to fuse, for the coal cakes into a continuous mass—**caking coal.** Caking coals furnish a hard compact coke. Other bituminous coals do not cohere in this way when heated—**non-caking coals.** These furnish a pulverulent coke. There are all gradations between the two sub-types. **Anthracite coal** has a low proportion of volatile hydrocarbons, and a greater amount of fixed carbon than the other varieties. It is hard, black, and brittle ; it presents no trace of vegetable structure ; it ignites with difficulty and burns with a short flame with a high calorific power.

The dry distillation of coal.—As in the case of wood, when coal is heated in a retort to about 400°, it is carbonized, and a comparatively small quantity of gaseous, and a relatively

large quantity of liquid, products are obtained. The gas, when purified from sulphur, etc., is called **coal gas.** It is mainly a mixture of hydrocarbon gases consisting mainly of members of the methane and ethylene series along with hydrogen. The gas varies in composition with the nature of the coal, the temperature of decomposition, etc. The by-products tar, carbon dioxide, sulphur and ammonia compounds, etc.—produced during the distillation of the coal—are removed from the gas, and finally, when the distillation is conducted in the neighbourhood of 1000°, purified coal gas contains approximately :

Hydrogen.	Methane.	Ethylene.	Carbon monoxide.	Carbon dioxide.	Nitrogen.	Oxygen.
49	35	4	4	½	4	½ per cent.

The approximate proportions of the by-products produced at the same time, are, per ton of coal :

	lbs.	per cent.
Coal gas (10,000 c. ft.)	380	17·0
Tar	115	5·1
Gas liquor (without water from scrubbers)	177	7·9
Coke	1568	70·0

The retorts are arranged in tiers on a retort bench. Those illustrated in Fig. 209 are heated by means of producer gas made in the *gas producer.* The volatile products from the coal in the retorts pass into a *hydraulic main,* a certain amount of tar condenses in this tube and runs to the *tar well.* The hot gases pass into a series of iron pipes—*the condensers*—where they are partly cooled, any liquid products which condense collects in the tar well. The gas is drawn from the retorts and condensers by an *exhaust pump* so as to reduce the pressure in the retorts. The gas then passes up and down a tower—*the scrubbers*—which is filled with coke or pebbles, and down which a stream of water trickles. Ammonia and carbon dioxide are here washed from the gas. The gas then passes through chambers—*the purifiers*—containing trays of damp lime and ferric hydroxide (bog iron ore), which absorb sulphur compounds from the gas. The gas passing along is measured in the *station meter* and stored ready for distribution in the *gas holder.*

A hard variety of carbon—**gas carbon**—gradually collects on the inside of the retort near the exit. It is a good conductor of

electricity, and is used for the manufacture of carbon rods for electric lighting, and for plates for galvanic batteries. The liquid which collects in the tar well separates into two layers (*a*) the tar, (*b*) the ammonical liquor. *Tar*—**gas tar, coal tar**—is a black viscid foul-smelling liquid used as a protective paint for preserving timber; making tarred paper, waterproofing masonry, etc. Tar is a mixture of many "organic substances" which are separated by distillation at different temperatures. It furnishes carbolic and creasotic oils, benzene, naphtha, anthracene, dyestuffs, flavours, perfumes, oils, etc. The residue in the retort is *pitch*. *Asphalt* is a solution of pitch in heavy tar oils, and is used in making hard pavements, varnish, etc. **Ammonia.** The ammoniacal liquid

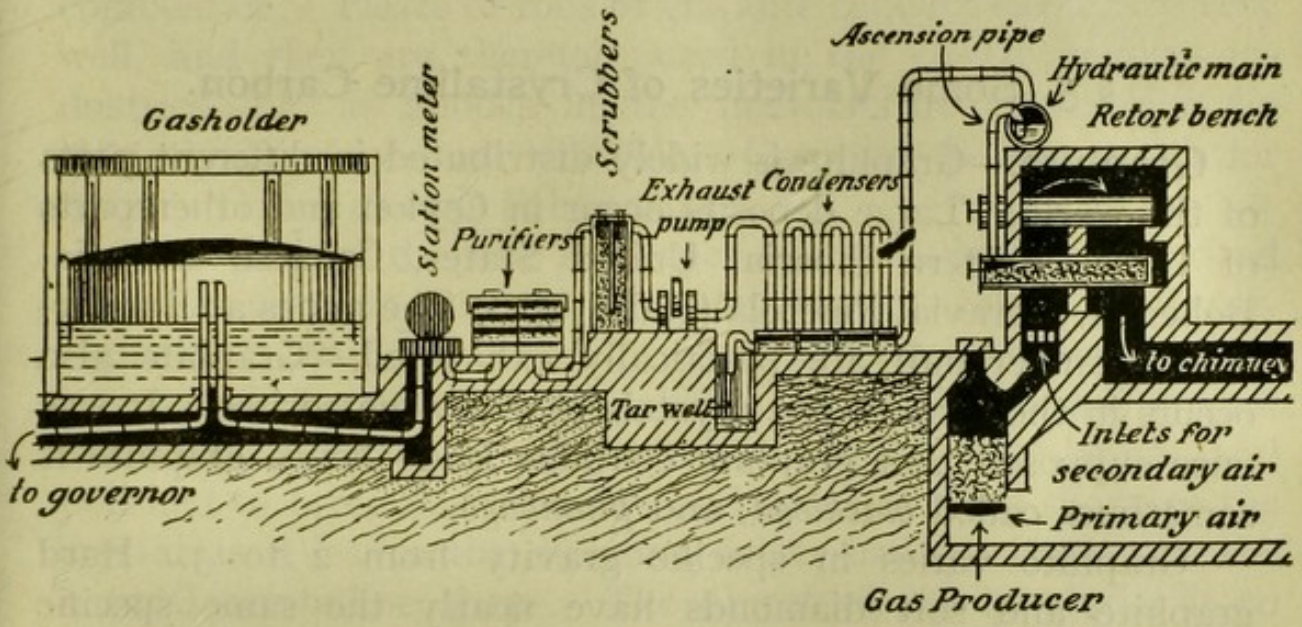


FIG. 209.—Coal Gas Works (Diagrammatic Section).

from the tar well and the scrubbers is boiled with milk of lime and the expelled ammonia is mixed with sulphuric acid. The tarry matters are separated, and the solution of ammonium sulphate is evaporated and crystallized for the market. **Gas lime.** The spent lime from the "purifiers" is used for agricultural purposes, and when the iron oxide has absorbed about 50 or 55 per cent. of sulphur it is said to be fouled, and is then sold to the manufacturer of sulphuric acid as **spent oxide.** It is then roasted to furnish sulphur dioxide. **Coke** remains behind in the retort.

§ 4. Coke.

Coke.—Coke is the residue obtained when coal is heated in a closed vessel out of contact with air. Coke generally contains about 90 per cent. of carbon. Coke is used in the manufacture

of iron and steel, and in a great many metallurgical operations, where its comparative freedom from sulphur and certain other impurities render it more suitable than coal. Coal may be converted into coke by heating it in closed vessels specially for the coke—gas, tar, and ammonia are then by-products; but if coal gas is being manufactured, coke, tar, and ammonia are the by-products. Coke may or may not be prepared under conditions where the by-products are recovered. The properties of coke depend upon the nature of the coal from which it is obtained, and upon the way the coal is "coked."

§ 5. Some Varieties of Crystalline Carbon.

Graphite.—Graphite is widely distributed in different parts of the world. Large deposits occur in Ceylon and other parts of India, Eastern Siberia, United States, Canada, Bavaria, Bohemia, Moravia, Pinerola (Italy), etc. The mines at Borrowdale (Cumberland) are practically exhausted. Graphite also occurs in the form of fine crystals in many meteorites. It was once supposed that graphite contains lead—hence graphite is sometimes called *blacklead*, and *plumbago*.

Graphite varies in specific gravity from 2 to 3. Hard graphite and soft diamonds have nearly the same specific gravity. Graphite occurs in two forms—crystalline and amorphous. The crystalline variety has a lamellar, scaly, or flaky structure, and is largely used in the industries. The amorphous variety is not of much industrial importance. Graphite is not readily attacked by acids, though it is less resistant than the diamond.

Uses of graphite.—Graphite when rubbed on paper leaves a black mark—hence the term graphite—from a Greek word meaning "to write." It is therefore used for making *lead pencils*. For this purpose the natural graphite is purified by grinding and washing so as to remove the grit. The purified graphite is mixed with a little washed clay and forced by hydraulic pressure through dies of the necessary shape. It is then stoved and cased in wood (red cedar for preference). Scaly graphite has been largely used, on account of its refractory

qualities and high heat conductivity, for the manufacture of *plumbago crucibles*. Other refractory goods are also made from graphite. Graphite is also used as a lubricant for machinery; a coating for iron to prevent rusting; coating for goods—say plaster of Paris—to be later electrotyped; preventative for boiler scale; stove polish; polishing powder for gunpowder; etc. Granular graphite is used as a resistance medium for electric furnaces. The resistance offered by this material to the passage of the electric current raises the temperature of the mass. If the mixture be suitably enclosed, very little graphite is lost by combustion. Plates or rods of graphite conduct electricity very well, and they are therefore used in the electrochemical industries—*e.g.* as anodes in the manufacture of chlorine by electrolysis of sodium chloride. Graphite is also used for battery plates, electric light carbons, etc.

The diamond.—For long ages diamonds have been prized as ornaments on account of their beauty, rarity, and permanence. Diamonds occur in their natural state as more or less rounded rough-looking pebbles not unlike pieces of gum arabic in appearance. The natural diamond must be cut and polished to bring out its lustre and sparkle. The shape of the crystal as it leaves the diamond cutter has no relation to the natural crystalline shape. The object of the lapidarist is to get the maximum reflection of light from the interior of the stone. The "brilliant," for instance, is a standard shape with a rather large flat face which is really the base of a pyramid with many sides (facets). The high reflecting and refracting power of the diamond are the particular qualities which make it supreme above other gems. In virtue of these qualities, the light falling on, say, the front face of a brilliant passes into the diamond, and is reflected from the interior surface of the facets. The reflected light is refracted into a wonderful play of "lightning flashes, and sparkling scintillations" as it passes into the air. The Cullinan is the largest known diamond. It was found near Pretoria (South Africa), January, 1905, and weighed over $1\frac{1}{4}$ lbs.; but stones over an ounce in weight are comparatively rare.

The occurrence of the diamond.—Diamonds are sparsely

distributed in different parts of the world. The chief localities are South Africa, Brazil, Ural, India, Borneo, and Australia. They have been found in meteorities—*e.g.* the Canyon Diablo meteorite (Arizona, U.S.A.) contained both black and transparent diamonds. Diamonds occur in river beds and in beds or pipes containing a heterogeneous mixture of fragments of various rocks cemented together with a bluish indurated clay known as "blue earth." The diamonds are found embedded in the blue clay. The clay crumbles on weathering, and the diamonds are readily detected in the disintegrated mass.

The varieties of the diamond.—Diamonds are usually tinged slightly yellow. The clearest and most nearly colourless diamonds without flaw are most prized as "diamonds of the first water." Diamonds are also occasionally coloured blue, pink, red, and green, owing to the presence of traces of foreign metals. Some diamonds are dark grey and even black. They exhibit a more or less imperfect crystalline structure, and are known as **black diamonds**—boart or bort, and carbonado. **Boart** is an imperfectly crystallized black diamond which has various colours, but no clear portions, and is therefore useless as a gem; boart is used in the drilling of rocks, and in cutting and polishing other stones. **Carbonado** is the Brazilian term for a still less perfectly crystallized black diamond. It is as hard as boart, and has similar uses. Boart and carbonado are usually regarded as intermediate forms between diamonds and graphite.

The diamond has a specific gravity about 3·5, and though brittle, is one of the hardest substances known. It is used for cutting glass. Few chemical reagents have any action on diamonds. When heated in oxygen or air, the diamond first blackens, and then burns to carbon dioxide.

The synthesis of diamonds.—Molten solids, on cooling, generally crystallize. Carbon, however, volatilizes at ordinary atmospheric pressures at about 3600° without passing through an intermediate liquid state. Arsenic also volatilizes at ordinary pressure without liquefying; but arsenic easily liquefies if it be heated under pressure. It is therefore inferred that if sufficient pressure could be obtained, carbon also would melt

to a liquid which would crystallize on cooling. Iron dissolves carbon and gives it up again on cooling. Other metals, especially silver, behave in a similar manner, but iron appears to be the best solvent. The solubility increases with the temperature. By heating iron with carbon to a high temperature and suddenly quenching the mixture in water, H. Moissan found some transparent diamonds, along with much boart and graphite, when the iron was dissolved away in hydrochloric acid. The diamonds were microscopic. It is supposed the outer layer of iron by being cooled suddenly is solidified, while the interior is fluid. When the interior expands in the act of solidification, it is supposed to have exerted enough pressure to liquefy part and crystallize part of the carbon.

TABLE XXXII.—COMPARISON OF THE PROPERTIES OF THE THREE FORMS OF CARBON.

Property.	Amorphous.	Graphite.	Diamond.
Appearance . . .	Amorphous black	Black, generally cystalline	Crystalline, colourless or coloured
Specific gravity . .	1·5 to 2	2 to 3	About 3·5
Lustre	Generally poor	Metallic	Brilliant, very hard
Hardness	Varies	There are two forms, hard and soft	
Conductor of heat and electricity	Fair	Fair	Poor
Specific heat . . .	0·24	0·20	0·15
Heat of combustion per 12 kilogrms.	93·24 Cals.	93·36 Cals.	96·98 Cals.
Action of a mixture potassium chlorate and nitric acid	Brown solution	Brown solid	Scarcely attacked

§ 6. Electric Furnaces.

It seems here advisable to emphasize the difference in some types of electric furnace indicated in this work. The student

is liable to confuse furnaces in which the electric current is used as a source of heat with those in which the electric current is used for electrolysis. The main types of electric furnace are :

1. **Arc furnace.**—In this, the heat is produced by one or more electric arcs. The arc may be established between one or more pairs of carbon or graphite poles as in Moissan's furnace—Fig. 210 ; or between the fused metal bath or

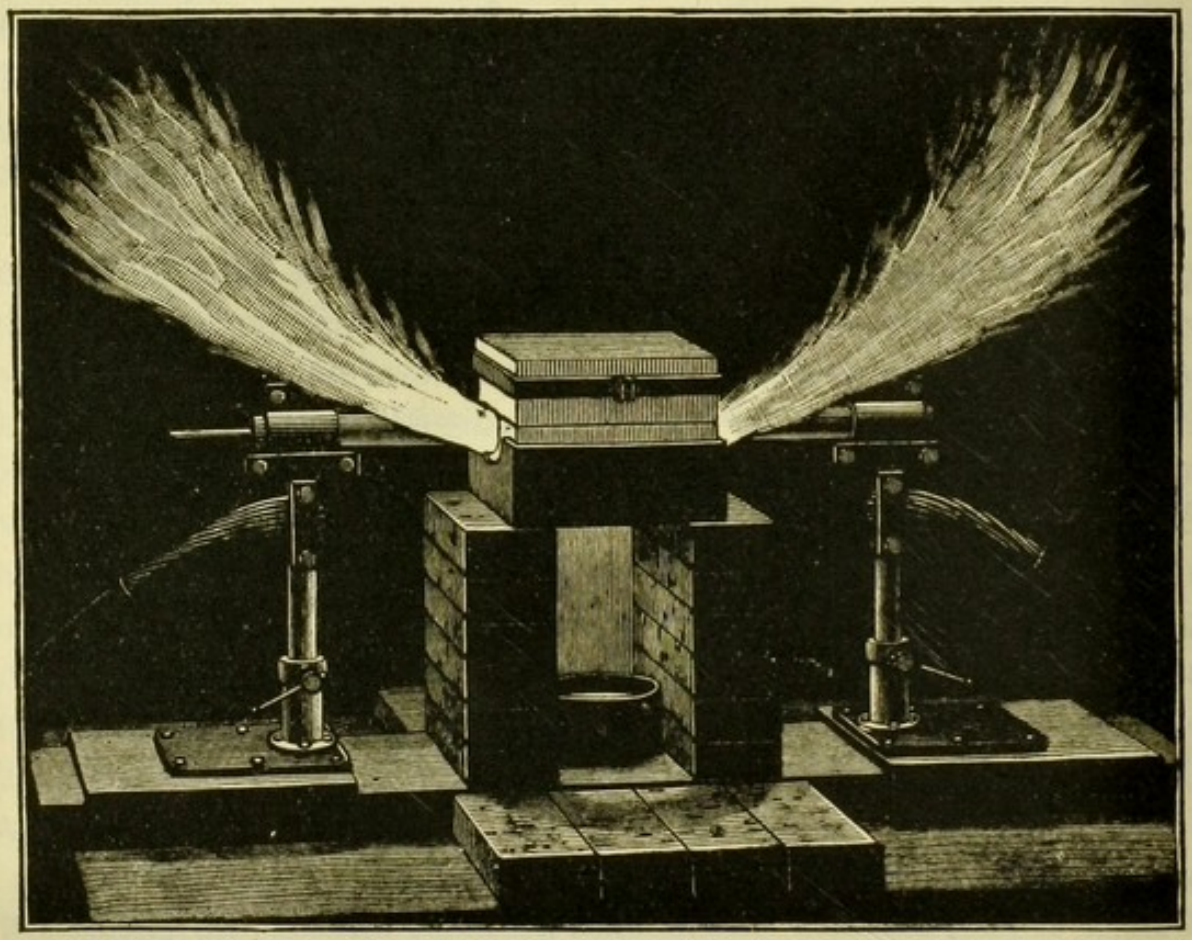


FIG. 210.—Moissan's Electric Arc Furnace.

fused slag and a carbon pole as in some furnaces used for reducing iron ores to pig iron, and in refining pig iron and steel.

2. **Resistance furnace.**—Here the heat is produced by the passage of an electric current through a solid or liquid resistor.

(*a*) A special resistance, *e.g.* nickel, ni-chrome, platinum wire, fragments of carbon, etc., is embedded between the inner and

outer walls of the furnace. The inner wall may take the form of a muffle, tube, etc. These furnaces are fairly common in chemical laboratories.

(*b*) The charge in the furnace constitutes the resisting medium. The resistance of the medium raises the temperature of the charge, *e.g.* the phosphorus furnace (Fig. 199); the calcium carbide furnace (Fig. 210); the carbon disulphide furnace (Fig. 212); and the carborundum furnace (Fig. 224).

3. Electrolytic furnace.—A continuous current splits the fused electrolyte into its component parts. The heating effect of the current may or may not suffice to keep the contents of the furnace in a fluid condition. The aluminium furnace (Fig. 186) illustrates the former; and Castner's sodium furnace (Fig. 174) the latter.

§ 7. Compounds of Carbon with the other Elements.

Carbides.—Carbon also unites directly with many elements at high temperatures—*e.g.* with sulphur to form carbon disulphide (p. 568); with nitrogen to form cyanogen (p. 588); with hydrogen to form the hydrocarbons (p. 576); with silicon to form carborundum (p. 602); and with metals to form carbides. **Carbides are compounds of carbon with other elements—chiefly metals.** The most important of these, commercially, are silicon carbide and calcium carbide. Some of the carbides react directly with water, forming hydrocarbons.

Calcium carbide—CaC_2—is made by heating a powdered mixture of, say, 56 parts by weight of quicklime and 36 parts of coke in an electric arc furnace—estimated temperature 3000°—arranged so that the carbide, as it is made, moves away from the electric arc to enable a new charge to take its place. The reaction is represented by the equation: $3C+CaO \rightarrow CaC_2+CO$. The process can be imitated on a small scale by clamping a graphite crucible to an iron rod, and connecting it with the $-$pole of a current of 60 to 100 volts. The $+$ pole is an electric light carbon rod which is clamped to a retort stand—

Fig. 211. The retort stands rest on some insulating material. The carbon rod is allowed to touch the bottom of the crucible and withdrawn, by the insulated handle *a*, so as to form an arc. The mixture of coke and quicklime is then gradually added to the crucible.

Calcium carbide is a hard, brittle, crystalline solid, specific gravity 2·2. When pure, it is white, but commercial calcium carbide is dark grey or bronze coloured owing to the presence of impurities. Calcium carbide reacts with water forming acetylene (p. 576), and it is sold packed in tin cans to protect it from deterioration by exposure to the moisture of the atmosphere. Calcium carbide is also used in the manufacture of calcium cyanamide used as a fertilizer, and in the manufacture of cyanides.

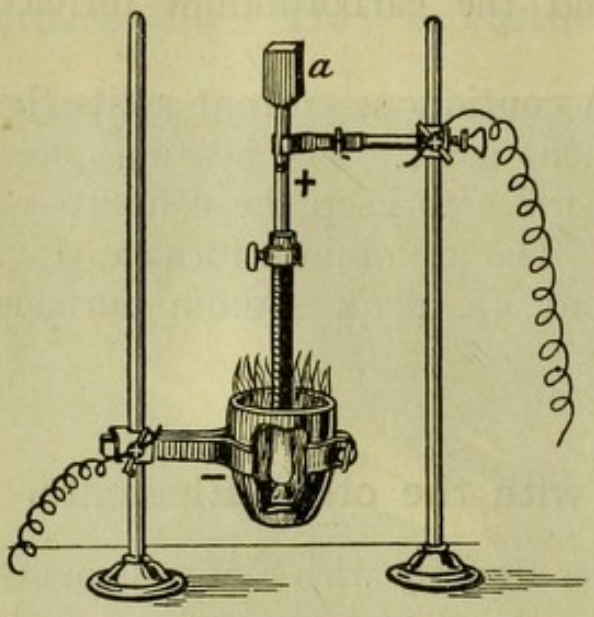


Fig. 211.—Laboratory Preparation of Calcium Carbide.

Carbon disulphide.—When sulphur vapour is passed over red-hot charcoal, the two elements combine, forming volatile carbon disulphide: $C + S_2 = CS_2$. The volatile compound of carbon and sulphur is condensed in vessels surrounded with cold water. The product is contaminated with free sulphur, which volatilizes with the carbon disulphide; some hydrogen sulphide is formed at the same time by the action of sulphur on the hydrogen in the charcoal.

In Taylor's electric process (1899) a cylindrical furnace 40 feet high and 16 feet in diameter is packed with coke from the top, Fig. 212; the coke is renewed through the side hopper *C*. An alternating current is sent through the electrodes *E* set at right angles to one another at the base of the furnace. The heat melts the sulphur on the floor of the furnace; the vapour of sulphur rises through the coke, forming carbon disulphide. Fresh sulphur is introduced through the hopper shown in the diagram. The carbon disulphide passes off at

the top of the furnace, and is condensed in the condensing coils. The electrical process is practically continuous and is free from troublesome leakages and heat losses incidental to the retort process. The crude product can be purified by repeated re-distillation and subsequent agitation with mercury, and distillation from white wax; but the manufacturing process of purification is a "trade secret."

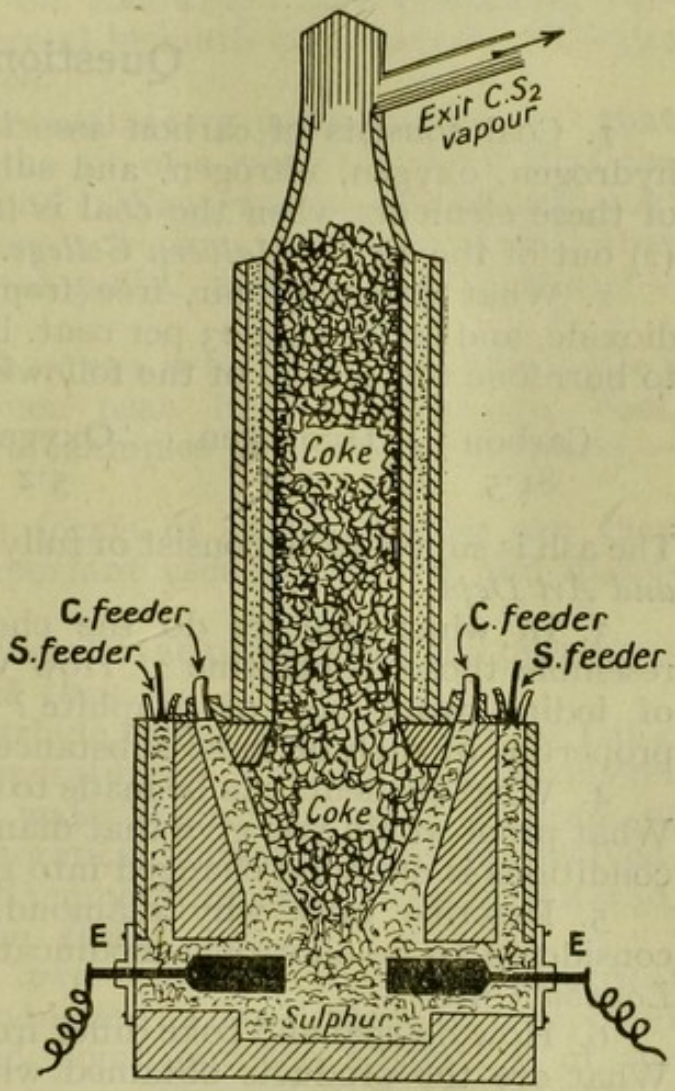


FIG. 212.—Taylor's Carbon Disulphide Furnace.

Properties. — Carbon disulphide, if pure, is a colourless, mobile, refractive liquid, with an aromatic smell not at all displeasing, although the smell of commercial carbon disulphide is usually disagreeable and rancid. If breathed constantly, in small quantities, it is injurious to health, and in large quantities, fatal. It is nearly $1\frac{1}{4}$ times as heavy as water. It freezes at $-116°$, melts at $-110°$, boils at 46°. 100 grams of water at 20° dissolve 0·1 gram of carbon disulphide. It mixes in all proportions with alcohol, ether, benzene, and essential oils. It is also a good solvent for sulphur, phosphorus, iodine, bromine, camphor, gums, resins, waxes, fats, and caoutchouc; and it is largely employed in the industries on account of its solvent properties. It is also used as an insectide.

There is a curious analogy between this compound and carbon dioxide which is accentuated by the fact that a **thiocarbonic acid** H_2CS_3 analogous with H_2CO_3 is known; the **thiocarbonates** also recall the carbonates. A compound **carbon**

monosulphide, CS, the analogue of carbon monoxide, CO, is known ; and **thiocarbonyl chloride** $CS.Cl_2$ analogous with carbonyl chloride, further emphasizes the similarity between oxygen and sulphur in their relations with carbon.

Questions.

1. Coal consists of carbon associated with small quantities of hydrogen, oxygen, nitrogen, and sulphur ; what becomes of each of these elements when the coal is heated (1) in contact with air, (2) out of the air ?—*Malvern College.*

2. What weight of air, free from aqueous vapour and carbon dioxide, and containing 23 per cent. by weight of oxygen, is needed to burn one ton of coal of the following percentage composition :—

Carbon	Hydrogen	Oxygen	Nitrogen	Ash
81·5	5·0	5·2	1·6	6·7

The ash is supposed to consist of fully oxidized substances.—*Science and Art Dept.*

3. In what respects do the chemical properties of bromine resemble those of chlorine ? How would you distinguish a piece of iodine from one of graphite ? Describe the characteristic properties of each of these substances.—*London Univ.*

4. What elements can be made to combine with carbon directly ? What proof would you give that diamond is carbon ? Under what conditions is diamond changed into graphite ?—*London Univ.*

5. Describe fully why diamond, graphite, and charcoal are considered to be allotropic modifications of the element carbon.—*London Univ.*

6. How do coal and coke differ from each other in composition ? What are the products obtained when (*a*) air, and (*b*) steam are separately passed over red-hot coke ?—*London Univ.*

7. How can charcoal be converted into graphite, and into diamond ? What experiments would you make in order to show that the three substances contain only the same element ?—*London Univ.*

8. The specific gravity of carbon is said to be about 1·2 and yet common charcoal floats in water. Why is this, and how can charcoal be made to sink ?—*Science and Art Dept.*

9. How could carbon monoxide be obtained from carbon and oxygen ? Using coke, which contains one-eighth of its weight of ash, what weight of coke would be required for the production of 56 lbs. of carbon monoxide ? (C=12, O=16.)—*Sydney Univ.*

10. What is meant by an allotropic form of one element ? Describe the chief properties and uses of the allotropic forms of

carbon, and state what evidence we have that they consist of carbon and of nothing else.—*Cambridge Senr. Locals.*

11. Under what conditions does carbon dioxide react with other substances to form bodies other than carbonates? What volume of carbon dioxide can be formed by the action of hydrochloric acid on 100 grms. of the following: acid potassium carbonate, calcium carbonate, normal bismuth carbonate? (K=39; Ca=40; Bi=210.)—*Owens Coll.*

12. How would you demonstrate experimentally (1) that carbonic acid was present in the air of a room; and (2) that the carbonic acid contained carbon? What weight of carbonic acid gas could be made by burning 100 grms. of carbon, and what volume would this gas occupy at 546° C. and 112 mm. pressure?—*Vict. Univ.*

13. What is charcoal and how can it be made on a large scale? Describe the difference between peat, lignite, bituminous coal, anthracite and graphite. Give examples of allotropic elements.—*Panjab Univ.*

14. Name the amorphous forms of carbon. How are they obtained? Mention their important uses in the arts and manufactures.—*Calcutta Univ.*

15. What is a carbide? Describe the preparation and properties of this class of bodies.—*Panjab Univ.*

16. A sample of calcium carbide contains 96 per cent. of CaC_2. On a day when the room temperature is 21° C. and the barometer stands at 762 mm., excess of water is dropped on to 10 grms. of the carbide. Calculate the theoretical volume of acetylene evolved, the gas being measured at room temperature and pressure. (Ca=40, C=12.)—*Adelaide Public Exam. Board.*

17. Describe briefly any two processes in which electrical energy is employed in the production of an element or compound of industrial importance, and point out the advantage of the electrical process over the one previously employed.—*Sydney Univ.*

18. State the natural sources of graphite, and describe those properties which distinguish it in a marked degree from amorphous carbon, and which render it especially useful. In what arts and manufactures is it usefully employed?—*Science and Art Dept.*

19. A blue flame is often seen at the top of a coke or charcoal fire. To what substance is it due, and how is this substance formed? Supposing that the coke used contained 90 per cent. of carbon, and it was entirely converted into this substance, how much coke would be needed to make 10,000 litres, measured at 15° and 750 mm.?—*London Univ.*

20. By what means can each of the three phosphoric acids be obtained using common "phosphate of soda" as the primary material in each case? Draw up a tabular statement by which

these acids may be distinguished from one another.—*Science and Art Dept.*

21. Explain the production of the gaseous hydrides of arsenic and antimony in the ordinary analytical tests for those elements; point out the distinctive characters of the hydrides, and explain the chemical changes which occur when each gas is led into a solution of silver nitrate.—*Science and Art Dept.*

22. How are the different kinds of phosphoric acid prepared? Give the formulæ of the corresponding sodium phosphates.—*Science and Art Dept.*

23. If several substances were given you and were said to contain nothing but the element carbon, what properties might they have? What experiments would you make to identify each?—*Oxford Junr. Locals.*

CHAPTER XXXII

Compounds of Carbon with Hydrogen and Nitrogen

§ 1. Methane.

Preparation.—Methane is usually prepared by the following process: Ten grams of fused sodium acetate are intimately mixed with three times that weight of soda lime or barium oxide in a mortar. Introduce the dry mixture in a glass or copper flask, or in a copper tube retort. Close the copper flask *A*, Fig. 213, with a cork to which a delivery tube is attached. The flask is strongly heated, and when all the air is expelled, the methane is collected over water in the usual manner. Soda lime or barium oxide is used in place of sodium hydroxide because of the fusibility of the latter. Soda lime is a mixture of calcium hydroxide and sodium hydroxide.

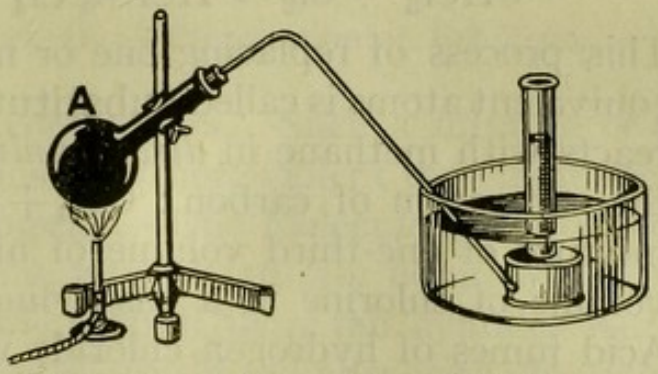


Fig. 213.—Preparation of Methane.

Properties.—Pure methane is free from colour, and is without smell. The gas prepared by the ordinary process usually has a slight smell, but this is due to the presence of impurities. Methane is lighter than air. 100 volumes of water at 20° dissolve $3\frac{1}{2}$ volumes of the gas. Methane is rather more soluble in alcohol. Methane has no well-defined physiological action on the system other than diluting the oxygen and so inducing suffocation. It is also called "marsh gas" because it occurs contaminated with other gases in the bubbles of gas which

sometimes rise from marshes, bogs, and swamps; and the "fire-damp" of coal mines contains much methane.

Combustion and explosion of methane.—When a lighted taper is plunged into a cylinder of this gas, held mouth downwards (Fig. 44), the taper is extinguished (non-supporter of combustion), and the gas burns at the mouth of the jar (combustible). The gas, if pure, burns with a pale blue non-luminous flame, forming carbon dioxide and water: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.

Action of chlorine.—When a mixture of equal volumes of chlorine and methane is exposed to *diffuse daylight*, they gradually react, forming methyl chloride—CH_3Cl. Thus: $CH_4 + Cl_2 \rightarrow HCl + CH_3Cl$. If more chlorine be present, the chlorine gradually replaces all the hydrogen. The successive stages in the action of chlorine on methane can be represented:

$CH_4 + Cl_2 \rightarrow HCl + CH_3Cl$ (methyl chloride)
$CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_3$ (dichloromethane)
$CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3$ (chloroform)
$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4$ (carbon tetrachloride)

This process of replacing one or more atoms in a molecule by equivalent atoms is called **substitution.** If an excess of chlorine reacts with methane in *direct sunlight* an explosion occurs with the separation of carbon: $CH_4 + 2Cl_2 \rightarrow 4HCl + C$. Shake a mixture of one-third volume of methane with two-thirds of a volume of chlorine in a gas cylinder; apply a lighted taper. Acid fumes of hydrogen chloride will be formed, and soot will be deposited in the cylinder.

§ 2. Ethylene.

Preparation.—Ethylene is most conveniently prepared by the action of dehydrating agents (sulphuric acid, or phosphoric acid) upon ordinary alcohol—C_2H_5OH. For this purpose put 50 c.c. of syrupy phosphoric acid in a 250 c.c. flask furnished with a two-hole rubber stopper fitted with a tap-funnel drawn out into a capillary end, and also a thermometer, *T* (Fig. 214). The side neck of the flask is connected with a delivery tube leading to an empty wash-bottle, and finally to the gas trough. The flask is heated to about 200° on a sand-bath or metal plate. Ethyl alcohol is slowly run from the tap-funnel below the surface

of the phosphoric acid. The alcohol is decomposed into water and ethylene. The water is retained by the phosphoric acid. The reaction is represented in symbols :

$$C_2H_5OH \rightarrow H_2O + C_2H_4$$

Properties.—Ethylene is a colourless gas with a peculiar ethereal odour. It has nearly the same density as air. 100 volumes of water at 20° dissolve 15 volumes of the gas ; the gas is nearly 13 times as soluble in alcohol. The gas behaves like methane towards a lighted taper, but it burns with a luminous smoky flame unless it be diluted with hydrogen or methane. One volume of the gas requires three volumes of oxygen, or 14·3 volumes of air for complete combustion. Such a mixture is a powerful explosive. The explosion is more violent than methane.

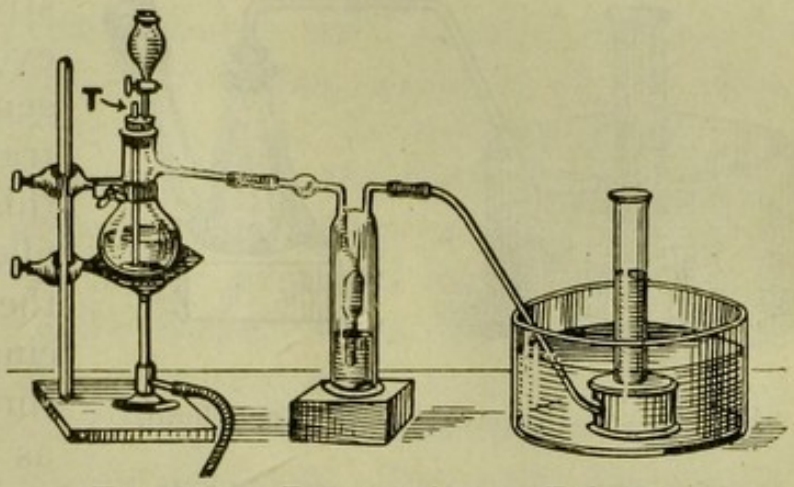


FIG. 214.—Preparation of Ethylene.

The action of the halogens.—One molecule of ethylene readily combines with chlorine, forming an oily liquid which is **ethylene dichloride**—$C_2H_4Cl_2$. Half fill a tall cylinder with ethylene, carefully but quickly fill up the cylinder with chlorine, and allow the cylinder to remain in the trough ; the water gradually rises in the cylinder ; and the ethylene dichloride will be seen floating on the surface of the water. Hence ethylene was once called *olefiant gas*. The oily ethylene dichloride was once termed *Dutch liquid*. Similarly with bromine, a litre flask filled with ethylene and 2 c.c. of bromine will form a colourless oil of $C_2H_4Br._2$, **ethylene dibromide,** on the bottom of the flask. Fill a cylinder one-third with ethylene, and two-thirds with chlorine. Mix the gases well, and apply a light ; acid fumes are formed with much soot :

$$C_2H_4 + 2Cl_2 = 4HCl + 2C.$$

The ethylene molecule also combines directly with sulphuric

acid, hydrogen bromide, etc. The compounds of ethylene with chlorine, bromine, etc., are called **addition products.**

§ 3. Acetylene.

Acetylene is most conveniently prepared by placing fragments of calcium carbide in a dry flask provided with a tap-funnel and delivery tube. On gradually admitting water from the tap-funnel, a stream of acetylene is evolved. A modified generating flask is illustrated in Fig. 215. In this case the flask is filled with water, and the fragments of calcium carbide are added through the side tube as required. The reaction between the water and the calcium carbide is presented by the equation : $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$.

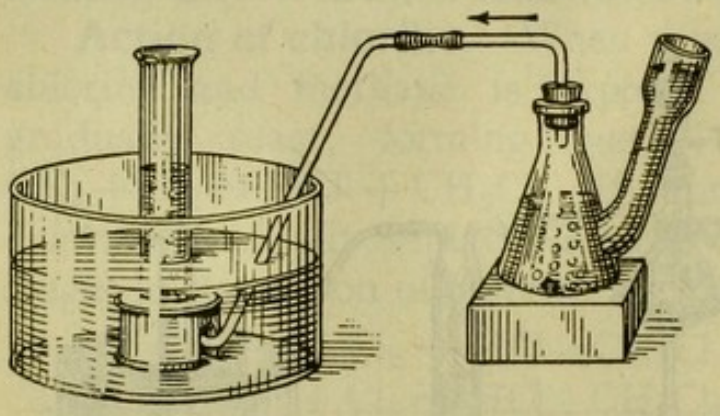


FIG. 215.—Preparation of Acetylene.

Properties.—Acetylene is a colourless gas, which, when pure, has an ethereal odour which is not unpleasant. As usually prepared and purified the gas has traces of impurities which impart to it an offensive smell reminding one of garlic. Acetylene is rather lighter than air. 100 volumes of water at 20° dissolve 103 volumes of acetylene. Alcohol dissolves about six times its own volume at ordinary temperatures. Acetylene, like ethylene, is absorbed by fuming sulphuric acid, but methane is not absorbed unless it is allowed to stand a long time in contact with the gas. Hence, with fuming sulphuric acid in an absorption pipette, Fig. 90, ethylene and acetylene and unsaturated hydrocarbons generally, can be removed from methane. Acetylene is poisonous and soon induces headache.

Action of chlorine.—If a gas cylinder be partly filled with acetylene, and chlorine be allowed to pass into the cylinder bubble by bubble, the acetylene flashes as the chlorine enters, and deposits soot on the walls of the cylinder. Note that methane and ethylene when mixed with chlorine must be ignited

before the soot is deposited. This experiment can be varied in an interesting manner by filling a cylinder about one-fifth full with a fresh solution of "chloride of lime," add some hydrochloric acid. The cylinder will soon be filled with chlorine gas. Add a few pieces of calcium carbide the size of a pear. As soon as the acetylene comes in contact with the chlorine, it bursts into flame with the separation of large volumes of soot: $C_2H_2+Cl_2=2C+2HCl$.

Combustion.—Acetylene burns with a luminous smoky flame, but, like the other hydrocarbon gases, it extinguishes a lighted taper plunged into the gas. If acetylene be burned from a jet with a very fine aperture the flame is not smoky, but it is exceedingly luminous. In most acetylene burners the gas issues from two small jets, so arranged that the jets strike one another to produce a flat flame. Other holes are arranged in the tubes leading to the jet, so that air is drawn in and mixed with the gas as it rushes through the nozzle—*e.g.* the gas jet of an ordinary acetylene bicycle lamp. The great luminosity of the acetylene flame, coupled with the easy preparation of the gas from "carbide," has led to the extensive use of acetylene for bicycle lamps, houses, etc., where coal gas is not convenient; acetylene is also used to increase the luminosity of other inflammable gases.

§ 4. Composition.

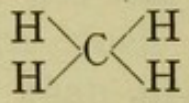
1. Methane.—If a measured volume of methane be mixed with an excess of air or oxygen, and exploded in a eudiometer, the contraction in volume determines the amount of hydrogen present, since the corresponding amount of water condenses to a liquid whose volume is negligibly small in comparison with the gas. The carbon dioxide can be absorbed by potassium hydroxide and the corresponding contraction represents the amount of carbon dioxide formed. In illustration, 10 c.c. of methane were mixed with 40 c.c. of oxygen in a Hempel's burette, Fig. 98. The mixed gases were driven into the Hempel's explosion pipette, and exploded. The gases were returned to the burette, and the volume measured 30 c.c.

instead of the original 50 c.c. The contraction was therefore 20 c.c. Water vapour contains its own volume of hydrogen, hence 10 volumes of methane contains the equivalent of 20 volumes of hydrogen. Again, the gases were transferred from the burette to the absorption pipette charged with potassium hydroxide solution, Fig. 201. On returning the gases to the burette, the volume measured 20 c.c. The contraction due to the absorption of the carbon dioxide was 10 c.c., and the 20 c.c. excess oxygen remained in the burette. One volume of carbon dioxide is equivalent to one volume of oxygen and one atom of carbon. Hence the analysis has furnished the following data :—

$$\underset{1\text{ vol.}}{\text{Methane}} + \underset{2\text{ vols.}}{2O_2} \rightarrow \underset{1\text{ vol.}}{CO_2} + \underset{2\text{ vols.}}{2H_2O_{steam}}$$

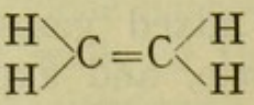
where the atoms of carbon and hydrogen must be united in the ratio 1 : 4, or the formula is $(CH_4)_n$, where the value of n has to be determined.

The relative density of methane (air = 1) is 0·559 ; and for hydrogen = 2, we have $28{\cdot}755 \times 0{\cdot}559 = 16{\cdot}07$. If $H_2 = 2$, the vapour density of CH_4 will be $12 + 4 = 16$. Hence the formula for methane is CH_4. If hydrogen be univalent, the only possible plane graphic formula is :



which makes carbon quadrivalent.

2. Ethylene.—The composition of ethylene can be determined by volumetric analysis as in the case of methane. The result shows that ethylene is $(C_2H_4)_n$. The vapour density ($H_2 = 2$) is nearly 28. Hence the formula for the gas must be C_2H_4. The graphic formula for ethylene with carbon quadrivalent and hydrogen univalent is not possible if all the valencies have to be saturated or "satisfied." Hence the graphic formula involves two sleeping or unsaturated valencies. On joining the carbon atoms by a double bond, we get—



3. Acetylene.—The composition of acetylene has been

established in a similar way. The vapour density 26·5 corresponds with the formula C_2H_2, and the graphic formula is represented:

$$H-C\equiv C-H$$

with three sleeping valencies.

§ 5. The Hydrocarbons.

The properties of the three gases—methane, ethylene, and acetylene, may now be summarized.

TABLE XXXIII.—COMPARISON OF THE PROPERTIES OF METHANE, ETHYLENE, AND ACETYLENE.

Property.	Methane.	Ethylene.	Acetylene.
Colour	nil	nil	nil
Smell (if pure) . .	nil	" ethereal "	" ethereal "
Litmus ; lime-water	nil	nil	nil
Combustible ? . .	yes	yes	yes
Supporter of combustion	no	no	no
Flame (if pure) . .	non-luminous	luminous ; smoky	luminous ; very smoky
Comparison of luminosity of flame	1 unit	20 units	50 units
Weight of a litre under standard conditions (air = 1)	0·555	0·978	0·92
100 volumes of water at 20° dissolve	3·5 vols.	15 vols.	103 vols.
Liquefies	−164°	−103°	− 81·6°
Solidifies	−184°	−169°	− 83·5
Action of chlorine .	Substitution in daylight (explodes sunlight) ; if ignited soot separates	Addition forming oily liquid ; if ignited soot separates	Decomposes flash and separation soot
Ammoniacal solution copper chloride	nil	absorbs	red precipitate
Ammoniacal solution silver nitrate	nil	absorbs	grey precipitate
Fuming sulphuric acid	not absorbed	absorption	absorption

Between 250 and 300 compounds of carbon and hydrogen are known, and they can be arranged in a few series the members of which have many properties in common. The first member of each of the following three series has just been briefly discussed, and all the series are discussed in organic chemistry.

Paraffin Series.		Boiling point.	Olefine Series.		Boiling point.	Acetylene Series.		Boiling point.
Methane	CH_4	−164°	—			—		
Ethane	C_2H_6	−93°	Ethylene	C_2H_4	−105°	Acetylene	C_2H_2	−83·6°
Propane	C_3H_8	−45°	Propylene	C_3H_6	−40°	Allylene	C_3H_4	−23·5°
Butane	C_4H_{10}	1°	Butylene	C_4H_8	1°	Crotonylene	C_4H_6	−27°
Pentane	C_5H_{12}	38°	Amylene	C_5H_{10}	39°	Valylene	C_5H_8	48°
Hexane	C_6H_{14}	70°	Hexylene	C_6H_{12}	69°	Hexoylene	C_6H_{10}	80°
. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
General formula	C_nH_{2n+2}		General formula	C_nH_{2n}		General formula	C_nH_{2n-2}	

Any member of a series is represented by the general formula of its series. Each series is called an **homologous series** because there is a constant difference—CH_2—between any one compound and the next higher or lower member, so that all the compounds of the series appear to be closely related. Corresponding derivatives of the hydrocarbons also form homologous series, and the study of these compounds is a special branch of chemistry, called "Organic Chemistry"—*See* Appendix.

§ 6. Petroleum and Related Products.

Occurrence.—Crude petroleum—also called *rock oil*—is a thick viscid liquid varying in colour from straw-yellow to greenish-black, and most varieties show a greenish fluorescence by reflected light. Petroleum is a complex mixture of many hydrocarbons belonging principally to the paraffin series along with small quantities of nitrogen and sulphur compounds. Petroleum occurs in the Baku district in Russia; in California, Colorado, Indiana, Kansas, Kentucky, New York, Ohio, and Texas in the United States; in Mexico, Canada, India, Egypt, South and West Africa, Peru, Trinidad, Barbadoes, Borneo, Australia, New Zealand, etc.

The oil apparently occurs underground, and in some places it issues from the earth without man's assistance. It is usually

necessary to "bore" through the overlying strata and insert a pipe in the "oil basin." When first "tapped," the oil often "shoots" out of the "well," but the velocity of the stream gradually subsides,[1] and, after a time, the oil is "pumped" to the surface; conveyed by pipes to a central reservoir for storage; and afterwards distributed. Fig. 216 is a diagrammatic sketch through the strata of an oilfield, and it is intended to give a rough idea of the way the oil and gas are associated in some oilfields. The gas and oil here collect near the summit on the underside of an anticlinal (concave downwards) fold capped by an impervious rock—called "cap-rock." If the gas is under pressure, it is easy to understand, from Fig. 216, how the oil from the "bore" shown in the diagram would be expelled with some violence until the pressure is relieved. Saline water is usually associated with oil and gas. In some cases the oil is obtained from a horizontal stratum of porous sandstone or limestone saturated with oil.

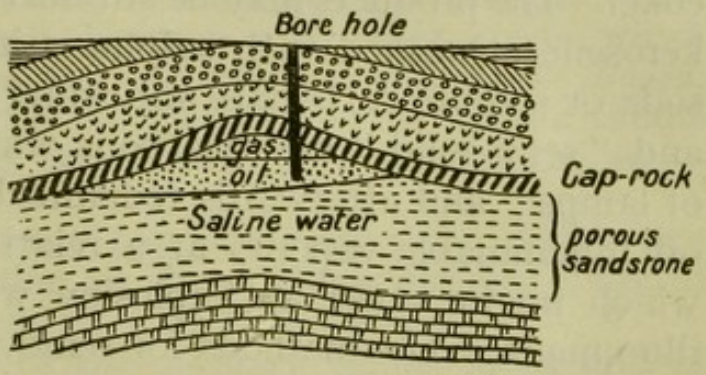


FIG. 216.—Geological Section of Oil-well (Diagrammatic).

Refining.—Crude petroleum is used as a fuel in many industries—metallurgy, locomotives, fire-engines, steamships, etc. A great deal of petroleum is purified or refined. The treatment of petroleum oil and its products is a vast industry. Over 200 different commercial products are derived from the purification and refining of petroleum. The crude petroleum is placed in a retort—"still"—connected with condensing tubes and receiving tanks. The temperature is gradually raised. At first, the lighter substances are volatilized and condensed in suitable receivers. The receivers are changed when the specific gravity of the distillate has attained a certain value, or when the temperature of the retort has risen sufficiently

[1] When the Lucas oil-well (Beaumont, Texas) was first "tapped" in 1901, a six-inch stream of oil is said to have spouted 160 feet high for 9 days at the rate of 75,000 barrels per day.

high. The chief fractions are: petroleum ether, gasoline, petrol, ligroin, naphtha, benzine (not benzene), benzoline, kerosene, photogene, and the so-called paraffin oil, variously used as solvents, fuel, and illuminants.

The residue in the retort is transferred to another still, and further heated to a high temperature. It furnishes lubricating oils; vaseline used for ointments, etc.; paraffin used for candles, insulating, etc. The residue in the retort is mainly coke. The products may be still further purified. For instance, kerosene is washed with sulphuric acid, and then with caustic soda or sodium carbonate and water to get rid of tarry matters and "semi-solid" hydrocarbons which might choke the wicks of lamps; and afterwards redistilled to remove oils which give off inflammable vapours at a relatively low temperature, and which might cause an explosion when the oil is used as an illuminant. The methods for removing sulphur from these oils are mainly trade secrets.

Oil shales.—These shales are associated with the sandstones, clays, and limestones in the Mid- and West Lothian and other parts of Scotland, etc. The oil shales of New South Wales are also called "kerosene shales." Good oil shales can often be lighted with a match, when they burn with a steady flame resembling a candle. When heated to dull redness in vertical retorts, they furnish gas and a liquid distillate which separates into two layers—the lower aqueous layer consists of ammonium compounds; the upper layer has a greenish-brown colour consisting of oil and tar. The latter closely resembles petroleum, and gives similar products on fractional distillation. Scotch shales furnish from 18 to 50 gallons of crude oil per ton; New South Wales shales are said to yield up to 100 or 150 gallons of crude oil per ton.

Questions.

1. How would you distinguish (1) between nitrous oxide and nitric oxide; (2) between hydrogen and marsh gas; (3) between hydrochloric and hydrobromic acid; (4) between carbon monoxide and carbon dioxide?—*London Univ.*

2. Explain exactly what is implied by the formula C_2H_4.—*London Univ.*

3. Two bottles are given. One contains hydrogen and the other marsh gas. How would you ascertain by experiments which of the two contains marsh gas ?—*London Univ.*

4. How is olefiant gas prepared ? How could you show that it contains carbon and hydrogen ? By what properties can olefiant gas be distinguished from marsh gas ?—*London Univ.*

5. What is the nature and composition of ordinary fuel ? Describe the chemical changes which occur in a coal fire.—*London Univ.*

6. Copper oxide suffers reduction when heated in a stream of coal gas. What does this mean ? What is it in the gas which brings about the reduction ? Mention any other oxide which might be reduced in the same way.—*Adelaide Public Exam. Board.*

7. Describe and explain the changes that occur when a candle is burnt in air (1) as regards the candle, (2) as regards the air.—*Staffs. County Schol.*

8. Give an account of what happens during the destructive distillation of coal, and mention all the products directly obtained in the process.—*Bombay Univ.*

9. Discuss the structure of the ordinary candle flame and of the non-luminous flame of the Bunsen burner, pointing out the difference between the two.—*Cape Univ.*

10. Describe the preparation of coal gas. Explain the character of the coal gas flame (1) when the air holes of a Bunsen burner are open, (2) when they are closed. Upon what does the luminosity of a flame chiefly depend ? Show one or two experiments in support of your view.—*Panjab Univ.*

11. 15 c.c. of marsh gas are exploded with an excess of oxygen, what change in volume would take place, and what volume of carbon dioxide would be produced ? It is assumed that all the gaseous measurements are made at 20° C. and 740 mm. pressure, the gas being in every case saturated with moisture.—*Staffs. County Schol.*

12. Give an account of the manufacture and purification of coal gas, indicating also as far as you can the nature and importance of any of the by-products obtained.—*Staffs. County Schol.*

CHAPTER XXXIII

Compounds of Nitrogen and Carbon

§ 1. Ferrocyanides and Ferricyanides.

Potassium ferrocyanide, K_4FeCy_6.—When nitrogenous refuse (blood, horns, leather scraps, etc.) is charred, and the black mass is ignited with potash and iron filings, something is formed which passes into solution when the mass is lixiviated with water. The aqueous solution on evaporation gives yellow crystals of potassium ferrocyanide with the empirical composition, $K_4FeC_6N_6.3H_2O$. It is convenient to represent the univalent group " CN " by the symbol " Cy," and accordingly the formula is written $K_4FeCy_6.3H_2O$. The salt is soluble in water, the solution has a bitter taste, but is not poisonous. The crystalline yellow salt loses its " water of crystallization " on warming, and the anhydrous salt remains behind as a white powder. Potassium ferrocyanide is decomposed when heated, forming potassium cyanide, KCy, and an impure iron carbide generally employed: FeC_2. The reaction is written: $4K_4FeCy_6 \rightarrow 4KCy + FeC_2 + N_2$, although it is probably much more complicated than this. When warmed with *dilute* sulphuric acid, hydrogen cyanide (*q.v.*) is formed; with *concentrated* sulphuric acid, carbon monoxide is evolved:

$$K_4FeCy_6 + 6H_2O + 6H_2SO_4 = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

When a saturated solution of potassium ferro-cyanide, freed from dissolved air by boiling, is treated with concentrated hydrochloric acid in the cold, a white crystalline powder called **ferrocyanic acid** is formed; it has the empirical formula,

H_4FeCy_6 Ferrocyanic acid turns blue on exposure to the air owing to the partial decomposition of the salt and the formation of Prussian blue. Potassium ferrocyanide is also called *yellow prussiate of potash*, while the next salt to be described, potassium ferricyanide, is also called *red prussiate of potash*.

Potassium ferricyanide, K_3FeCy_6.—If an aqueous solution of potassium ferrocyanide be treated with oxidizing agents like chlorine, bromine, nitric acid, hydrogen peroxide, etc., it acquires a dark reddish colour, and crystals of potassium ferricyanide separate when the solution is concentrated by evaporation: $2K_4FeCy_6 + Cl_2 = 2KCl + 2K_3FeCy_6$. The potassium ferricyanide is separated from potassium chloride by recrystallization. Potassium ferrocyanide decomposes when ignited out of contact with the air and forms a complex mixture of potassium cyanide, iron carbide, etc. When a saturated solution is treated with concentrated hydrochloric acid, in the cold, reddish-brown crystals of **ferricyanic acid,** H_3FeCy_6, separate from the solution.

TABLE XXXIV.—PROPERTIES OF THE FERRO- AND FERRICYANIDES OF SOME METALS.

	Ferrocyanides added to	Ferricyanides added to
Ferric chloride	Deep blue, precipitate of **ferric ferrocyanide** also called **Prussian blue,** insoluble in hydrochloric acid, soluble in oxalic acid.	No precipitate in neutral solutions, but the solution is coloured green or blue.
Ferrous chloride	Bluish-white precipitate which rapidly darkens on exposure to air, or by adding a drop of bromine.	Deep blue precipitate of **ferrous ferricyanide** also called **Turnbull's blue.**
Copper sulphate	Reddish-brown precipitate.	Yellowish-green precipitate.
Zinc sulphate	White precipitate.	Orange precipitate.
Silver nitrate	White precipitate.	Reddish-brown precipitate.

Various salts of ferrocyanic and ferricyanic acids have characteristic colours, and consequently, potassium ferrocyanide and ferricyanide—particularly the former—are used in qualitative analysis. The reactions of both salts with ferrous and ferric salts should be noticed particularly.

§ 2. Hydrocyanic Acid and the Cyanides.

Potassium cyanide, KCy.—Potassium cyanide was formerly made by heating potassium ferrocyanide either alone or mixed with potassium carbonate in an iron crucible to a red heat: $K_4FeCy_6 + K_2CO_3 = 5KCy + KCyO + Fe + CO_2$. The mass was lixiviated with water, and the solution evaporated to dryness, fused, cast into sticks and sold as potassium cyanide. The commercial salt always contains some potassium cyanate, KCyO. Potassium cyanide is extensively used in electroplating, gilding, the extraction of gold from quartz, and in photography. Fused potassium cyanide is a powerful reducing agent, and it liberates metals from their oxides, and is at the same time converted into potassium cyanate: $SnO_2 + 2KCy = 2KCyO + Sn$. Hence potassium cyanide is used in metallurgy and in analytical work. The potassium cyanate, KCyO, can be extracted by lixiviating the mass with dilute alcohol, and subsequent evaporation. When heated alone, potassium cyanide fuses without decomposition in the absence of air, but if air be present, it is partially converted into potassium cyanate. Potassium cyanide is soluble in water and in hot alcohol. When potassium cyanide or ferrocyanide is boiled with water holding yellow mercuric oxide in suspension, **mercuric cyanide,** $HgCy_2$, is formed. The reaction with potassium ferrocyanide is symbolized: $K_4FeCy_6 + 3HgO + 3H_2O = Fe(OH)_2 + 4KOH + 3HgCy_2$.

A. Frank and N. Caro patented a process in 1895 for the fixation of the nitrogen of atmospheric air by heating calcium or barium carbides in an atmosphere of nitrogen between 1000° and 1100°. Nitrogen, it will be remembered, is a by-product in the process for separating oxygen from liquid air. The absorption of nitrogen by the carbides commences about 700°, but the reaction is incomplete; at 1100°, however, the absorption

is practically complete, and **calcium cyanamide,** $CaCN_2$, that is, Ca=N—Cy is formed: $CaC_2+N_2 \rightarrow CaCN_2+C$. A large amount of heat is evolved at the same time. The mixture of carbon and calcium cyanamide so obtained is known in commerce as *nitrolime* or *Kalkstickstoff*. When treated with superheated steam, calcium cyanamide forms calcium carbonate and **ammonia**: $CaCN_2+3H_2O=CaCO_3+2NH_3$. Calcium cyanamide is used as a nitrogenous fertilizer, and in the manufacture of cyanides, for if calcium cyanamide be melted with a suitable flux—sodium chloride—or carbonate, sodium cyanide is produced: $CaCN_2+C=CaCy_2$; and $CaCy_2+Na_2CO_3=CaCO_3+2NaCy$.

Hydrogen cyanide, HCN.—Hydrogen cyanide is made by distilling a mixture of powdered potassium cyanide with a

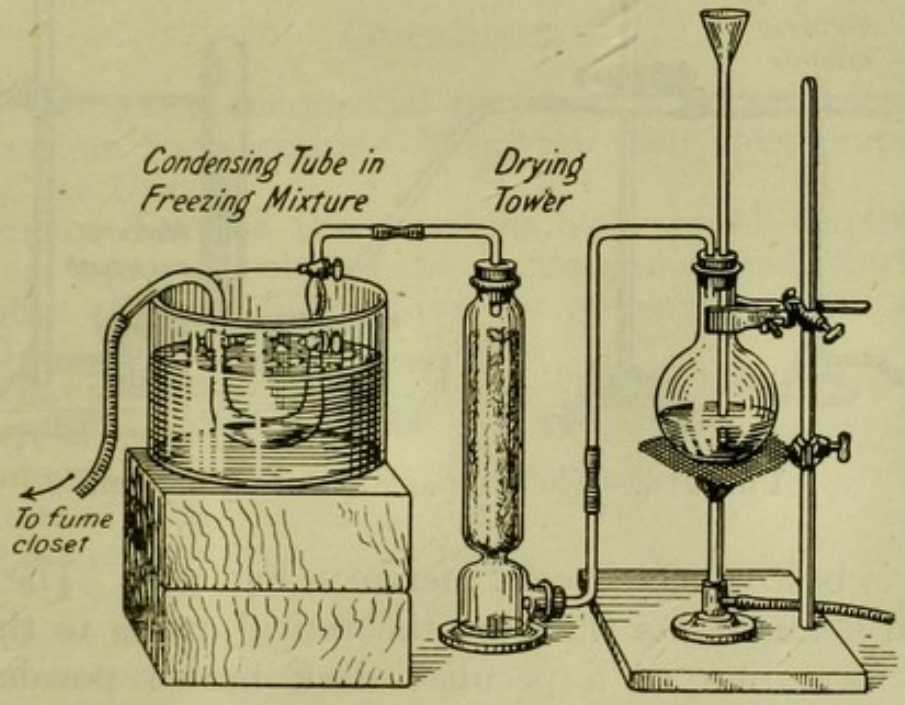


FIG. 217.—The Preparation of Anhydrous Hydrogen Cyanide.

mixture of equal volumes of sulphuric acid and water; if concentrated acid be used, a considerable amount of carbon monoxide is evolved. Instead of collecting the distillate in a receiver, Fig. 22, if the vapour be passed through a tower containing calcium chloride to remove the water, and the dry hydrogen cyanide led through a U-condensing tube surrounded by ice, the gas condenses to a colourless liquid, Fig. 217. It is not

probable that the teacher will allow a young student to make the acid or the gas. *Pure hydrogen cyanide is one of the most deadly poisons known, and hence great care must be taken in experiments with the gas, and indeed with cyanides generally.* The liquid boils at 26·5°, and freezes at −15° to a white solid. It dissolves in water in all proportions, and the solution—called **hydrocyanic acid**—has the smell of bitter almonds. Hydrocyanic acid is monobasic, and the salts, as indicated above, are called **cyanides.** Hydrocyanic acid is one of the weakest of acids, and very dilute solutions are used in medicine under the name of **prussic acid.**

Cyanogen.—Cyanogen, Cy_2, is a gas made by heating mercuric or silver cyanide in a hard glass tube: $HgCy_2 = Hg + Cy_2$.

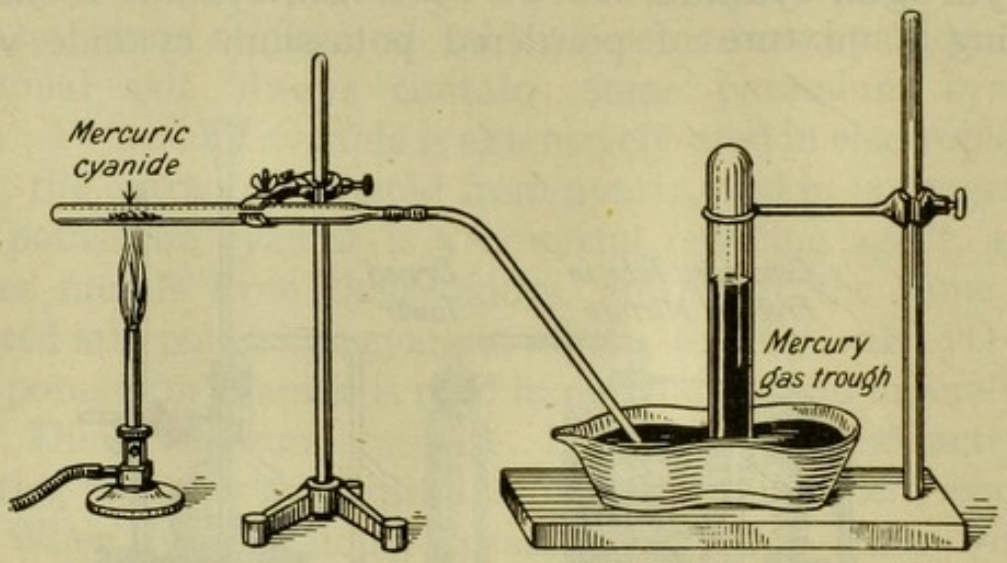


FIG. 218.—The Preparation of Cyanogen.

The gas is best collected over mercury, Fig. 218. The yield of cyanogen is much less than the theoretical owing to the simultaneous formation of a peculiar dark brown powder called **paracyanogen.** This substance appears to be a polymer of cyanogen, because if continually heated it furnishes ordinary cyanogen. Cyanogen is a colourless poisonous gas with a faint odour which reminds some people of the smell of peaches. Cyanogen burns with a violet-coloured flame forming carbon dioxide and nitrogen. Analyses and vapour density determinations correspond with the formula C_2N_2.

Thiocyanic acid and the thiocyanates.—If the alkaline cyanides be fused with sulphur, a change, analogous with the

oxidation of the alkaline cyanide, occurs, and the so-called **thiocyanates,** or **sulpho-cyanides,** are formed : $KCy + S = KCyS$. The fused mass, when cold, is lixiviated with dilute alcohol, and the alcoholic solution, when concentrated by evaporation, furnishes colourless deliquescent crystals of potassium thiocyanate, KCNS. The acid is made by distilling the potassium salt under pressure with dilute sulphuric acid. Ammonium thiocyanate is conveniently made by digesting concentrated ammonia with carbon disulphide : $4NH_3 + CS_2 = NH_4SCy + (NH_4)_2S$. The thiocyanates give a blood-red ferric thiocyanate with ferric salts, and no coloration occurs with the ferrous salts if ferric salts be absent. Hence, this reagent is used in qualitative analysis.

Questions.

1. Describe the commercial preparation of potassium cyanide and potassium ferrocyanide. What are their chief properties and uses ?—*Cape Univ.*

2. Briefly describe the reactions you would employ in preparing an aqueous solution of hydrocyanic acid starting from nitrogenous animal refuse. Give the properties of the anhydrous acid.—*Adelaide Public Exam. Board.*

3. What are the products generated by the complete combustion in oxygen of sulphuretted hydrogen, ammonia, carbon monoxide, and cyanogen ? What bulks of these products are formed from one volume of each combustible gas, all substances being measured in the gaseous or vaporous state and at the same temperature or pressure ?—*Science and Art Dept.*

4. What changes take place when the following salts are heated with concentrated sulphuric acid : (*a*) common salt, (*b*) nitre, (*c*) borax, (*d*) yellow prussiate of potash ? Give equations.—*Science and Art Dept.*

CHAPTER XXXIV

Silicon

§ 1. Silica, or Silicon Dioxide.

There is a quaint Scandinavian fable which says that the kobolde—dwarfs or goblins—which inhabited mines and caves in the earth gathered metals and fashioned them into weapons which they presented to mortals whom they favoured. If the kobolde be surprised, the dwarfs immediately assume the form of beautiful crystals, which are therefore called "quartz."

Quartz.—Quartz occurs in hexagonal prisms terminating in hexagonal pyramids. A single quartz crystal weighing very nearly one ton was found at Calaveras (U.S.A.). The purest varieties of quartz—called *rock crystal*, Fig. 219—are colourless with a specific gravity 2·67, and are hard enough to cut glass. The crystals are sometimes coloured with traces of various oxides. Thus, manganese oxide gives *amethyst quartz*; *smoky quartz* probably owes its colour to the presence of carbonaceous matter; *milky quartz* owes its opacity to the presence of innumerable air bubbles. Quartz also occurs massive in quartzite and quartose rocks. Quartose sands and sandstones are also more or less impure quartz. Rock crystal was one of the first crystallized minerals to attract the attention of the early philosophers, and they believed it to be a form of ice "so hard and dry that it becomes crystal," but, says the old historian Pliny, "it is not easy to explain why the crystals grow six-sided." G. Agricola (1550) reported his belief that "rock crystal is not ice, but a denser product of cold." The Greek word for ice (*crystallos*) has been extended to cover the whole science of crystals—crystallography.

Amorphous silica.—Amorphous silica occurs in nature associated with 3 to 12 per cent. of water in the mineral *opal*, which may be colourless or tinted yellowish-brown, etc., with iron oxide, organic matter, etc. Chert, flint, chalcedony, kieselguhr, jasper, contain more or less amorphous silica associated with quartz so difficult to recognize that these minerals were once thought to be amorphous silica. They are said to be *crypto-crystalline*—from the Greek word for hidden.

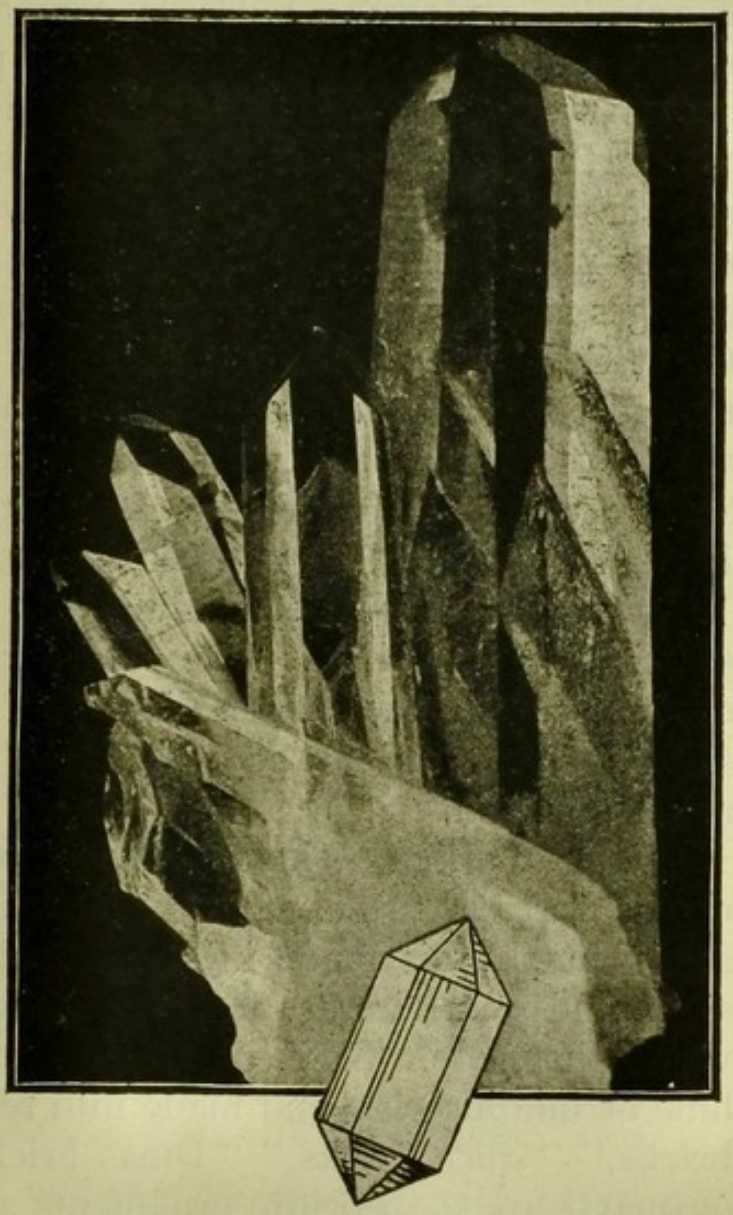


FIG. 219.—Group of Quartz Crystals from Duaphine.

Properties of silica.—Silica melts to a colourless glass—quartz glass—in the oxyhydrogen blowpipe. The melting-point of quartz is not well defined. Melting commences about 1600°. Silica can be vaporized in the electric furnace. The specific gravity of vitreous silica is about 2·22. The coefficient of thermal expansion of vitreous quartz is remarkably small—nearly 0·0000005—so that quartz glass can be very rapidly cooled without cracking. For instance, quartz glass can be heated red hot in the blowpipe and plunged in cold water without fracture; under the same conditions, ordinary glass—with a coefficient of thermal expansion of 0·000008—would shatter into small fragments.

Crystalline and vitreous silica appear to be insoluble in water and in all acids except hydrofluoric acid. Fused silica is readily attacked by phosphoric acid and by the alkalies. Crystalline silica is slowly attacked by aqueous solutions of alkaline hydroxides and carbonates, but the amorphous variety is rapidly attacked. Silica is also attacked by superheated water, and a small quantity may pass into solution. The necessary conditions seem to prevail in deep-seated cavities in the earth. The water rising to the surface is cooled, and the pressure reduced. Some of the dissolved silica is then deposited at the mouth of the spring as a thick jelly. This afterwards changes into a hard white porous mass called *geyserite*. The Great Geyser of Iceland, for instance, is surrounded by a large mound or hillock of silica with a funnel-like cavity from which the geyser discharges. Similar geysers occur in the Hot Springs of New Zealand, the Mammoth Springs of Yellowstone Park, U.S.A., etc. In many cases—*e.g.* the mineral springs at Yellowstone Park—the alkalinity of the water facilitates the solution of the silica. The alkaline silicates so formed are decomposed by the carbon dioxide of the atmosphere, and the silica is deposited as geyserite or "siliceous sinter" in the neighbourhood.

Uses of silica.—Quartz glass is used for the manufacture of elastic threads to suspend the delicate parts of electrical instruments. It is made into tubes, flasks, dishes, etc. Sandstone and quartzite are used for building stones, grindstones, whetstones, etc. Sand or sandstone is ground with a little lime or binding clay and made into refractory bricks "ganister bricks," "silica bricks," "Dinas bricks," etc. Many varieties of quartz are shaped into ornaments and gems. Diatomaceous earth—also called tripoli, kieselguhr, or (wrongly) infusorial earth—is used as a polishing powder, in the manufacture of cement, soluble glass, dynamite, and refractory bricks.

History.—The element does not occur free in nature, but its oxygen compound—silica—is well known. The process of manufacturing glass from silicates has been known from ancient times, and J. J. Becher believed that these silicates contained a peculiar earth which he called *terra vitrescibilis* (vitrifiable

earth); this is now called "silica." It was known in the seventeenth century that Becher's vitrifiable earth does not fuse when heated alone, and that a fusible glass is formed when it is heated with other earths. O. Tachenius (1660) noticed that the vitrifiable earth had acid rather than alkaline properties; K. W. Scheele (1773) showed it to have the characteristics of a refractory acid.

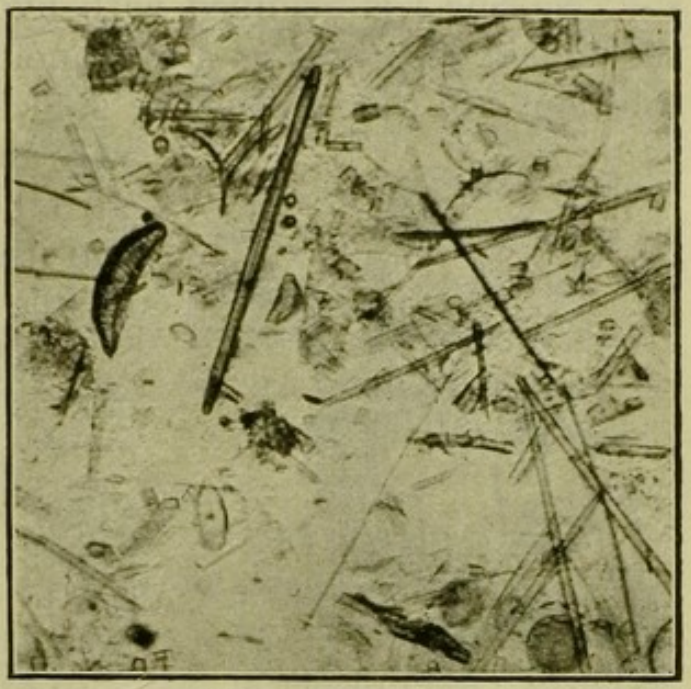


FIG. 220.—Kieselguhr from Unterluss near Hannover.

Silica is one of the most important compounds in the "half-mile crust" of the earth. It occurs abundantly in the mineral kingdom, and it is also common in the connective tissue of animals, fibres of vegetables, etc. The so-called *kieselguhr* or "diatomaceous earth" is a mass of the siliceous skeletons of dead diatoms illustrated by the micro-photograph, Fig. 220. Silica, SiO_2, occurs in nature free and combined with various bases to form numerous mineral silicates. Free silica occurs crystalline and amorphous. There are three types of crystalline silica: quartz, tridymite, and cristobalite.

§ 2. The Silicic Acids and the Silicates.

If the soluble alkaline silicates be treated with acids, an amorphous gelatinous mass called "silicic acid" is obtained. This is appreciably soluble in water and in acids, and is readily dissolved by dilute solutions of the alkalie hydroxides and carbonates. The jelly-like mass, when dried in air, retains about 16 per cent. of water; and at 100°, about 13 per cent. The mass is then practically insoluble in water and acids. By heating above 500°, anhydrous silica is formed.

A dilute solution of sodium carbonate—say, 5 per cent.—

dissolves all the silicic acids. Native quartz is almost insoluble in 5 per cent. sodium carbonate, but if finely powdered, appreciable quantities are dissolved in a short time.

When a solution of water glass (sodium or potassium silicate, say, Na_2SiO_3) is acidified with hydrochloric acid, some of the silicic acid separates as a gelatinous mass, and some remains in solution. If the solution be sufficiently dilute, the silicic acid will all remain in solution along with the excess of hydrochloric acid, and the sodium chloride formed in the reaction: $Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl$. The hydrochloric acid and the sodium chloride can be separated from the silicic acid by dialysis because it passes through parchment very slowly while sodium chloride and hydrochloric acid pass through quickly. The apparatus illustrated by Fig. 221 can be used; it is called a **dialyzer,** and the operation **dialysis.** The liquid to be dialyzed is placed in the bag of parchment tied to the glass vessel, closed by a plug of cotton wool. A current of water is kept circulating about the outside of the dialyzing membrane. The dialyzing surface is relatively great so that the operation is fairly rapid.

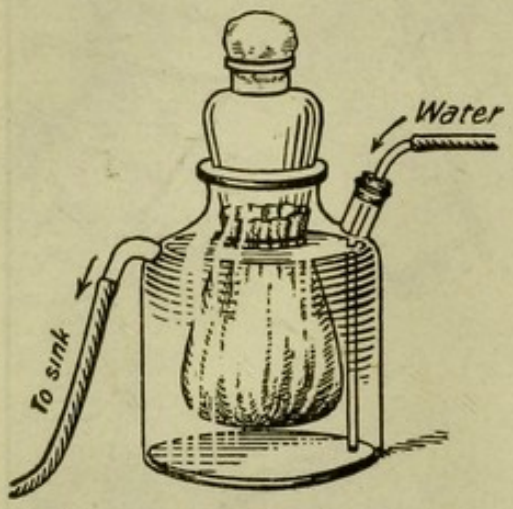


FIG. 221.—Proskauer's Dialyzer.

Silicates.—Although chemically inactive at ordinary temperatures, silica acts as a powerful acid anhydride at high temperatures, combining with the bases and many metallic oxides to form more or less fusible **silicates.** The more fusible silicates—*e.g.* lead silicate—are used in making glasses and pottery glazes. Potassium and sodium silicates are soluble in water, and the aqueous solution is sold as **water glass,** and the solid as **soluble glass.** The powerful acid character of silica at high temperatures turns on the fact that most of the acid anhydrides—SO_3, P_2O_5, etc.—volatilize at much lower temperatures, and consequently, as soon as ever so little, say, sulphur trioxide is displaced, the volatile anhydride passes

away and ceases to compete with the silica for the base. At lower temperatures, sulphur trioxide rapidly displaces silica from the bases when competing under equal conditions.

Many of the simple silicates are attacked by hydrochloric acid, particularly if they have been first roasted at a dull red heat. The silicic acid then separates as a gelatinous mass. The insoluble silicates are usually brought into solution for analysis, by fusion with sodium carbonate, and the cold " cake " broken down by treatment with dilute hydrochloric acid. When the solution is evaporated to dryness, nearly all the silica separates in a form insoluble in dilute hydrochloric acid.

The formation of metallic silicates is well illustrated by familiar experiment—*Silica garden:* a litre beaker is filled with a solution of sodium silicate (sp. gr. 1·1) and crystals of, say, cobalt nitrate, cadmium nitrate, copper sulphate, ferrous sulphate, nickel sulphate, manganese sulphate, zinc sulphate, etc., are allowed to fall into the beaker so as to rest on different parts of the bottom. The whole is allowed to stand overnight in a quiet place, when plant-like shoots are obtained which have a form and colour characteristic of the salts used (Fig. 222).



FIG. 222.—Silica Garden.

Assuming silica has the formula SiO_2, silicon acts as a quadrivalent element. The corresponding acids will be orthosilicic acid, H_4SiO_4, and metasilicic acid, H_2SiO_3. These three substances are represented by the graphic formulæ:

$O = Si = O$

Silica, SiO_2.

$O = Si\langle^{OH}_{OH}$

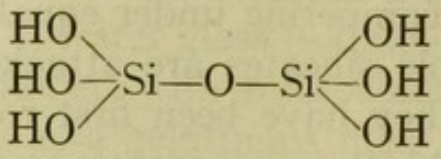
Metasilicic acid, H_2SiO_3.

$HO\rangle Si\langle^{OH}_{OH}$
$HO\rangle$

Orthosilicic acid, H_4SiO_4.

Salts of these acids occur free in nature, thus *willemite*, Zn_2SiO_4, is a **zinc orthosilicate,** and *wollastonite* a **calcium metasilicate.** Still more complex silicates are considered to be derived from the union of several molecules of the silicic acids with the loss of one or more molecules of water. Thus, *serpentine* is considered to be a magnesium salt of a polysilicic acid

derived from the union of two molecules of the ortho-acid and the loss of one molecule of water :



The constitution is probably much more complex when the silicates are associated with aluminium, and such form compounds which are called **alumino-silicates.**

§ 3. The Weathering of Rocks.

The hills are shadows and they flow
From form to form and nothing stands;
They melt like mists, the solid lands
Like clouds they shape themselves and go.

HUTCHINSON.

When potash felspar and many other natural silicate rocks are exposed to certain natural influences, they are finally converted into an insoluble crystalline or amorphous (colloidal) powder—clay, and other materials. The more important agents which facilitate the decomposition and disintegration—weathering—of the aluminium silicates are : (1) Volcanic gases (steam, hydrofluoric acid vapours, etc.). (2) Water draining from peat bogs ; and coal beds—this water contains organic acids in solution. (3) Spring or rain water containing carbon dioxide, etc., in solution.

Formation of clays.—The early stages of the decomposition —weathering—of the felspar is indicated by the apparent clouding of the crystals of felspar ; the felspar becomes more and more opaque ; and finally disintegrates. Consequently, granitic rocks, with felspar as a matrix, Fig. 37, disintegrate and leave behind the clay mixed with the more or less resistant varieties of mica, quartz, and other minerals which originally formed the granitic rock. The clay may be leached by streams of water from the place where it was formed, transported from the hills, and deposited at lower levels. All kinds of *débris* from the rocks and soils, etc., over which the clays are carried may be with the clay. Transported clays are usually, but not always,

less pure than the residual or primary clays. The residual clays formed by the weathering of the less ferruginous granitic rocks, after an elaborate process of washing and settling, furnish white *china clay* or *kaolin*, which has very nearly the empirical composition : $Al_2O_3.2SiO_2.2H_2O$. The object of the washing is to separate the china clay from the unweathered quartz, mica, etc. The term *clay* is applied industrially to a fine grained mixture of various minerals which has these qualities : (1) It is plastic enough to be moulded when it is wet ; (2) It retains its shape when dried in spite of a certain amount of contraction ; and (3) When the moulded mass is heated to a high temperature it sinters together forming a hard coherent mass without losing its original contour. These properties have given clays an important place—probably third or fourth—in the world's industries. Clays are used in the manufacture of building bricks, tiles, firebricks, crucibles, gas retorts, sanitary goods, pottery, etc. ; china clay is also extensively employed for filling paper, cotton, etc.

Pottery and bricks.—British pottery is generally made from a plastic mixture of white-burning clay, with flint quartz, and felspar or Cornish stone. The mixture is moulded into the desired shape, dried, and fired between 1000° and 1200° according to the kind of ware being made. This forms the so-called " biscuit " body. A fusible mixture—containing lead borosilicate, clay, felspar, etc., ground together to form a " slip " with water—is then spread over the surface of the " biscuit body," and the whole is refired to 900° or 1000°. The melted mixture covers the surface of the " body " with a glassy film or " glaze." There are many modifications. The ware may be decorated by painting coloured oxides on the biscuit body before glazing ; or by painting fusible enamels on the glaze and refiring ; or the glaze itself may be coloured with suitable oxides. Glaze and body may be fired in one operation with or without a preliminary baking of the body. There are also considerable variations in the composition of the body and glaze. The chief varieties of pottery are *earthenware*—made from white burning clays, Cornish stone, and flint ; *hard porcelain*, made—principally on the Continent—from clays, felspar,

and quartz—with or without a little lime; *bone china*—made chiefly in England—from bone ash, clay, and Cornish stone; and the commoner varieties of pottery made from special mixtures—often local clays glazed with a mixture containing galena. *Drain pipes* are also made from local clays, which burn a buff or red colour—and glazed by throwing salt into the kiln. The salt decrepitates, volatilizes, and then attacks the surface of the drain pipe and covers it with a glass-like skin—*salt glaze*. *Tobacco pipes* (unglazed) are made from siliceous clays, that is, from clays containing more or less finely divided silica. *Firebricks* are made from refractory clays which soften at about 1650°. The refractory clay is moulded by hand or machinery, and fired to about 1100°–1200°. *Common building bricks* are usually made from less refractory clays fired at a lower temperature.

Glass.—Glass is a congealed solution of several silicates—most commonly potassium, calcium, and lead—which has not crystallized on cooling. It is made by fusing together a mixture of clean sand, limestone, or whiting or lime, sodium or potassium carbonate, and litharge or red lead in the right proportions. Traces of manganese dioxide or selenium are sometimes added to neutralize the yellow or green tinge due to the presence of ferrous or ferric oxide present as impurity in the ingredients used in making the glass. The mixture is melted in fireclay pots, and when the molten mass has cooled to the right temperature, a portion is collected at the end of an iron tube and brought to the desired shape by forcing it into a mould, or blowing into the tube and twisting or swinging the plastic mass of glass as required. Details of the procedure vary with the particular objects being made. Rapidly cooled glass is brittle and liable to fracture, hence the glass is annealed in an annealing kiln, where it can be cooled as slowly as desired. If cooled too slowly the glass devitrifies.

Window glass is a soda-lime silicate. This type of glass is sometimes called "soda glass" or "soft glass," and it is used for making chemical glass ware. *Window glass, plate glass,* and glass for table ware, and bottles are also made from the same constituents in different proportions and of different degrees of

purity. *Bohemian glass* is a potash-lime silicate. It is a hard glass and fuses only at a high temperature, hence it is used for making chemical apparatus designed to withstand high temperatures. It also resists the solvent action of water better than soda-glass. *Jena glass* and Bohemian glass are varieties of potash-lime glass. *Flint glass* is a lead potash silicate. It is lustrous, and refracts light much better than other types of glass. It is used for making lenses for optical purposes. Some varieties are made into artificial gems and ornamental glass. *Cut glass* is a variety of lead glass which is ground or "cut" on emery or carborundum wheels. Besides these special admixtures, metallic oxides may be added to colour the glass. *Translucent or opal glass* is made by the addition of bone ash, or fluorspar, or cryolite. Boric acid is also used in the manufacture of glass with a high refractive index.

§ 4. Silicon Fluoride and the Fluosilicates.

Silicon tetrafluoride, SiF_4.—This gaseous compound is important; it is made by the action of hydrofluoric acid upon silica or on a silicate—*e.g.* glass: $SiO_2 + 4HF \rightarrow 2H_2O + SiF_4$. Silicon tetrafluoride is usually made by the action of hydrofluoric acid derived from a mixture of calcium fluoride and sulphuric acid upon silica. The mixture is heated in a flask—illustrated in Fig. 223—fitted with a safety funnel containing mercury. An excess of sulphuric acid is used to absorb the water formed during the reaction. Silicon tetrafluoride is a colourless gas with a pungent odour resembling hydrogen chloride. The density of the gas is 104·2 (oxygen = 32). This corresponds with the formula SiF_4. Boron fluoride and chloride can be made by a similar process, but not silicon chloride. This is supposed to be due to the fact that boron trichloride is not so readily hydrolized by water as silicon tetrachloride.

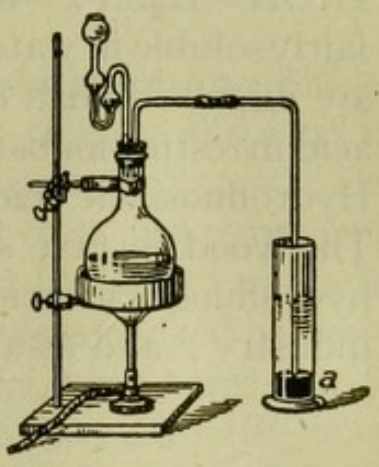


FIG. 223.—Preparation of Hydrofluosilicic Acid.

Hydrofluosilicic acid, H_2SiF_6.—If silicon tetrafluoride be

passed into water, it decomposes, gelatinous silicic acid is precipitated, and hydrogen fluoride is formed: $SiF_4 + 4H_2O = Si(OH)_4 + 4HF$. The hydrogen fluoride immediately combines with a molecule of silicon tetrafluoride producing an aqueous solution of hydrofluosilicic acid. The whole reaction is written: $3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6$. In order to prevent the choking of the delivery tube by the separation of silicic acid when the silicon tetrafluoride is passed into water, it is well to let the delivery tube dip below a little mercury, *a*, Fig. 223, placed at the bottom of the vessel of water. The aqueous layer is frequently stirred to prevent the formation of channels of silicic acid through which the gas can escape into the atmosphere without coming in contact with the water. This is a good method of making hydrofluosilicic acid. The silicic acid is separated from the aqueous solution by filtration; the aqueous solution cannot be concentrated very much by evaporation because it decomposes into silicon tetrafluoride and hydrogen fluoride.

Hydrofluosilicic acid reddens blue litmus, and it is neutralized by the bases forming salts, **fluosilicates**. For instance, with potassium hydroxide, it forms potassium fluosilicate, $2KOH + H_2SiF_6 = K_2SiF_6 + 2H_2O$. Most of the fluosilicates are fairly soluble in water, but the potassium and barium fluosilicates are dissolved with difficulty. Hence the use of hydrofluosilicic acid in testing for barium salts, and in the estimation of potassium. Hydrofluosilicic acid is used for giving wood a stone-like surface. The wood is first soaked in lime water and then treated with hydrofluosilicic acid. The acid is also used in the paper industry; and as an antiseptic in medicine.

§ 5. Silicon.

Silicon.—The element can be made by heating potassium or sodium in an atmosphere of silicon chloride or silicon fluoride: $SiF_4 + 4K = Si + 4KF$. The brown mass so formed—called **amorphous silicon**—is washed with water and hydrofluoric acid, heated at a dull red heat, and finally washed and dried. If silica be heated with metallic magnesium a **crystalline silicon** remains when the magnesia is dissolved away with hydrochloric

acid. The reaction is symbolized: $SiO_2 + 2Mg = 2MgO + Si$; if an excess of magnesium be employed, **magnesium silicide,** Mg_2Si, is formed. A more or less impure crystalline silicon has been made commercially by heating quartz with coke in the electric furnace: $SiO_2 + 2C = 2CO + Si$. If too much coke be employed a carbon silicide is formed. Silicon so prepared is sold in metallic-looking lumps and used in the manufacture of alloys.

Crystalline silicon forms dark grey opaque needle-like crystals or octahedral plates. It is hard enough to scratch glass. Its specific gravity varies between 2·34 to 3, according to the temperature to which it has been heated. It burns when heated in chlorine and fires spontaneously in fluorine. Silicon is insoluble in acids, but dissolves in a mixture of nitric and hydrofluoric acids. Crystalline silicon slightly conducts electricity, amorphous silicon does not. Chemically, crystalline silicon resembles amorphous silicon, but it is not so active. Silicon combines with the metals forming **silicides.** **Siloxicon** is the trade name for a greyish-green granular powder formed by heating a mixture of silica with carbon to about 2500° in an electric furnace. It varies in composition between Si_2C_2O and Si_7C_7O. It is used as a refractory material when shaped into bricks, furnace linings, etc.

Silicon carbide, carbon silicide, carborundum—SiC.—This compound is made by fusing a mixture of coke and sand in an electric resistance furnace—estimated temperature 3500°. The furnace is a large oblong box with permanent ends, and temporary sides. Large carbon electrodes are fitted into the two ends, and project into the furnace. Granulated coke is packed between the electrodes. A mixture of sand and coke, with some salt to make the mass fusible, and some sawdust to make the mass porous, are packed about the carbon core and held in place by the side walls of loosely packed bricks. The furnace is illustrated diagrammatically in Fig. 224. A powerful current of electricity is sent through the charge. The change which takes place is represented by the symbols: $SiO_2 + 3C \rightarrow SiC + 2CO$. The operation is over in about eight hours. The furnace is then allowed to cool; the side walls are removed, and the silicon carbide removed. The best grades are found nearest the core.

The product is crushed and treated with sulphuric acid to remove impurities ; it is then washed, dried, and graded according to size.

Carborundum crystallizes in hexagonal plates when pure ; it may be transparent and colourless, or vary in tint from emerald green to brown or black. The latter varieties are most common. The specific gravity is 3·2. It is not attacked by acids—even hydrofluoric acid. It is decomposed by fusion with alkaline hydroxides. It is nearly as hard as the diamond, and accordingly is largely used as an abrasive powder and made into whetstones, hones, grinding wheels, polishing cloths, etc. It is also very

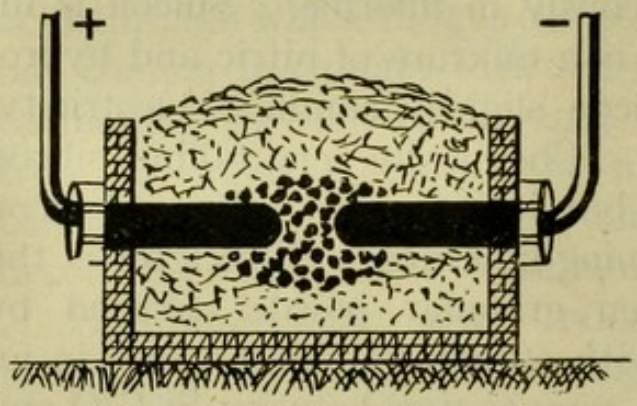


FIG. 224.—Carborundum Furnace (Diagrammatic).

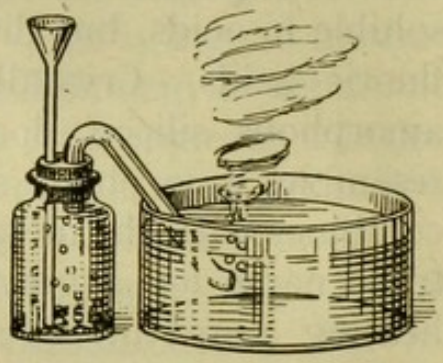


FIG. 225.—Hydrogen Silicide.

refractory, and when mixed with clay has special uses as a refractory material for protecting furnace walls, etc.

Hydrogen compounds.—There are three compounds of silicon and hydrogen : silicon-methane or gaseous silicon hydride, SiH_4, corresponding with methane, CH_4 ; silico-ethane or liquid silicon hydride, Si_2H_6, corresponding with ethane, C_2H_6 ; and silico-acetylene or solid silicon hydride, Si_2H_2, corresponding with acetylene, C_2H_2.

Silico-methane, SiH_4, or silicane.—This gas is most conveniently made by the action of concentrated hydrochloric acid on magnesium silicide whereby hydrogen gas containing 4 or 5 per cent. of silicane and a trace of silico-ethane is formed. The latter is spontaneously inflammable in air, the former is not. Hence the gas prepared by the above described process is spontaneously inflammable in air. This property is generally illustrated by apparatus shown in Fig. 225. The magnesium

silicide is placed in the bottle fitted up as shown in the diagram and the delivery tube and bottle filled with water. Hydrochloric acid is then added and the bubbles of gas ignite as they rise to the surface of the water in the dish, forming rings of silicon dioxide.

Questions.

1. Silica has no taste and does not act on blue litmus. Why is this substance sometimes called silicic acid ?—*London Univ.*

2. What is the action of sulphuric acid on the following substances : limestone, copper, zinc, fluorspar, and common salt ? Represent the reactions by equations, and very briefly describe the chief properties of the products.—*London Univ.*

3. Give a short account of the forms of silica met with in nature, and point out the chief characters by which crystallized silica and diamond can be distinguished.—*London Univ.*

4. What meaning have you been taught to attach to the word " salt " ? Discuss the title of potassium hydroxide and hydrogen chloride to be called salts. Arrange the following elements according to their usual *valency :* sodium, chlorine, copper, silicon, carbon, oxygen, zinc, bismuth, arsenic, iron, calcium, phosphorus ; and indicate those cases in which the valency apparently varies.—*Science and Art Dept.*

5. Given a mixture of sand and sulphur, how would you separate them from each other ? What would be the effect of heat on each of these substances ? Are they both elements ?—*London Univ.*

6. Under what circumstances, if any, does water react chemically with the following substances : sodium peroxide, sodium amalgam, calcium carbide, silicon tetrafluoride, and phosphorus pentachloride ? Explain briefly the nature of the chemical changes taking place in each case.—*Board of Educ.*

7. How would you prepare from flints specimens of pure silica, and of silicon fluoride ? Give equations. In what respects does silicon resemble carbon ?—*Owens Coll.*

8. How is hydrofluoric acid prepared ? Explain its action upon quartz, glass, zinc, and sodium carbonate.—*Science and Art Dept.*

9. Given some sodium silicate in a platinum dish, how would you get rid of the silicon ?—*Cape Univ.*

10. A little finely powdered calcium fluoride is mixed in a test tube with an equal weight of pure sand (silica). The mixture is moistened with concentrated sulphuric acid and then gently warmed. A gas is evolved. A glass rod with a drop of water at its lower

end is held in this gas. The water drop becomes enclosed in a thin white solid shell. Explain the action and give equations.—*Bombay Univ.*

11. State the chemical composition of each of the following substances : diamond, quartz, opal, glass, marble, bone ash, borax. How could diamond and quartz be distinguished from one another ? —*Sydney Univ.*

12. A crystal is given to you, and you are requested to ascertain by chemical experiment whether it is a diamond or rock crystal. Describe an experiment which will furnish the required information. —*London Univ.*

13. How can you prove that the constituent of flint has properties similar to other acids ? and how can this substance be obtained dissolved in water ?—*London Univ.*

14. Under what conditions can compounds of hydrogen with the following elements be produced : iodine, bromine, nitrogen, antimony, and silicon ? Describe the properties of each compound.

CHAPTER XXXV

Tin and Lead

§ 1. Tin.

History.—Discoveries of tin in Egyptian tombs show that the metal was fairly common in olden times. It is not certain if the Hebrew word "bedil" in the Pentateuch, translated by the Greek word κασσίτερος (cassiteros), and by the Latin word *stannum*, really means tin. The word "stannum" appears to have been used by the Romans to designate certain alloys containing lead. It is not certain whether the Phœnicians obtained their tin from India, Britain, or Iberia. The resemblance between the Sanscrit word "castîra" and the Greek "cassiteros" has been used as an argument in favour of the Indian origin of Phœnician tin. Pliny states that "cassiteron" was obtained from "Cassiterides (British Isles) in the Atlantic Ocean." This no doubt refers to the tin then obtained from the Cornish mines, for "certain islands north of Spain" were often referred to as the *Insulæ Cassiterides* (Tin Islands). The Romans appear to have distinguished lead from tin by calling lead *plumbum nigrum*, and tin *plumbum candidum*. The word "stannum" was later restricted to tin proper. The alchemists called tin "Jupiter," and represented it by ♃, their symbol for the planet Jupiter.

Occurrence.—There are several reports of the occurrence of metallic tin in nature. Practically *tinstone* or *cassiterite* is the sole source of commercial tin. This mineral occurs in tetragonal crystals coloured brown or black by impurities, chiefly iron. Cassiterite is stannic oxide, SnO_2, contaminated with more or less arsenical pyrites, copper pyrites, tungstates, and various metallic sulphides. "Lode" or "vein" tin is cassiterite which

is obtained from veins or lodes in primary deposits; while "stream" tin is cassiterite from alluvial secondary deposits where it occurs in more or less rounded lumps. The miners speak of tinstone as "tin" or "black tin" to distinguish it from the metal which is called "white tin." It is comparatively rare. About one-third of the world's output of tin is produced in the Malay peninsula. Tin is also produced in the Malay archipelago, Bolivia, Australia, Cornwall, South Africa, Bohemia, and Saxony, etc.

Extraction.—The ore is first concentrated by washing away the earthy impurities. The high specific gravity of tinstone —6·8 to 7·0—and the low specific gravity of the earthy matters—2·5 to 3—enables this to be done without much trouble. This process usually works well with stream tin; but vein tin usually requires more complex treatment. The crushed ore is first washed to remove earthy matters. The arsenic and sulphur are removed by an oxidizing roast. The ore is passed through an intense magnetic field, when most of the mechanically mixed impurities are removed.

The extraction of tin from the ore, or the "concentrates," as they are called, involves a reduction in a blast furnace or in a reverberatory furnace. To do this, the "concentrated" ore —tinstone—is heated with coal in a reverberatory furnace. The oxide is reduced: $SnO_2 + 2C = 2CO + Sn$. The molten tin which collects on the bottom of the furnace is drawn off and cast into ingots or blocks—*block tin*—which contain about 99·5 per cent. of metallic tin. The slag obtained in this operation is also worked up to recover the 20 to 40 per cent. of metal it contains. The tin is sometimes still further purified.

Properties.—Tin is a white lustrous metal with a pale blue tinge. The metal retains its lustre unimpaired by exposure to air. The metal is soft enough to be cut with a knife, but it is harder than lead, and not so hard as zinc. Tin is very ductile, for it can be beaten into foil—tinfoil—and drawn into wire. Tin has a marked tendency to crystallize on solidification. If a bar of tin be bent, it emits a low crackling noise—"tin cry" —said to be due to the rubbing of the crystal faces upon one another. If the surface of a block of tin be treated with warm

dilute aqua regia, the surface of the metal immediately assumes a crystalline appearance. The crystals are best shown by cooling molten tin in a crucible until part has solidified, and pouring out the liquid portion. The walls of the crucible will be lined with crystals of tin. Tin appears to be dimorphous, for electrolytic tin, *i.e.* tin deposited from a solution by the electrolysis of a tin salt, and malleable tin, form tetragonal crystals ; while the " brittle " tin, mentioned above, is rhombic. Tetragonal tin passes into the rhombic form between 170° and 200°. Tin melts at 232°. The metal takes fire when heated between 1500° and 1600°, burning with a white flame to stannic oxide, SnO_2. When the metal is heated just above its melting-point in air for some time, it forms a yellowish-white scum which is also stannic oxide.

Grey tin.—When cooled to a low temperature, tin crumbles to a grey friable powder. Several cases have been reported where tin, during an exceptionally cold winter, has crumbled to powder ; for instance, Erdmann (1851) noticed some tin organ-pipes crumble to powder. The disease is called the " tin pest." Grey tin appears to be a third allotropic modification of the element.

	Rhombic tin.	$\overset{170°}{\rightleftharpoons}$ Tetragonal tin.	$\overset{18°}{\rightleftharpoons}$ Grey tin.
Specific gravity . .	7·25	6·55	5·8

The transition temperature is 18°. Hence, excepting in warm weather, all ordinary white tin is in an unstable condition. E. Cohen has pointed out that the speed of the transformation is exceedingly slow at ordinary temperatures, but it proceeds with a maximum velocity at −48°. If a piece of tin which has already commenced to change be allowed to remain in contact with a piece of ordinary white tin, the unchanged tin is more quickly affected with the " disease."

The action of acids and alkalies.—Tin dissolves slowly in dilute hydrochloric acid, and rapidly in the concentrated acid, forming **stannous chloride,** $SnCl_2$, and hydrogen : $Sn + 2HCl \rightarrow SnCl_2 + H_2$. Tin is but slowly attacked by cold sulphuric acid, but the hot concentrated acid dissolves the metal, forming **stannous sulphate** and sulphur dioxide : $Sn + 2H_2SO_4 \rightarrow$

$SnSO_4 + SO_2 + 2H_2O$. The action of nitric acid depends upon the temperature and concentration of the acid. With cold very dilute nitric acid, **stannous nitrate,** $Sn(NO_3)_2$, is formed : $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$, with possibly a little stannic nitrate, $Sn(NO_3)_4$. With nitric acid of moderate concentration (specific gravity 1·24), copious fumes are evolved, and a bulky white insoluble precipitate of meta-stannic acid separates. Very concentrated nitric acid is said to have little or no action on the metal. Boiling alkaline hydroxides form **alkaline stannates,** *e.g.* K_2SnO_3, and hydrogen :

$$Sn + 2KOH + H_2O \rightarrow K_2SnO_3 + 2H_2.$$

Uses.—The resistance of tin to ordinary corrosive agents is utilized in protecting iron from rusting, " tin plate " is made by dipping thin sheets of steel into molten tin, whereby the steel is coated with a thin film of tin. The plated tin so made is used in the manufacture of tin cans, and similar articles. Copper coated with tin is also used for cooking vessels. Tin amalgam is used in coating mirrors.

Alloys.—Many useful alloys contain tin. The addition of tin to lead lowers the melting-point of lead ; and the addition of lead to tin lowers the melting-point of the tin. Tin melts at 232°, and lead at 327° ; an alloy of 37 per cent. lead with 63 per cent. of tin melts at the eutectic temperature 180°, as indicated in Fig. 226. *Common solder* has one part of tin to one part of lead, but solders generally vary from 66 to 33 per cent. of tin.

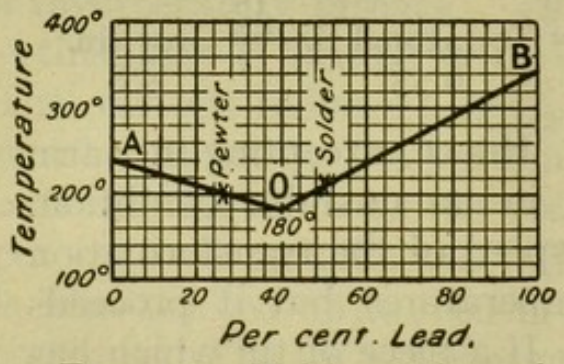


FIG. 226.—Melting-Points of Tin-lead Alloys

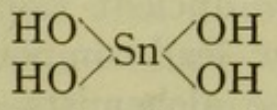
Pewter is a tin-lead alloy containing 75 per cent. of tin with 25 per cent. of lead. It will be observed that an alloy of two metals or a salt solution may appear to have two freezing-points : (1) the temperature at which an excess of one constituent freezes along the lines *AO*, *OB*, Fig. 226 ; and (2) the temperature at which the eutectic freezes *en bloc*. During the cooling of plumber's solder, for instance, say tin 40, lead 60,

solid lead begins to separate at 240°, and continues separating until the mother liquid contains 37 per cent. of lead, when the whole mass solidifies. Between these two temperatures, 180° and 240°, the cooling alloy seems to be in a " pasty " condition, and this enables the plumber to " wipe " a joint being made with such an alloy.

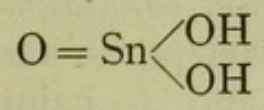
§ 2. Compounds of Tin

Tin forms two series of compounds corresponding with the two oxides, **stannous oxide,** SnO, and **stannic oxide,** SnO_2. **Stannous chloride** $SnCl_2$ prepared as indicated above, furnishes crystals, $SnCl_2.2H_2O$, called *tin crystals*, and they are used by dyers. If stannous chloride be treated with a little aqua regia, a solution of **stannic chloride,** $SnCl_4$, is formed. Anhydrous stannic chloride is formed as a fuming colourless liquid when metallic tin is heated in a stream of dry chlorine. The two sulphides, **stannous sulphide,** SnS, and **stannic sulphide,** SnS_2, correspond with the two oxides. Stannous chloride is used as a reducing agent. It changes mercuric chloride first to mercurous chloride ($2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$), and finally to mercury itself ($SnCl_2 + 2HgCl = 2Hg + SnCl_4$) ; ferric salts are likewise reduced to ferrous salts ($2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$).

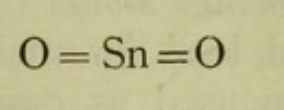
The stannic acids.—If a solution of stannic chloride be treated with an alkaline hydroxide, or ammonia, **stannic hydroxide,** $Sn(OH)_4$, is precipitated : $SnCl_4 + 4KOH = Sn(OH)_4 + 4KCl$. This substance is also called **orthostannic acid.** If dried over concentrated sulphuric acid in a desiccator (Fig. 83), this stannic acid, $Sn(OH)_4$, is said to pass into a substance of the composition $SnO(OH)_2$, and called **metastannic acid.** The graphic formulæ are :



Orthostannic acid, $Sn(OH)_4$.



Metastannic acid, $SnO(OH)_2$.



Stannic oxide, SnO_2.

A metastannic acid of the same alternate composition is made by treating tin with hot nitric acid (sp.gr. 1·3), but with quite different properties. To distinguish between the two, the first

named metastannic acid is called the **α-stannic acid,** and the last one, **β-stannic acid.** The properties of the two acids can be contrasted in the following manner :—

TABLE XXXV.—PROPERTIES OF THE METASTANNIC ACIDS.

α-Metastannic acid.	β-Metastannic acid.
Salts dissolve in water easily without decomposition. More basic than the β-acid.	Salts dissolve in water with difficulty and decompose forming insoluble basic salts and free acid. Less basic than the α-acid.
When moist, dissolves readily in nitric acid.	Insoluble in nitric acid.
Soluble in dilute sulphuric acid and the solution does not gelatinize when boiled.	Insoluble in sulphuric acid even if concentrated.
Easily soluble in hydrochloric and the solution remains clear when boiled.	Unites with hydrochloric acid forming a substance insoluble in acid but soluble in water. The aqueous solution gelatinizes when boiled.

The cause of the difference is supposed to be due to a difference in the formation of the molecules of the two acids.

§ 3. Lead.

History.—Lead was known to the ancient Egyptians. It is mentioned several times in the Old Testament. It appears to have been confused with tin (*q.v.*), and Pliny seems to have distinguished between *plumbum nigrum* (black lead) and *plumbum album* or *plumbum candidum.* The ancient Romans used lead for making water-pipes, and some lead compounds were used as cosmetics, and as paint. The alchemists connected lead with the slow-moving planet Saturn, and accordingly represented lead by a scythe ♄, the symbol for Saturn.

Occurrence.—Small quantities of metallic lead are occasionally found in nature. In combination with sulphur, lead occurs as sulphide, *galena,* PbS This is the most abundant ore of

lead. Commercial lead is obtained almost exclusively from galena. Lead ores come from England, United States, Germany, Mexico, Spain, New South Wales, South America, etc.

Extraction.—The galena is roasted in a current of air at a low temperature in a reverberatory furnace, so that one part of the lead sulphide, PbS, is oxidized to lead monoxide, PbO, and another part is oxidized to lead sulphate: $2PbS+3O_2=2PbO+2SO_2$; $PbS+2O_2=PbSO_4$. The mixture of lead sulphide, lead sulphate, and lead monoxide so obtained is heated to a higher temperature with the air "shut off." The sulphide reacts with the sulphate and the lead monoxide, forming metallic lead: $PbSO_4+PbS=2Pb+2SO_2$; and $2PbO+PbS=3Pb+SO_2$; and towards the end of the operation, when the lead sulphide begins to fuse: $PbS+3PbSO_4=4PbO+4SO_2$. In dealing with ores low in lead, *e.g.* some Spanish ores, the ore is sometimes reduced by heating with iron, or a mixture of iron ore and coke. Metallic lead and iron sulphide are formed: $PbS+Fe=Pb+FeS$. The lead made by these processes usually contains antimony, tin, copper, etc. These impurities make the lead hard and brittle. A large proportion can be removed by heating the metal in a shallow flat-bottomed reverberatory furnace whereby most of the impurities are oxidized before the lead, and rise to the surface as a scum. This operation is known as "softening lead." The silver is usually extracted by Parkes' process.

Properties of lead.—Lead is a bluish-grey metal with a bright metallic lustre when freshly cut, but the lustre soon disappears in ordinary air. Perfectly dry air, and air-free water, have no action on the metal, but if moist air be present, or if the metal be immersed in aerated water, lead is soon covered with a film, probably an oxide, and this is ultimately converted into a basic carbonate. Lead is soft enough to be cut with a knife and scratched with the finger nail. It leaves a grey streak when drawn across paper. Small traces of impurity—antimony, arsenic, copper, zinc—make the lead much harder. Lead is not tough enough to be hammered into foil or drawn into wire; but it can be pressed into pipes, or rolled into thin sheets or foil. The specific gravity of lead varies

from 11·25 to 11·4 according as the metal is cast or rolled. Lead melts at 326°. When cooled slowly, the molten metal forms a mass of octahedral crystals. Lead is also deposited as an "arborescent" mass of crystals"—called a "lead tree"—when a strip of iron or zinc is suspended in a solution of a lead salt.

Lead is rapidly dissolved by nitric acid, forming **lead nitrate**; but is little affected by dilute hydrochloric or dilute sulphuric acid in the cold, because a crust of insoluble lead chloride or sulphate is formed on the surface, and this protects the metal from further action. If either of these acids be added to a solution of lead nitrate insoluble **lead chloride** will be precipitated in the one case, and insoluble **lead sulphate** in the other. Powdered lead is quickly dissolved by boiling concentrated hydrochloric or sulphuric acid. Organic acids—acetic acid (vinegar)—also act as solvents for metallic lead. Hence, vessels plated with tin containing lead, if used for cooking purposes, may contaminate the food with poisonous lead compounds. Water containing sulphates and carbonates in solution forms a coating on the surface of lead which prevents further action. Lead is attacked by water holding ammonium salts and carbon dioxide in solution. In the latter case, a soluble acid carbonate may be formed. All lead salts are poisonous, and if the water supply of a town be pure enough to attack lead it is sometimes necessary to filter the water through limestone or chalk. The water then takes up enough carbonates to form a film on the interior of the lead pipes, which protects the lead from further action.

Uses.—Lead is largely used in the arts on account of the ease with which it can be worked, cut, bent, soldered, and on account of its power of resisting attack by water and many acids. It is used in the manufacture of pipes for conveying water; for the manufacture of sheaths for electric wires, sheets for sinks, cisterns, and roofs, lead chambers for sulphuric acid works, evaporation pans in chemical works, etc. It is used in making bullets, shot, accumulator plates, etc. Type metal, solder, pewter, and fusible alloys contain much lead. These alloys have been previously discussed.

§ 4. Lead Oxides.

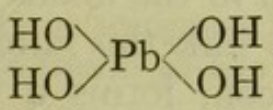
Lead forms a curious series of oxides :

Lead monoxide . . .	PbO	Litharge
Lead sesquioxide . .	Pb_2O_3	
Lead tetroxide . . .	Pb_3O_4	Red lead or minium
Lead dioxide . . .	PbO_2	Puce-coloured oxide of lead

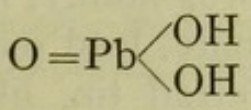
Lead monoxide, PbO.—This oxide is formed as a yellow powder when lead is oxidized in air at a low temperature—about 300°. This oxide fuses at 877°, and the fused mass forms reddish crystals. Litharge dissolves in nitric or acetic acid. If an alkali be added to the solution, a lead hydroxide $Pb(OH)_2$ is precipitated. If this hydroxide be shaken with an alkaline solution, and treated with an oxidizing agent—chlorine, hydrogen peroxide, etc.—**lead sesquioxide,** Pb_2O_3, is precipitated.

Red lead, Pb_3O_4.—This oxide is formed when lead monoxide is heated in air between 350° and 500°. It is a scarlet powder used in the manufacture of paint, matches, flint glass, pottery glazes, etc. If red lead be digested in dilute nitric acid, a brown powder remains undissolved. Its composition corresponds with the formula PbO_2, and it has oxidizing properties analogous with barium dioxide and manganese dioxide. Hence it is called **lead dioxide.**

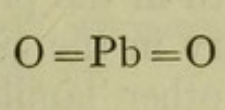
Lead peroxide is usually represented by the graphic formula O=Pb=O, lead quadrivalent, and it is considered to be the anhydride of **orthoplumbic acid,** $Pb(OH)_4$. It is further supposed that, like the stannic acids, a **metaplumbic acid,** $PbO(OH)_2$, is possible. Hence, graphically—



Orthoplumbic acid, $Pb(OH)_4$

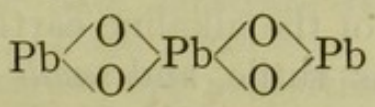


Metaplumbic acid, $PbO(OH)_2$

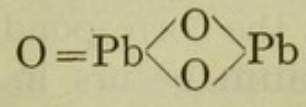


Lead peroxide, PbO_2

It is further supposed that red lead is the **lead orthoplumbate,** and lead sesquioxide is the **lead metaplumbate.** Graphically—



Lead orthoplumbate
Red lead, Pb_3O_4



Lead metaplumbate
Lead sesquioxide, Pb_2O_3

§ 5. The Relationships of the Carbon-Silicon-Tin Family.

The elements carbon, silicon, tin, and lead have a close family relationship. The physical properties, it will be seen, where known, vary with the atomic weight. Thus :

TABLE XXXVI.—PHYSICAL PROPERTIES OF THE CARBON-TIN FAMILY.

	Carbon.	Silicon.	Tin.	Lead.
Atomic weight .	12	28·3	119	207·1
Specific gravity .	2·3 to 3·5	2·35	5·8 to 7·3	11·4
Atomic volume .	4·15	12·04	18·25	18·18
Melting point .	—	about 1500°	231°	326°
Boiling point . .	—	about 3000°	2200°	1500°

The gradual change in the physical properties with rise in atomic weight is very manifest. The chemical properties have many interesting resemblances. They are all bi-, and quadrivalent, and there is a marked transition from acidic to basic qualities with rise of atomic weight. Carbon and silicon form hydrogen compounds, but the former element is unique in forming numerous complex compounds with hydrogen. Silicon resembles boron in many ways in spite of the fact that silicon is a tetrad, boron a triad. These relationships are best worked out by comparing the properties of the halides, the monoxides and peroxides, allotropic forms of the elements, etc. Like bismuth in the phosphorus family, lithium in the alkali family, mercury in the zinc family, lead seems to link this family with some other family. Tetrad tin, like silicon, forms a volatile tetrachloride—$SnCl_4$; and stannic oxide, like silicon dioxide, forms a series of salts—stannates. Dyad tin resembles copper. The tetrachloride of lead is easily decomposed. Lead dichlorides, $PbCl_2$, resembles silver and mercurous chlorides ; lead sulphate resembles the corresponding salts of the alkaline earths.

Titanium occurs in nature as rutile, and *small* quantities are found in most soils, clays, and rocks. It closely resembles silicon in its general properties.

Questions.

1. Distinguish clearly between white lead, black lead, and red lead.

2. How is red lead prepared ? What is its composition ? What substances would be produced if red lead and black lead were heated together in a crucible to a high temperature ?—*Panjab Univ.*

3. There are three oxides of lead which have the composition shown below :—

Pb	92·85	90·63	86·51 per cent.
O	7·15	9·37	13·49 per cent.

Illustrate the law of combination by multiple proportions by reference to the composition of these three oxides.—*Science and Art Dept.*

4. Describe the method by which metallic lead is obtained from galena. What compounds of lead and oxygen are known ? How are they prepared from metallic lead ?—*Science and Art Dept.*

5. Give the formulæ and describe the most important properties of the oxides of lead, copper, and mercury.—*Science and Art Dept.*

6. Give an account of the preparation of tin from native tinstone. For what practical purposes are tin and its commoner compounds employed ? By what tests would you identify a piece of metallic tin ?—*Delegacy of Local Exams.*

7. Give the preparation of silver from a mixture of lead and silver, and show what are the chief uses of silver.—*Sydney Univ.*

8. Compare the physical and chemical properties of lead and silver. How may these metals be separated when alloyed ?—*New Zealand Univ.*

9. How are the chlorides of tin prepared ? Explain the action of the lower chloride upon acidified aqueous solutions of (*a*) mercuric chloride, (*b*) ferric chloride, and (*c*) potassium dichromate.—*London Univ.*

10. Four compounds containing lead and oxygen were examined and were found to have the following composition :—

1·479 gm.	of the	first	contained	1·424 gm.	lead	and	0·55 gm.	oxygen.
1·94 ,,	,,	second	,,	1·8 ,,	,,		0·14 ,,	,,
2·031 ,,	,,	third	,,	1·819 ,,	,,		0·212 ,,	,,
1·763 ,,	,,	fourth	,,	1·526 ,,	,,		0·237 ,,	,,

From these data illustrate the law of combination in multiple proportion.—*Cape Univ.*

11. Describe the properties of carbon monoxide, orthophosphoric acid, potassium permanganate, arseniuretted hydrogen, stannous chloride.—*Cape Univ.*

12. Give an account of the preparation and properties of the oxides of copper and lead.—*Cape Univ.*

13. Give the names and chemical formulæ of the principal ores of tin and zinc. Mention the characteristic wet and dry reactions of these metals.—*Cape Univ.*

14. Write a brief account of the processes employed in the commercial manufacture of the following substances: potassium chlorate, sodium bicarbonate, potassium iodide, white lead.—*Science and Art Dept.*

15. What is the effect of a red heat upon the following compounds? Write equations where decomposition occurs. Zinc oxide, lead nitrate, mercurous oxide, lead dioxide, silver oxide, mercuric nitrate, manganese dioxide, sodium chloride.—*Science and Art Dept.*

16. How is lead extracted from the native sulphide and obtained in a commercially pure condition?—*Science and Art Dept.*

17. By what characters can lead be distinguished from other metals? How is lead nitrate prepared, and what effects are observed to follow the addition of hydrochloric acid and sulphuric acid to separate portions of a solution of lead nitrate?—*Science and Art Dept.*

18. What is the common ore of tin? How is the metal prepared? Name the principal alloys. What is the action of tin on (1) nitric acid, (2) hydrochloric acid, (3) aqueous caustic soda?—*Bombay Univ.*

19. By what characters, physical and chemical, would you distinguish specimens of the metals tin, lead, zinc, magnesium? What are the chief uses of lead and tin?—*Delegacy Local Exams.*

20. Trace the chemical relationship between the compounds of lead on the one hand, and those of tin on the other.—*Calcutta Univ.*

21. Describe and explain what happens when (*a*) tin oxide is added to fused potassium cyanide; (*b*) excess of a solution of stannous chloride is added to one of mercuric chloride; (*c*) metallic zinc is put into a solution of lead nitrate; (*d*) caustic soda solution is added in excess to one of copper sulphate, and the mixture then boiled; (*e*) a few crystals of potassium bichromate are dropped into a boiling solution of hydrochloric acid; (*f*) gold is dissolved in aqua regia and the solution evaporated to dryness on a water bath.—*Adelaide Public Exam. Board.*

22. Show how lead may be converted into (*a*) red lead, (*b*) white lead. How much "red lead" could be made from five tons of lead? (Pb=207, O=16.)—*Sydney Univ.*

23. If you were given in the laboratory silver chloride, also bismuth nitrate, also red lead, how would you obtain the metal from each?—*London Univ.*

24. How is tin extracted from its ores? Give the preparation and properties of its principal compounds.—*Cape Univ.*

25. Compare the chemical and physical properties of mercury and lead. State briefly the chemical differences existing between their chlorides and oxides.—*Cape Univ.*

26. What is the common ore of tin? How is the metal prepared? Name the principal alloys. What is the action of tin on (1) nitric acid, (2) hydrochloric acid, (3) aqueous caustic soda?—*Bombay Univ.*

27. Give the common and systematic names and chemical formulæ of the chief ores from which the metals mercury, zinc, lead, tin, chromium, and manganese are obtained.—*Science and Art Dept.*

CHAPTER XXXVI

The Platinum Metals

§ 1. Review of the Platinum Metals.

The "platinum metals" include platinum, Pt; iridium, Ir; osmium, Os; palladium, Pd; rhodium, Rh; and ruthenium, Ru. They occur in a metallic condition in gravels and sands associated together as mixtures or compounds along with magnetite, gold, chromite, etc., principally in Ural and Caucasus (Russia), and in smaller quantities in California, Sumatra, New Granada, Brazil, Australia, etc. The platiniferous sands and gravels are washed as in the case of alluvial gold. "Platinum concentrates" consist of rounded grains or flattened scales containing approximately the following percentage composition:

Platinum.	Iridium.	Rhodium.	Palladium.	Gold.	Copper.	Iron.	Osmiridium.	Sand.
76·4	4·3	0·3	1·4	0·4	4·1	11·7	0·5	1·4

The *osmiridium* is a native metallic alloy containing approximately:

Platinum.	Iridium.	Rhodium.	Osmium.	Ruthenium.
10·1	52·5	1·5	27·2	5·9

with traces of palladium, copper, and iron.

The metals are greyish-white and lustrous. They all melt at a high temperature. They are not acted on by air or oxygen at ordinary temperatures. Osmium alone burns when strongly heated, forming the tetroxide, OsO_4; the others are scarcely affected, chemically, at any temperature. Palladium dissolves in hot nitric acid, but the other metals are scarcely affected by hot acids. Aqua regia attacks osmium, forming osmium tetroxide, OsO_4; platinum forms the tetrachloride, $PbCl_4$;

ruthenium is slowly dissolved, while iridium and rhodium are not appreciably attacked. The metals are readily reduced from their compounds, which fact probably accounts for their occurrence free in nature. The metals fall naturally into two groups with nearly equal molecular weights. The **light platinum metals** include ruthenium, rhodium, and palladium; the **heavy platinum metals** include osmium, iridium, and platinum. Palladium is related with silver, and platinum with gold, as indicated in Table XXXVII.

TABLE XXXVII.—PROPERTIES OF THE PLATINUM METALS.

	Light.				Heavy.			
	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au
Atomic weight	101·7	103·0	106·0	107·88	191·0	193·0	194·8	195·7
Specific gravity	12·26	12·1	11·9	10·6	22·47	22·38	21·45	19·31
Atomic volume	8·3	8·5	8·9	10·1	8·5	8·6	9·1	10·1
Melting point .	*c.* 2000°	1650°	1549·2°	962°	2300°	2000°	1753·0°	1064°
Valency . .	3, 8	2, 3, 4	2, 4	1, 2, 3	2, 3, 4, 8	2, 3, 4	2, 4	1, 3

History.—There is supposed to be a reference to platinum in Pliny under the name "aluta." The term "platina del Pinto" for a white metal resembling silver, has been for a long time in general use by the Spaniards in South America. "Platina" is the diminutive form of the Spanish *plata*, silver, and "Pinto" has reference to the river where it was discovered. At one time its export from South America was forbidden by the Spanish Government, who ordered it to be thrown into the sea to prevent its being used for adulterating gold. In 1788, the Spanish Government bought it for about 8*s*. per lb., presumably for adulterating gold. It is now worth over £100 per lb. Platina del Pinto attracted the attention of Antonio de Ulloa (Columbia) in 1735. It was brought to Europe in 1740, and R. Watson described its properties in 1748. It attracted much attention at the time. Before 1823, most of the platinum in commerce came from South America. Platinum was discovered in Ural in 1819, and in 1824 Russia began exporting

platinum ; since that time, most of the platinum of commerce has come from that source.

Osmium and iridium were discovered by S. Tennant, 1802 to 1803 ; rhodium and palladium by W. H. Wollaston, 1803 to 1804 ; and ruthenium by A. Claus in 1845. All these metals were found during the study of native platinum. " Osmium " is named from a Greek term meaning a smell ; " iridium " is named from the Greek word for a rainbow, from the varying tint of its salts ; " rhodium " is named from the Greek word for a rose, from the rose-red colour of its salts ; " palladium " is named after the planet Pallas, discovered the same year as palladium, 1802 ; " ruthenium " is named after *ruthen*, for Russia.

§ 2. The Chlorides and their Complex Acids.

Platinum tetrachloride, PCl_4.—Platinum dissolves in aqua regia. If the solution be evaporated to dryness, and the residue gently heated, a solution of the residue in hot water deposits reddish-brown crystals of $PtCl_4.5H_2O$ on cooling. The anhydrous chloride, $PtCl_4$, can be made by drying the crystals over sulphuric acid and warming them in a current of chlorine. The tretachloride decomposes into **platinum dichloride,** $PtCl_2$, between 200° and 300°, and into the metal and chlorine at about 500°. Chlorides of all six platinum metals of the type $PtCl_4$ are known. **Palladium tetrachloride** is not known in a free state, but double chlorides with potassium, etc., are known. The dichloride is made when chlorine acts on the heated metal (250°). **Palladium chloride,** $PdCl_2$, is made by the action of a solution of chlorine in hydrochloric acid upon the metal. It gives an insoluble precipitate of **palladious iodide,** PdI_2, with the iodides, and the reaction is sometimes used for separating iodine from the other halogens.

Chloroplatinates.—If platinum chloride be crystallized from a solution acidified with hydrochloric acid, or if an aqua regia solution of the metal be evaporated a number of times with an excess of hydrochloric acid to drive off the nitric acid, reddish-brown deliquescent crystals of the complex acid $H_2PtCl_6.6H_2O$ are formed. This substance—the " platinum

chloride " of commerce—is really **hydrochloroplatinic acid.** The acid is dibasic, and it forms a characteristic series of complex salts—the chloroplatinates. **Potassium chloroplatinate,** K_2PtCl_6, for example, is a yellow crystalline precipitate made by adding the acid to a solution of potassium chloride. The solubility of **ammonium chloroplatinate,** $(NH_4)_2PtCl_6$, is low. The fact that the sodium salt is fairly soluble in 80 per cent. alcohol, while the potassium salt is almost insoluble, enables a mixture of the chloroplatinates of sodium and potassium to be separated. The ammonium salt behaves like the potassium salt. During the electrolysis of ordinary salts—silver nitrate, potassium chloride, etc.—the metal is deposited on the cathode ; with the chloroplatinates, the platinum is deposited on the anode. Again, silver nitrate precipitates Ag_2PtCl_6, not AgCl ; thus confirming the deduction that " $PtCl_6$ " is a bivalent complex acid radicle.

§ 3. The Properties and Uses of Platinum.

Platinum is a greyish-white metal with a brilliant lustre. It is harder than copper, silver, or gold. It is ductile and malleable, and usually comes on the market in the form of foil or wire. Platinum has also the valuable quality that it softens like iron before melting, so that, like iron, it can be welded. Platinum melts between 1750° and 1755°. Molten platinum, like molten silver, absorbs oxygen, which is given off as the molten metal cools, hence it is liable to " spitting." Platinum is not attacked by pure hydrofluoric, hydrochloric, nitric, and sulphuric acids. It is readily dissolved by aqua regia and by solutions containing chlorine (see " Gold "). When platinum is alloyed with silver, copper, lead, zinc, etc., it is attacked and partly dissolved by nitric acid, probably forming a **platinum nitrate.**

The high fusing temperature, and the fact that platinum is not attacked by air and strong acids, enable it to be used in the manufacture of apparatus—dishes, crucibles, stills, etc.—for many chemical operations which could not be readily performed with apparatus made from other available metals. The unfortunate steady advance in the price will lead to the

use of gold crucibles for many purposes. The analysis of many minerals could not be so readily conducted as at present if it were not for the valuable qualities of platinum. Platinum is attacked by alkalies, nitrates, cyanides, and phosphates under reducing conditions; and also by phosphorus, arsenic, and carbon. Platinum also alloys directly with metals like lead, silver, zinc, etc., but not mercury. Hence platinum crucibles must not be heated with these metals, nor in smoky flame.

Platinum has nearly the same coefficient of expansion as glass, and platinum wires can be fused in glass so as to make gas-tight joints. Platinum is also a good conductor of electricity, and large quantities are used in the electric light industry. Short pieces of platinum wire are fused into the glass at the base of the bulb, and connected with the filament inside. The bulb is then exhausted and sealed. The platinum wires outside are then put in communication with the wire carrying the current. The filament is thus heated under reduced pressure to form the "incandescent electric light." Platinum is used in dentistry, photography, in jewellery, and in making scientific and surgical instruments, etc.

Platinum-iridium alloys are hard and elastic; malleable and ductile; and less fusible than platinum. If more than 20 per cent. of iridium be present, the alloys are exceedingly difficult to work. An alloy of 10 per cent. iridium and 90 per cent. platinum was chosen by the International Committee on Weights and Measures for preserving the standards of length and weight. Platinum-iridium wire with platinum wire are used as thermocouples for temperatures up to 1000°; and platinum-rhodium wires are used with platinum in a similar way for temperatures up to 1400°. Commercial platinum has 2 per cent. of iridium, and it appears to gradually lose this constituent when heated to a high temperature. The result is that platinum crucibles made from commercial platinum lose in weight every time they are heated for some time in the gas blowpipe. This is a source of annoyance. The high fusing temperature of osmium has led to its use for the manufacture of filaments for incandescent electric lamps—"osmium lamps." An alloy of iridium and osmium is used for tipping gold nibs

on account of its hardness. The alloy is called *iridosmine* or *osmiridium*. Palladium is used for absorbing oxygen, for the detection of carbon monoxide, and for the separation of iodine as indicated above. Osmium is used for staining and hardening organic tissues in histology.

When platinum is precipitated from solutions of the tetrachloride by reducing agents, a velvet black powder called **platinum black** is obtained; when ammonium chloroplatinate is calcined, the metal remains behind as a spongy mass called **spongy platinum**; and if asbestos be soaked in a solution of platinum chloride and ignited, the asbestos permeated with platinum is called **platinized asbestos**. Platinum sponge, platinum black, and platinized asbestos absorb large quantities of oxygen gas, and they can then be used as oxidizing agents. Platinum black can absorb 100 times its volume of oxygen, and 110 times its volume of hydrogen. Palladium black absorbs over 600 times its volume of hydrogen. This property of occluding gases is shown in a less marked degree by iron, nickel, and cobalt, as well as by copper, gold, and silver. Spongy platinum will cause a mixture of hydrogen and oxygen to unite with explosion; spongy palladium, without explosion. A jet of hydrogen directed on to finely divided platinum will cause the platinum to glow and finally ignite the jet of gas. Alcohol dropped on to iridium black takes fire. Similarly, coal gas can be ignited, and this property is utilized in making the so-called "self-lighting Bunsen's burners." The catalytic properties of the finely divided platinum metals are used in some industries for promoting chemical changes, *e.g.* the contact process for sulphuric acid.

Questions.

1. What is aqua regia? What compounds are formed by its action upon gold and platinum?—*Science and Art Dept.*

2. State the special properties of each of the following metals, which render them useful either commercially or in the laboratory, and point out how their use depends upon these properties: copper, iron (steel and cast iron), aluminium, mercury, lead, and platinum.—*Sydney Univ.*

3. How is platinum found in nature? Describe methods of

obtaining it in a finely divided condition, and give one illustration of the use of the metal in an inorganic chemical preparation.—*Cape Univ.*

4. Give at least one example of each of the following: (*a*) a substance insoluble in water and acids, (*b*) a substance insoluble in water but soluble in hydrochloric acid, (*c*) a substance more soluble in hot than in cold water, (*d*) a substance more soluble in cold than in hot water, (*e*) an infusible substance.—*Staffs. County Schol.*

5. Explain both by description and equations the reactions which occur, and the properties of the products obtained when strong sulphuric acid is heated together with (*a*) copper, (*b*) platinum, (*c*) fluorspar, (*d*) chalk, (*f*) flint.—*Science and Art Dept.*

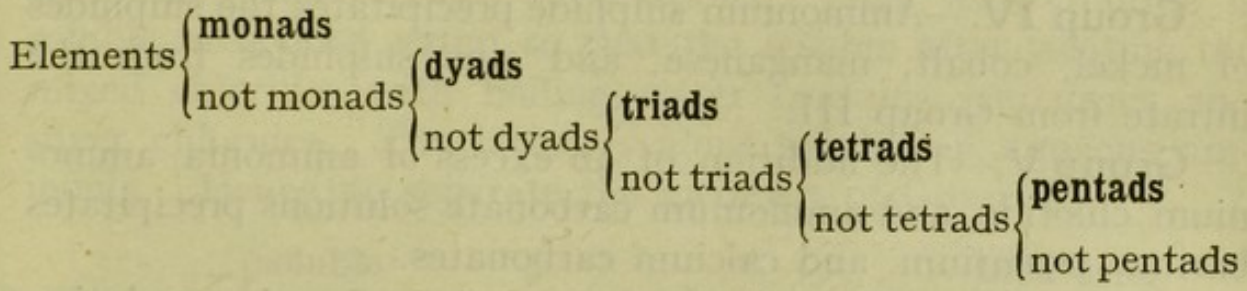
CHAPTER XXXVII

The Classification of the Elements

§ 1. The Analyst's Classification of the Elements.

The primary object of classification is to arrange the facts so that we can acquire the greatest possible command over them with the least possible effort.

The classification of the elements has long been an attractive subject. The elements have been classed into metals and non-metals, p. 159 ; into acidic and basic, or, what amounts to the same thing, into electronegative and electropositive elements, p. 415 ; and they have been classed according to their valency. Thus, the elements may be monads or not monads, if not monads, then dyads or not dyads, and so on.



In these systems an element appears in more than one class ; or elements with but few properties in common are grouped together. The properties of the elements used as the basis of classification may also vary with the conditions under which their properties are observed.

In analytical chemistry, the elements are classed according to their behaviour towards certain reagents which are conventionally taken as standards of reference. There are some differences in detail, but the general results are the same. First a few simple reactions are employed to allocate the given

substance in a certain dominant group or groups. Thus, assuming that a solution contains a mixture of all the important basic elements, they can be separated in the following manner :—

Group I.—The addition of hydrochloric acid precipitates silver, lead, and mercurous salts in the form of sparingly soluble chlorides. Lead chloride is slightly soluble in dilute acid, and consequently a little lead escapes precipitation and remains in solution.

Group II.—The elements whose sulphides are sparingly soluble in dilute hydrochloric acid (p. 314), are precipitated from the filtrate by hydrogen sulphide ; mercuric, lead, bismuth, copper, cadmium, tin, arsenic and antimony sulphides are precipitated. These elements can be divided into two subgroups, since tin, arsenic, and antimony sulphides are soluble in a mixture of ammonium sulphide and sodium hydroxide, while the others are not soluble.

Group III.—The addition of ammonia in the presence of ammonium chloride to the filtrate from Group II freed from hydrogen sulphide by boiling, precipitates ferric, chromic, and aluminium hydroxides.

Group IV.—Ammonium sulphide precipitates the sulphides of nickel, cobalt, manganese, and zinc sulphides from the filtrate from Group III.

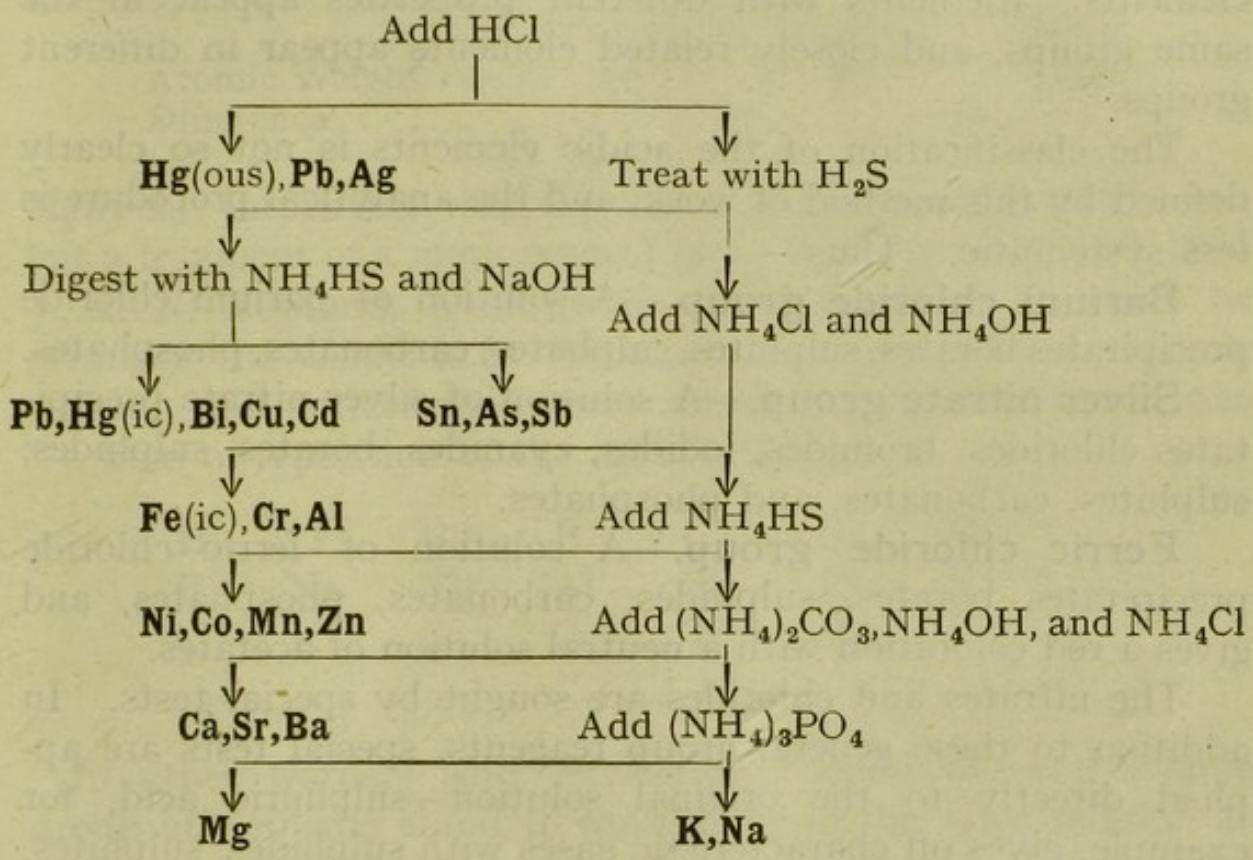
Group V.—The addition of an excess of ammonia, ammonium chloride, and ammonium carbonate solutions precipitates barium, strontium, and calcium carbonates.

Group VI.—The addition of ammonium phosphate solution precipitates magnesium phosphate from the filtrate.

Group VII.—Potassium and sodium remain as members of another group. Ammonium salts must be sought in a portion of the original solution (p. 518).

There are some difficulties, as indicated in our study (p. 314), of the action of hydrogen sulphide on solutions of these elements. In the presence of certain acidic radicles, too, there may be some interlapping.

To summarize (precipitates to left, solutions to the right):



Each of these groups and subgroups is further treated by methods described in laboratory text-books so as to separate them into still smaller subdivisions. Thus, lead chloride is soluble in boiling water, so that the residue after treating the mixed chlorides with boiling water contains mercurous and silver chlorides. The latter is alone soluble in aqueous ammonia. Hence, to separate the members of Group I,

Boiling water	soluble		**Lead salts**
	insoluble. Treat with NH_4OH	soluble	**Silver salts**
		insoluble (blackens)	**Mercurous salts**

Since the three members of Group I have been isolated, it is possible to apply special tests—the so-called **confirmatory tests**—without the reactions being obscured or masked by the presence of other elements. The other groups are separated into smaller and smaller subdivisions by suitable reagents until finally the individual elements are available for confirmatory tests. This system of classification is very suited for analytical

work, but not for a systematic study of the properties of the elements. Elements with different properties appear in the same groups, and closely related elements appear in different groups.

The classification of the acidic elements is not so clearly defined by this method of work, and the analytical procedure is less systematic. Thus—

Barium chloride group.—A solution of barium chloride precipitates borates, sulphites, sulphates, carbonates, phosphates.

Silver nitrate group.—A solution of silver nitrate precipitates chlorides, bromides, iodides, cyanides, borates, sulphides, sulphites, carbonates, and phosphates.

Ferric chloride group.—A solution of ferric chloride precipitates borates, sulphides, carbonates, phosphates, and gives a red coloration with a neutral solution of acetates.

The nitrates and chlorides are sought by special tests. In addition to these general group reagents, special tests are applied directly to the original solution—sulphuric acid, for example, gives off characteristic gases with sulphides, sulphites, carbonates, cyanides, and acetates. Details can be found in laboratory text-books.

§ 2. The Law of Octaves—J. A. R. Newlands.

In all chemical changes one thing at least remains unaltered, and the more successful systems of classification have been based on this constant, the atomic weights of the elements. The early efforts in this direction were seriously hampered by the uncertainty in the numerical values of the atomic weights. But after chemists had cleared up the confusion associated with the atomic theory left by Dalton, and obtained a consistent system of atomic weights, the results were more promising. True enough between 1816 and 1829, J. W. Dobereiner noticed some regularities in the atomic weights of certain related elements, for he found that most of the chemically related elements either exhibited almost the same atomic weight—*e.g.* iron, cobalt, and nickel—or else exhibited a constant difference when arranged in sets of three. Thus, selecting one

set from Dobereiner's list, and rounding off the modern atomic weights,

	Calcium.		Strontium.		Barium.
Atomic Weight . .	40		87		137
Difference		47		50	

Many felt intuitively that the list of **Dobereiner's triads** was but a fragment of a more general law. Between 1863 and 1866 J. A. R. Newlands published a series of papers in which he arranged the elements in the ascending order of their atomic weights, and noticed that every succeeding eighth element was "a kind of repetition of the first." Thus,

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe
. . .	. . .	. . .	. . .			

"In other words," said Newlands, "members of the same group of elements stand to each other in the same relation as the extremities of one or more octaves in music. This peculiar relationship I propose to provisionally term **the law of octaves.**" Newlands noticed that elements belonging to the same group "usually" appeared in the same column, and he declared that all the numerical relations which had been observed among the atomic weights "including the well-known triads, are merely arithmetical results flowing from the existence of the law of octaves."

The "law of octaves" did not attract much attention probably because faulty atomic weights seriously interfered with the arrangement.[1] Similar remarks apply to some papers by A. E. B. de Chancourtois in 1862, where it was proposed to classify the elements by their atomic weights. Chancourtois' ideas were so much entangled with extraneous matters, and the

[1] When Mr. Newlands read a paper on "The Law of Octaves" at a meeting of the London Chemical Society in 1866, Prof. G. F. Foster said that any arrangement of the elements would present occasional coincidences, and ironically inquired if Mr. Newlands had ever examined the elements according to their initial letters. Twenty-one years later the Royal Society awarded Newlands the Davy Medal for his discovery.

truth was so much obscured by useless and faulty speculations, that his work lay buried for nearly thirty years, and it was only resurrected after Mendeléeff's system had become famous.

§ 3. The Periodic Law—D. I. Mendeléeff and L. Meyer.

> The periodic series is a brilliant and adequate means of producing an easily surveyed system of facts which by gradually becoming complete will take the place of an assemblage of the known facts.—E. MACH.

D. I. Mendeléeff and L. Meyer, quite independently and, so far as we can tell, quite in ignorance of Newland's and Chancourtois' work, obtained a far clearer vision of the "law of octaves" about 1869. Mendeléeff said: "When I arranged the elements according to the magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties." Otherwise expressed, if the elements be arranged in the order of increasing atomic weights, their *properties* vary from member to member in a definite way, but return more or less nearly to the same value at fixed points in the series. Mendeléeff continued: "I designate by the name 'periodic law' the mutual relations between the properties of the elements and their atomic weights, these relations are applicable to all the elements, and have the nature of a periodic [1] function." Expressed more concisely, **Mendeléeff's periodic law: The properties of the elements are a periodic function of their atomic weights.** The early tables were very imperfect for the reasons stated above. Mendeléeff's tables of the atomic weights were designed to tabulate the elements in such a way as to exhibit the greatest number of relationships. The original tables were afterwards amended and modified owing to improved data and the discovery of new elements. The symbols of the elements with their atomic weights have been arranged on a helix, on a spiral, and in numerous other ways. Table XXXVIII., not very different

[1] A periodic function is one whose value repeats itself at regular intervals. The interval is called a "period."

Table XXXVIII.—The Periodic Series of the Elements.

	Series.	Group 0	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_2	Group VII RH R_2O_7	Group VIII Transition elements RO_4
	1		H 1·008	—	—	—	—	—	—	——
Short Period	2	He 3·99	Li 6·94	Be 9·1	B 11·0	C 12·00	N 14·01	O 16·00	F 19·0	——
Short Period	3	Ne 20·2	Na 23·00	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·07	Cl 35·46	——
Long Period	4	A 39·88	K 39·1	Ca 40·07	Sc 44·1	Ti 48·1	V 51·0	Cr 52·0	Mn 54·93	Fe 55·84; Co 58·97; Ni 58·68
	5		63·57 Cu	65·37 Zn	69·9 Ga	72·5 Ge	74·96 As	79·2 Se	79·92 Br	
Long period	6	Kr 82·92	Rb 85·45	Sr 87·63	Yt 89·0	Zr 90·6	Nb 93·5	Mo 96·0	—	Ru 101·7; Rh 102·9; Pd 106·7
	7		107·88 Ag	112·40 Cd	114·8 In	119·0 Sn	120·2 Sb	127·5 Te	126·92 I	
Long period	8	Xe 130·2	Cs 132·81	Ba 137·37	La 139·0	Ce 140·25	—	—	—	——
	9		—	—	—	—	—	—	—	
Long period	10	—	—	—	—	—	Ta 181·0	W 184·0	—	Os 190·9; Ir 193·1; Pt 195·2
	11	—	197·2 Au	200·6 Hg	204·0 Tl	207·10 Pb	208·0 Bi	—	—	
? Long period	12	Nt 222·5	—	Ra 226·4	—	Th 232·4	—	U 238·5	—	——

in style from one of Mendeléeff's first tables, is one of the simplest modes of arrangement, perhaps the best.[1]

The nine vertical columns are usually styled **groups,** and the thirteen horizontal lines **series** or periods. We have already studied (pp. 298 *et seq.*) the properties of the more familiar elements and compounds from the point of view of this system of classification. A brief review of the families or groups will therefore suffice to emphasize the relationships of the members of any given group. Each **short period,** it will be observed, contains eight elements ; and each **long period** either contains nineteen elements of which three are the so-called **transition elements,** or else it has provision made for nineteen elements. Hyphens are inserted in the spaces where the corresponding element is unknown. The elements in the first short series are sometimes called **group elements** or **bridge elements,** since they show a notable gradation of properties from one to the other, and serve as links or bridges between the different groups. The next short period or series 3, are called **typical elements** because they have the typical properties and characteristics of the group, and show a rather wide divergence from neighbouring groups. Each typical element of the different groups diverges into two **sub-groups.**

This table also emphasizes the fact that while the atomic weights of the elements progressively increase, their properties recur at definite intervals ; no well-known elements are omitted from the scheme ; with three exceptions the order is that of the atomic weights, and the elements fall into virtually the same groups as would have been obtained had they been grouped according to their chemical behaviour.

Most of the well-defined physical and chemical properties of the elements are periodic—valency, specific gravity, atomic volume, melting point, hardness, malleability, ductility, compressibility, coefficient of expansion, thermal conductivity, latent heat of fusion, refraction equivalents for light, colour, electrical conductivity, magnetic power, etc. When the

[1] Other schemes have advantages as well as disadvantages over Mendeléeff's arrangement so that there is no special reason why any one should be here given preference.

numerical values of these properties and the atomic weights of the elements are tabulated on squared paper, a curve is obtained which is broken up into periods, as illustrated by Fig. 227. The properties of analogous compounds of the elements—molecular volumes, melting points, boiling points, stability of the hydroxides, colour, etc.—are very often periodic. The specific heats of the elements are unique in furnishing a non-periodic curve. According to Dulong and Petit's law, if x

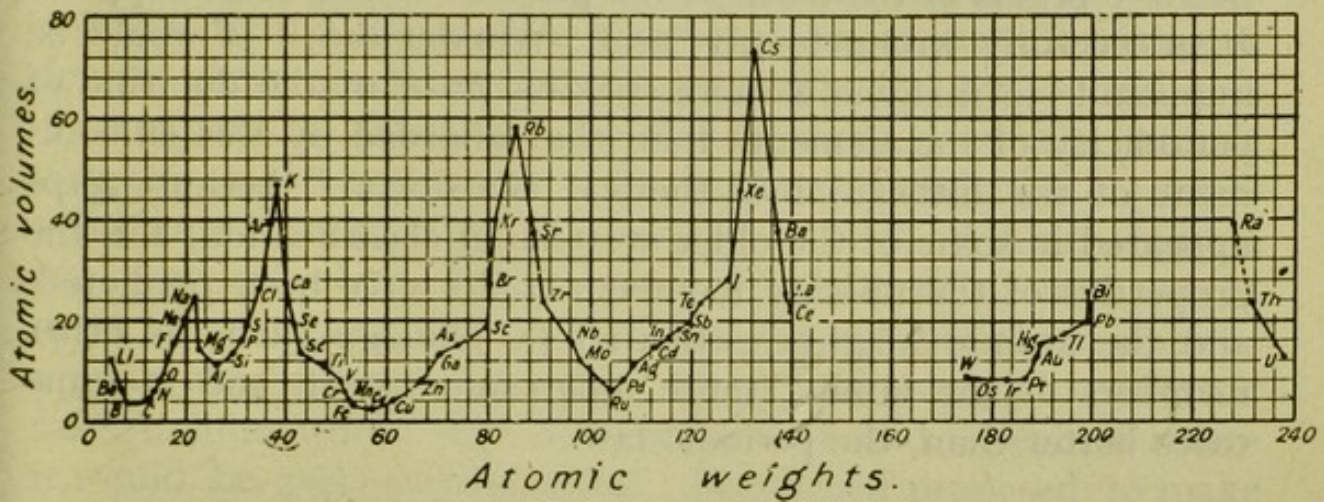


FIG. 227.—Relation between atomic weights and atomic volumes of the elements.

denotes the specific heat of an element with an atomic weight, y, we have $xy = 6$.

§ 4. The Gaps in Mendeléef's Tables of the Elements.

Both Meyer and Mendeléeff considered it necessary to leave gaps in their tables for undiscovered elements, and more particularly in order to keep certain related elements in the same vertical column. Mendeléeff boldly prophesied that the **missing elements** would be discovered later, and in some cases even predicted the anticipated properties in considerable detail. For instance, when Mendeléeff announced the law, there were two blank spaces in Group III, the missing elements were called **eka-aluminium** and **eka-boron** respectively; and another space below titanium in Group IV, the missing element in this case was called eka-silicon. The subsequent discovery of gallium, scandium, and of germanium with properties

practically identical with Mendeléeff's audacious prognostications, attracted considerable attention, and served to strengthen the faith of chemists in the fundamental truth of the periodic law. The confirmation of Mendeléeff's predictions of the properties of eka-aluminium (gallium), and of eka-boron (scandium) were equally striking. This dramatic achievement focussed attention on the generalization ; and it is only fair to say that the predictions and their subsequent verification are not such positive proofs of the truth of the periodic law as some suppose. It is certainly wrong to say, as C. Winkler did, "it would be impossible to imagine a more striking *proof* of the doctrine of periodicity of the elements than that afforded by this embodiment of the hitherto hypothetical eka-silicon," because gaps appeared in some of the older systems of classification, and the properties of the missing members could have been predicted, and the atomic weights estimated by analogy with the other members of the family, quite independently of, and in some cases better than, the periodic law.

§ 5. The Applications of the Periodic Law.

> A natural law only acquires scientific importance when it yields practical results, that is, when it leads to logical conclusions which elucidate phenomena hitherto unexplained, when it directs occurrences till then unknown, and especially when it calls forth predictions which may be verified by experiment.—D. I. MENDELÉEFF.

Mendeléeff pointed out that the periodic law could be employed in : 1. The classification of the elements ; 2. The estimation of the atomic weights of elements not fully investigated ; 3. The prediction of the properties of hitherto unknown elements ; and 4. The correction of atomic weights.

1. The classification of the elements.—T. H. Huxley (1864) has said : "By the classification of any series of objects, is meant the actual or ideal arrangement together of those which are like, and the separation of those which are unlike ; the purpose of this arrangement being to facilitate the operations of the mind in clearly conceiving and retaining in the

memory the characters of the objects in question." The periodic system is undoubtedly superior to all the older methods of classification, for the law make it possible to build up a system of the greatest possible completeness, free from much arbitrariness, and it furnishes strong circumstantial evidence of the correctness of the reasoning employed by Cannizzaro to deduce values for the atomic weights of the elements.

2. The estimation of the atomic weights of the elements.—On account of practical difficulties, it is not always possible to fix the atomic weight of an element by vapour density determinations (Avogadro's rule), and by specific heat determinations (Dulong and Petit's rule), and the atomic weights of these elements were frequently assigned on somewhat uncertain grounds. According to C. L. Winkler, indium has the equivalent weight 37·8. The correct atomic weight must be some multiple of this, and for no special reason, the atomic weight was once taken to be $37{\cdot}8 \times 2 = 75{\cdot}6$. In that case, indium would fall between arsenic and selenium where it would be quite mis-matched. Mendeléeff proposed to make indium tervalent, like aluminium, so that the atomic weight became $37{\cdot}8 \times 3 = 113{\cdot}4$, and the element fell in the table between cadmium and tin where it fits very well. The subsequent determination of the specific heat of indium, 0·0577, corroborated the change made by Mendeléeff in the atomic weight from 75·6 to 113·4. Beryllium, uranium, and a number of the rare earths at one time did not fit very well into the table, but Mendeléeff's alteration of the supposed atomic weights to make these elements fit the table were subsequently justified by vapour density determinations of the volatile chlorides, or by specific heat determinations.

3. The prediction of the properties of hitherto undiscovered elements.—In order to avoid introducing new names when speaking of unknown elements, Mendeléeff designated them by prefixing a Sanscrit numeral—eka (one), dwi (two), tri (three), etc.—to the name of the names of the next lower analogous elements of the odd or even numbered series of the same group. Thus, the unknown elements of Group I will be called eka-cæsium, and dwi-cæsium. Were niobium

unknown, it would be called eka-vanadium. In addition to the prediction of germanium, gallium, and scandium already discussed, Mendeléeff foretold the possible discovery of eka- and dwi-cæsium; eka-niobium—En=146; of eka-tantalum—Et =235; of dwi-tellurium—Dt=212; and of the analogues of manganese: eka-manganese—Em=100; and tri-manganese —Tm=190.

The case of the **inert gases** of elements is of more recent date. The discovery of argon and helium could not have been predicted from Mendeléeff's periodic law, but after these elements had been discovered, they were accommodated in the periodic table between the strongly acid halogen family and the strongly basic alkali metals, the probable existence of other similar inert gases was indicated. When an exhaustive search was made krypton, neon, and xenon were discovered with properties and atomic weights which could have been predicted from the arrangement made for argon and helium in Mendeléeff's table.

4. The correction of the values of atomic weights.—If the atomic weight of an element does not fit with the regular course of, say, the atomic volume curve, Fig. 138, the atomic weight is probably in error. Thus, the atomic weights of platinum, iridium, and osmium at that time were probably too high, and subsequent determinations verified this inference. Thus the atomic weights of these elements were:

	Platinum.	Iridium.	Osmium.
In 1870	196·7	196·7	198·6
In 1912	195·2	193·1	190·9

There are also some **misfits** in the table as we have it to-day, owing to the fact that at least three pairs of elements would be mis-matched if they were simply classed according to their atomic weights: argon (39·88) and potassium (39·10); cobalt (58·97) and nickel (58·68); and tellurium (127·5) and iodine (126·92). The case of **iodine and tellurium** has been studied very closely. Iodine most certainly belongs to the same group as the other halogens, and tellurium to the selenium group, and these elements are accordingly placed in these groups

in spite of the fact that if their atomic weights were alone considered tellurium would be ranked with the halogens, and iodine with selenium. B. Brauner supposes that ordinary tellurium is a complex containing *a*- and *b*-tellurium ; but tellurium has been melted, sublimed, oxidized, hydrogenized, phenylated, dissolved, crystallized, and precipitated ; yet nothing but failure has followed all attempts to get an atomic weight lower than iodine. Hence in spite of the fact that "the laws of nature admit of no exception" (p. 80), faith in the law has led chemists to allocate these discordant elements according to their chemical properties and not according to their atomic weights. This method must be dubbed "unscientific," [1] but the circumstantial evidence justifies the procedure, in the expectation that a consistent system will ultimately grow from the truth and error engrafted into the "law." It is not very probable that the principle underlying the periodic law will be abandoned, because it is founded on a vast assemblage of facts of different kinds ; and because it seems to be plastic enough to fulfil subsequent requirements.

[1] Bode's law of astronomy successfully *predicted* the asteroids and allocated their proper place in the solar system ; but the subsequent discovery of Neptune did not agree with Bode's law. The "law" was accordingly abandoned, and it is now regarded as a curiosity.

APPENDIX

Some Organic Compounds

§ 1. The Source of Cellulose.

The harmony of Nature is revealed most clearly in her tiniest objects.—Pliny.

Plant cells.—When the tissue of a young plant is examined under a microscope, it can be resolved into a vast host of what Robert Hooke (1665) called "little boxes or cells which are distinct from one another." The normal shape of a single cell is approximately spherical, but when the cells are crowded together, they are squeezed into more or less polygonal forms. This is illustrated by the photograph, Fig. 228, of a thin slice cut across the stem of an equisetum. Every plant cell is enveloped by a **cell-wall** of cellulose (Latin *cellula,* a little cell).

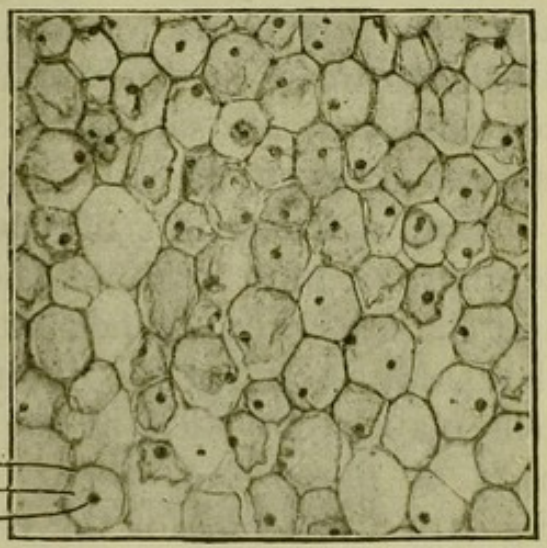


Fig. 228.—Part of a Section across the Stem of an Equisetum. (×90.)

The cell is not usually a hollow chamber, but is more or less completely filled with a translucent, colourless, viscid substance called **protoplasm** (πρῶτος) (protos), first; (πλάσμα) (plasma), a moulded thing. The protoplasm usually contains a small rounded body which appears to be a denser and thicker

form of protoplasm. It is called the **nucleus**. The cell-walls, protoplasm, and nuclei, of a mass of cells are illustrated by the photograph of the cell-tissue of the equisetum, Fig. 228.

The jelly-like protoplasm is common to animal and vegetable organisms. It has a complex composition. It contains carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulphur, as well as small proportions of potassium, calcium, magnesium, and iron. How these elements are combined is not known. The most remarkable property of protoplasm is the possession of life. In this it differs from all other substances. The living protoplasm of the cells is the seat of all the vital processes of the plant. The cell-wall is formed by the protoplasm, and the subsequent elaboration of the older plant cells is due to its activity. The plant grows by the sub-division of certain cells into two ; each daughter cell increases in size, and again sub-divides. So the process continues an indefinite time.

Cell contents.—Besides protoplasm the cell usually contains a number of lifeless bodies—food granules (starch, proteids, etc.) ; pigmented bodies (green chlorophyll, etc.) ; drops of oil ; excretory matters of no evident use to the plant ; the alkaloids—strychnia, morphia, nicotin, etc. Some of the alkaloids are the active principles of medicines. The cells and contents are also saturated with water holding different substances—organic and inorganic—in solution.

The elaboration of the plant cells.—The protoplasmic contents of most cells, as they grow old, gradually disappear, and the cells are modified into a great variety of forms so that they may be fitted for different functions in the plant. The cells may be crowded in one direction so as to form elongated bags or fibres—*e.g.* fibres of cotton, hemp, etc., illustrated Fig. 229 ; the ends of the elongated cells may be absorbed so as to form continuous tubes and fibres ; the cell-wall may remain simply a thin film of cellulose, or it may be more or less thickened by secretions from the protoplasm as is the case with the cellulose of the date-stone. The cellulose may be impregnated with secondary substances to form the *lignin* of wood, the *suberin* of cork, etc.

The different parts of all plants, trees, etc., are made up of

dead or living cells, and consequently, as soon as the cell-sap of a plant is dried, little remains but cellulose along with secondary substances which were once present in the cell-sap or which were formed by the elaboration of the cellulose. *Cellulose is the predominating constituent of all vegetable tissue;* and botanists call it "the structural basis of plants." Wood is impure cellulose; cotton, flax, hemp, ramie, and linen are nearly pure forms of cellulose. Cellulose is applied to many useful purposes in the arts—*e.g.* paper manufacture.

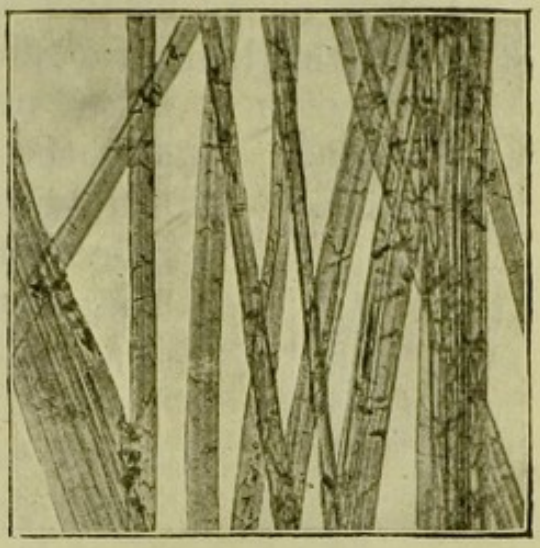


FIG. 229.—Fibres of China Grass (×60).

Paper. — Paper is made by pulping flax or linen rags. This is effected by boiling the rags with an alkali (sodium or calcium hydroxide) and agitating them in a disintegrating machine so as to produce a uniform pulp. This may or may not be bleached (p. 143). The pulp is then spread evenly on a wire cloth, pressed between rollers, and dried. Wood, straw, and other plant fibres are used for the cheaper kinds of paper. Filter paper is almost pure cellulose.

§ 2. Osmotic Pressure.

Water with dissolved salts is absorbed by the root from the soil. This produces a comparatively large pressure—*root pressure*—which "drives" water up the vessels in the stem of the plant. This root-pressure is easily demonstrated by cutting through the stem of a young bean plant in active growth, and, by means of rubber tubing, *B*, Fig. 230, attaching an **S**-shaped glass tube, *CD*, to the stump of the stem. The long tube *D* is clamped in a vertical position and a little mercury poured through *C* into the long leg. The glass tube *C* is filled with water and closed by a rubber stopper. The root pressure drives the mercury up the stem, as is shown by the difference in the levels of the mercury towards the beginning and the end

of the experiment.[1] How does the water carrying the salts in solution pass through the cellulose cell walls at the growing tips of the rootlets ?

A piece of wet bladder is stretched and wired over the head of a wide thistle-headed funnel with a stem about 10 cm. long. When nearly dry, the bladder is removed and the hot funnel is smeared about the rim with marine glue. The bladder is immediately wired securely in position. The thistle-headed funnel is nearly filled with a concentrated solution of cane sugar and joined by means of pressure tubing or a rubber stopper with a piece of capillary tubing of $\frac{1}{2}$ mm. bore bent **S**-shaped as indicated in Fig. 231. The funnel is immersed in a jar of water. The level of the index of coloured water in the capillary tube is marked with gummed paper, and the apparatus is allowed to stand overnight. In the morning the liquid in the capillary will have risen about 10 cm. Water has obviously passed from the beaker through the membrane into the sugar solution.

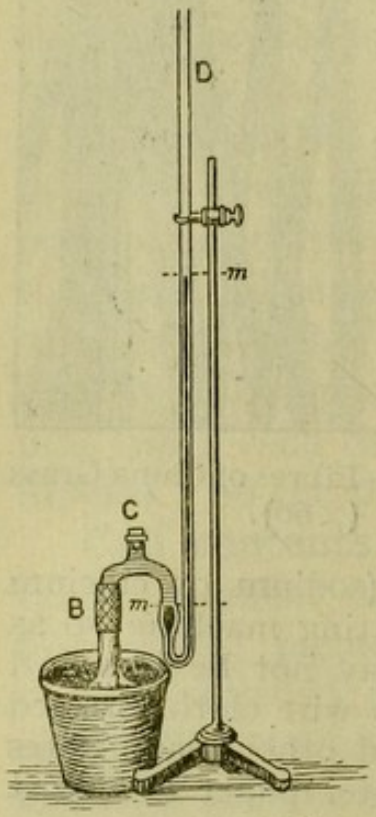


FIG. 230.—The Root Pressure of Plants.

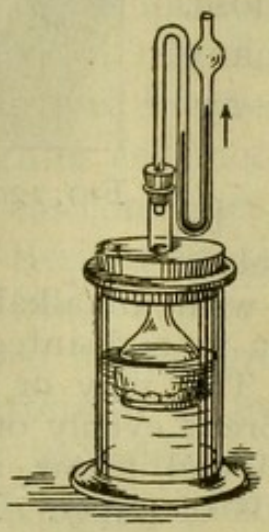


FIG. 231.—Illustration of Osmotic Pressure.

The passage of water through a membrane in this manner is called **osmosis**—from the Greek ὠσμός (osmos), a push. If the osmosis be inwards, towards the solution, it is called **endosmosis**; if outwards, **exosmosis**. The membrane permeable to the solvent, impermeable to the dissolved substance, is called a **semipermeable membrane**. The extra pressure exerted upon the membrane by the sugar solution was styled, by W. Pfeffer (1877), " the osmotic

[1] The stem may at first temporarily absorb water. The soil about the plant is supposed to be sufficiently wet to permit the free play of the forces at work.

pressure of the sugar solution." Solutions with the same osmotic pressure are said to be *is-osmotic* or **isotonic.**

The action is curious. In the ordinary nature of things the sugar would diffuse into the solvent until the whole system had one uniform concentration. The membrane prevents this. If the sugar cannot get to the solvent, the solvent goes to the sugar—a case of Mohammed and the mountain. Molecules of sugar and molecules of water attempt to pass through the membrane ; the way is open for the molecules of water, but not for the molecules of sugar. Water can pass freely both ways. The extra pressure on the solution side of the membrane—the **solution pressure**—is supposed to be due to the bombarding of the membrane by the molecules of sugar. Equilibrium occurs when the number of molecules of water passing downwards through the membrane is equal to the number passing in the opposite direction. The resulting pressure is the solution pressure or the osmotic pressure of the solution.

Here, then, we have a pressure somewhat analogous to root pressure. The cellulose membrane of the cells of the root hairs of the plant is permeable to very dilute solutions. The cell-sap in the rootlets of a plant is a comparatively concentrated solution, the soil-water is a comparatively dilute solution. Hence, a larger amount of water diffuses inwards by endosmosis, than outwards by exomosis. In this way the plant is able to get certain food it requires from the soil even though there is a non-porous membrane separating the interior of the plant from the soil. In a similar way, the nutritive constituents of food, in solution, can pass through the membrane walls of the intestines of animals into the blood.

§ 3. The Properties of Cellulose.

Cellulose is a white, colourless, non-crystalline compound, insoluble in water, alcohol, and most of the ordinary solvents. It slowly dissolves when boiled with acids and alkalies, and it is readily dissolved by an ammoniacal solution of cupric hydroxide—*Schweitzer's reagent.* A substance like cellulose is precipitated from the solvent by the addition of an acid. The

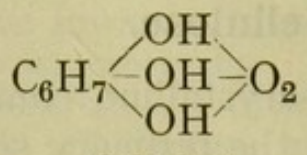
action of heat on cellulose resembles its action on wood (p. 557). The analysis of cellulose furnishes

Carbon.	Hydrogen.	Oxygen (by difference).
44·4	6·2	49·5 per cent.

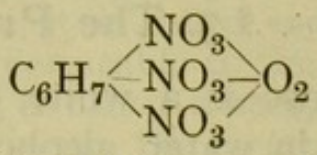
This agrees with the empirical formula $C_6H_{10}O_5$. We do not know the molecular weight, and consequently as a first approximation this symbol—$C_6H_{10}O_5$—can be taken to represent the constituents of the molecule.

The action of sulphuric acid on cellulose.—Concentrated sulphuric acid converts cellulose into a sugar-like substance—**dextrose** or **grape sugar**; but if placed for a few seconds in an evaporating dish containing a mixture of equal volume of sulphuric acid and water, cellulose is converted into a parchment-like substance. The acids can be removed by washing with water and dilute ammonia. If paper be so treated, the so-called **parchment paper** is formed; this is used to cover jams, pickles, etc.

The action of nitric acid on cellulose.—When clean dry cotton is dipped for about five minutes in a mixture of fuming nitric acid with three volumes of concentrated sulphuric acid, and then washed in water until free from acid, the dried cotton retains its general appearance—colour, structure, etc.—but it increases nearly fifty per cent. in weight. When struck with a hammer, on an anvil, it explodes with a loud report, although if ignited with a match, it burns rapidly without explosion. The cotton treated as just described is called **gun-cotton** or **trinitrocellulose.** The analysis of gun-cotton furnishes the empirical formula $C_6H_7N_3O_{11}$. It is sometimes assumed that the fuming nitric acid removes three hydroxyl (OH) groups, and introduces three nitroxyl (NO_3) groups



Cellulose.



Trinitrocellulose or gun-cotton.

Often enough these formulæ are doubled as if the cellulose molecule was $C_{12}H_{20}O_{10}$. It is supposed that the function of the sulphuric acid in the preparation of gun-cotton is to remove

the water as fast as it is formed so that the strength of the nitric acid is maintained.

Collodion.—If cellulose be treated with ordinary nitric acid, in place of the fuming acid, a **dinitrocellulose,** $C_6H_8(NO_3)_2O_3$, is formed. This is commercially known as **pyroxylin** or **soluble gun-cotton.** Unlike cellulose and gun-cotton, pyroxylin is soluble in alcohol and ether. The solution is called **collodion.** Collodion is used in surgery and photography. If collodion be spread on a clean glass plate a transparent tough elastic film remains when the ether has evaporated. Celluloid is prepared from gun-cotton, camphor, etc.

§ 4. Starch.

The extraction of starch.—The cells of the potato, wheat, maize, etc., contain a multitude of rounded white starch granules ranging from 0·05 to 0·0025 mm. in diameter. The starch granules, and minute granules of a nitrogenous substance called **gluten** or **vegetable albumen,** appear to be stored by the plant, either for the nutrition of the young embryo when the seed germinates; or to feed young plants; etc. Arrowroot, sago, tapioca, etc., used as food-stuffs are starches derived from certain tropical plants.

The starch can be removed by pounding, say, a potato into a pulp with water, and allowing the mass to stand for a few days to ferment. The mixture is then strained through a fine cotton cloth. The fluid which passes through the sieve has a white milky appearance; cellulose, etc., remains on the filter cloth. The white turbid liquid is allowed to settle, and white granules of starch collect as a sediment. The starch is allowed to drain on blotting paper and dried in a warm room. Roots, tubers, and seed grains of various kinds can be rasped and treated in a similar way.

The properties of starch.—When starch granules are examined under the microscope—particularly in polarized light—their curious striated structure becomes apparent. Since the starch granules of different plants has a characteristic structure, the different starches can usually be readily distinguished by a microscopic examination. Hence, when food-stuffs with the more expensive starches are adulterated with cheaper varieties, the fraudulent adulteration can be readily

detected. The analysis of starch furnishes numbers similar to those obtained for cellulose ; and the empirical formula is the same, viz. $C_6H_{10}O_5$. The molecular weight is not known. Starch is virtually insoluble in cold water, but when placed in boiling water, the granules swell and finally form a paste-like fluid—*starch paste*. Starch paste dries to a stiff horn-like mass. Hence the word " starch " is derived from the German *stark*, strong, because the paste is used for stiffening linen and other fabrics. A solution of iodine in an aqueous solution of potassium iodide colours starch blue. The colour fades if the solution be heated, but reappears on cooling. The coloration is characteristic of iodine, and hence is utilized in analysis (p. 271).

Dextrin.—When heated to about 200–220°, starch forms a kind of dextrin. A similar substance is formed when starch is boiled with a dilute solution of sulphuric acid (2 per cent.), or nitric acid (2 per cent.) until the mixture no longer gives a blue coloration with iodine. When the resulting solution is evaporated, a syrupy liquid is obtained which is used as a gum for envelopes, stamps, etc. The analysis of dextrin shows that it has the same empirical formula as cellulose and starch—$C_6H_{10}O_5$. Dextrin is readily soluble in water, and the solution bends a ray of polarized light to the right. Hence the term (Latin *dexter*, right-handed). When boiled with concentrated sulphuric acid, starch, dextrin, and cellulose furnish carbon dioxide, carbon, and sulphur dioxide. A solution of dextrin is coloured red by iodine.

§ 5. Sugars.

Sugars of many kinds are found in the sap of many plants. Thus, *cane sugar* is found in the sugar-cane, and a somewhat similar variety is found in the sugar maple and in the root of the beet, carrot, etc. ; *mannite* in the dried sap of many species of ash, etc.

The extraction of cane sugar.—Cane sugar is extracted by crushing the cane between heated rollers, and neutralizing the somewhat acid juice with milk of lime. The clarified liquid is evaporated under reduced pressure until it reaches the point of crystallization. The mother-liquid—called *molasses*—is drained from the crystals of raw sugar. The raw sugar is refined by solution in water, filtration with animal charcoal in order to remove the colouring matters, and the colourless syrup is evaporated under

reduced pressure—in *vacuum pans*—until a mass of crystals and a syrup is obtained. The hot liquid is placed in conical moulds and allowed to cool. The liquid syrup is drained off and the resulting *loaf-sugar* is dried. The so-called *crystalline sugar* is made by separating the syrup from the crystals in a centrifugal machine.

The properties of cane sugar or saccharose.—Cane sugar forms large white transparent crystals which melt at 160°. The amber-coloured non-crystalline mass formed on cooling is *barley sugar*. When heated to about 210°, sugar loses water, swells, and forms a brown mass, called *caramel*, which is used for colouring beer, vinegar, etc. The analysis of cane sugar agrees with the empirical formula $C_{12}H_{22}O_{11}$. An aqueous solution of cane sugar deflects a ray of polarized to the *right;* after a prolonged boiling in water, the solution deflects the ray to the *left*. The sugar is then said to be *inverted*. Invert sugar is a mixture of two varieties of sugar—one is called **levulose** or **fructose,** and the other **dextrose** or **glucose.** The former bends a ray of polarized light to the left, and the latter bends it to the right. Both these varieties have the same empirical composition—$C_6H_{12}O_6$. Hence during inversion cane sugar unites with a molecule of water and probably splits two parts. The reaction is symbolized :

$$C_{12}H_{22}O_{11} \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Cane sugar. Fructose. Glucose.

The presence of very dilute acids —even carbonic acid—accelerates the speed of the inversion of cane sugar in a wonderful way.

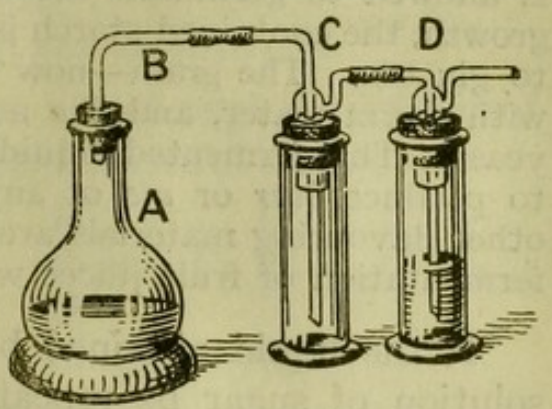


FIG. 232.—The Fermentation of Sugar.

Fermentation.—If about 50 c.c. of treacle in 400 c.c. of water be placed in a litre flask *A*, Fig. 232, along with a few c.c. of yeast, and the flask be connected by means of a delivery tube *B* with an empty wash-bottle *C*, and another wash-bottle *D*, containing clear lime-water, the liquid in the flask, if kept warm, soon begins to froth—ferment. The lime-water becomes turbid owing to the

evolution of carbon dioxide during the fermentation. Cane sugar does not ferment in this way until inversion has set in. It appears that the yeast plant secretes a substance—named **invertase**—which changes cane sugar into invert sugar ; and a second secretion of the yeast plant—**zymase**—breaks down the invert sugar into carbon dioxide and ethyl alcohol. In symbols

$$\text{I. Invertase : } C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$$
$$\text{II. Zymase : } C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

where the symbol C_2H_5OH represents a molecule of ethyl alcohol, ethyl alcohol is one product of the fermentation of sugar. Note that sugar, starch, and cellulose are compounds of carbon, hydrogen, and oxygen, and that in each, the hydrogen and oxygen are in the proportions required to form water—hence the name **carbohydrates** has been given to these three types of compounds.

§ 6. Alcohol.

Alcoholic beverages.—When the grain of cereals, say, barley, is allowed to germinate for a time and then heated to stop the growth, the contained starch is converted into a sugar very similar to glucose. The grain—now called *malt*—is crushed and agitated with warm water, and the aqueous solution treated with a little yeast. The fermented liquid is filtered and diluted with water to produce *beer* or *ale* of any desired concentration. Hops and other flavouring materials are added. *Wines* are produced by the fermentation of fruit juices which contain glucose.

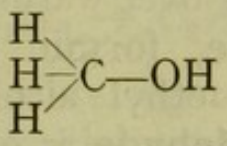
If the liquid obtained by the fermentation of an aqueous solution of sugar be repeatedly distilled, a liquid containing about 84 per cent. of alcohol is obtained. It is called *rectified spirit.* By the repeated distillation of rectified spirit from recently ignited quicklime, the so-called *absolute alcohol* is obtained.

Spirituous liquids. — Wines and beers contain from about 3 to 15 per cent. of alcohol. If the " beer " obtained from rye, corn, or potatoes be distilled the distillate, called *whisky*, contains about 50 per cent. of alcohol ; if wine be similarly treated, *brandy* containing up to 70 per cent. alcohol is obtained ; while rum and

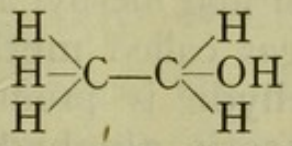
gin—containing about 75 per cent. of alcohol—are derived from molasses. All these distilled liquids contain minute quantities of volatile flavouring materials which are distilled from the fermented liquid along with the alcohol and water.

The so-called *methylated spirit*, or *denatured alcohol*, is ethyl alcohol to which wood spirit, benzene, or pyridine has been added in order to make its use in beverages and medicines impossible.

The properties of alcohol.—Ethyl alcohol, derived from the fermentation of saccharine liquids, and methyl alcohol, derived from the destructive distillation of wood (p. 557) are closely related. They are, in fact, the first two members of a homologous series of alcohols of the general formula: $C_nH_{2n-1}OH$. They are both colourless liquids, with agreeable smell. They mix with water in all proportions; they burn with a bluish flame. Ethyl alcohol boils between 78° and 79°, methylated about 65°. Analyses and vapour density determinations correspond with the formulæ:

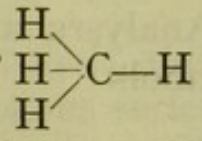


Methyl alcohol—CH_3OH.

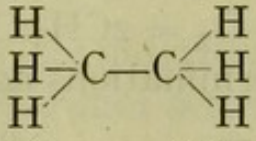


Ethyl alcohol—C_2H_5OH.

Methyl alcohol is thus regarded as a hydroxyl derivative of methane, and ethyl alcohol, a hydroxyl derivative of ethane.



Methane—CH_4.

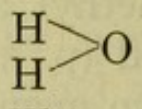


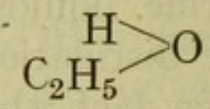
Ethane—C_2H_6.

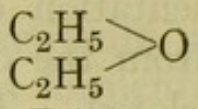
Glycerol or glycerine is an alcohol derived from the next higher homologue of the series—propane, C_3H_8. Normal propyl alcohol has a composition corresponding with C_3H_7OH; in the glycerol molecule (p. 655), three of the hydrogen atoms of propane are replaced by OH radicles, and accordingly, the formula of glycerol is written $C_3H_5(OH)_3$.

Ethers.—When ethyl alcohol is heated with sulphuric acid at about 140°, a highly inflammable vapour is given off. If the vapour be passed through a well-cooled condenser, a distillate

is obtained which separates into two layers. The lower aqueous layer is rejected ; the upper layer is treated with a concentrated solution of sodium hydroxide, and the volatile liquid which floats on the soda solution is shaken with anhydrous calcium chloride, and afterwards distilled. The resulting liquid—called *ether*—is very volatile, and it has a pleasing odour. Ether has a composition corresponding with $(C_2H_5)_2O$. The relationship of ether to water and alcohol is illustrated by the following scheme :—

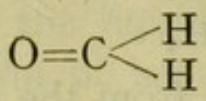

Water.

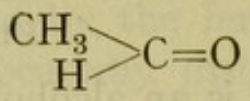

Ethyl alcohol.

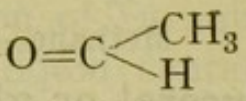

Ether.

Ether is a good solvent for waxes, fats, oils, and organic compounds. It is used as an anæsthetic. Ethyl ether, $(C_2H_5)_2O$, is one member of a large group of related substances, *e.g.* **methyl ether,** $(CH_3)_2O$; **methyl ethyl ether,** $CH_3.C_2H_5O$, etc.

Aldehydes.—When alcohol is oxidized, say by passing a mixture of air and methyl alcohol vapour over warm platinized asbestos, a *gas* called **methyl aldehyde, formic aldehyde,** or **formaldehyde** is produced. With ethyl alcohol, **ethyl aldehyde, acetic aldehyde,** or **acetaldehyde** is obtained as a colourless liquid, boiling nearly at 21°. The effect of the oxidation in both cases is to remove two atoms of hydrogen per molecule. Thus, $2CH_3OH + O_2 = 2H.COH + 2H_2O$; and $2C_2H_5OH + O_2 = 2CH_3.COH + 2H_2O$. Analyses and vapour density determinations agree with the symbols :

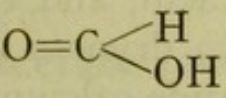

Formaldehyde—H.CO.H.


Acetaldehyde—$CH_3.CO.H$.

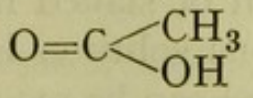


When a warm solution of ammoniacal silver nitrate is treated with either aldehyde, the silver is reduced to the metallic state which is deposited as a mirror-like film on the glass. With formaldehyde, for instance, $H.CO.H + Ag_2O = 2Ag + H.COOH$. A chlorine substitution product of ethyl alcohol—$CCl_3.CO.H$—related to acetic aldehyde—$CH_3.CO.H$—can be prepared by the prolonged action of chlorine upon ethyl alcohol. This compound

—called **chloral,** $CCl_3.CO.H$—crystallizes from its aqueous solution with a molecule of water to form the **chloral hydrate,** $CCl_3.CO.H(H_2O)$, of commerce. This is used in medicine for inducing sleep. When heated with caustic potash, chloral, or chloral hydrate is reduced to **chloroform,** $CHCl_3$, and the potassium salt of formic acid, viz. potassium formate—$CCl_3.CO.H + KOH = CHCl_3 + H.COOK$. When exposed to the air, or treated with certain oxidizing agents, the aldehydes are oxidized to the corresponding acids. Formaldehyde gives **formic acid,** $H.CO.OH$, and acetaldehyde gives **acetic acid,** $CH_3.CO.OH$.



Formic acid—$H.CO.OH$.



Acetic acid—$CH_3.CO.OH$.

Thus the aldehydes are intermediate products formed during the oxidation of the alcohols to the corresponding acids.

Paraffin.	Alcohol.	Aldehyde.	Acid.
CH_4	$\rightarrow CH_3OH$	$\rightarrow H.CO.H$	$\rightarrow H.CO.OH$
C_2H_6	$\rightarrow C_2H_5OH$	$\rightarrow CH_3.CO.H$	$\rightarrow CH_3.CO.OH$

By using more vigorous oxidizing agents, the alcohols can be oxidized to the acids without any signs of the intermediate formation of aldehydes.

§ 7. Acids.

The alcohols, aldehydes, and acids just indicated are members of homologous series related to the paraffin series as indicated in the following table :—

Alcohols.		Aldehydes.		Acids.	
Methyl alcohol	CH_3OH	Formaldehyde	$H.COH$	Formic acid	$H.COOH$
Ethyl alcohol	C_2H_5OH	Acetaldehyde	$CH_3.COH$	Acetic acid	$CH_3.COOH$
...	...	...	...	...	...

Formic acid, $H.CO.OH$, is produced during the oxidation of many organic substances, and it was originally discovered in the reddish liquid obtained by distilling water containing a number of red ants—*formica*, an ant—hence the name. Formic acid is likewise derived from stinging nettles. The inflammation produced by the sting of a bee is said to be due to the injection

of formic acid by the bee's sting. Formic acid is manufactured by heating oxalic acid with glycerol. It acts as a monobasic acid, forming a series of salts **formates**—*e.g.* **sodium formate,** H.COONa. Formic acid and the formates are strong reducing agents—thus mercuric chloride, $HgCl_2$, is reduced to HgCl, and finally to mercury itself: $2HgCl_2+H.COOH \rightarrow 2HgCl+2HCl+CO_2$, and $2HgCl+H.COOH \rightarrow 2Hg+2HCl+CO_2$.

Acetic acid, $CH_3.COOH$.—Acetic acid is formed during the dry distillation of wood, and it will be found in the crude "wood spirits" indicated on p. 557. The crude wood spirit is treated with soda ash or slaked lime to fix the acid, and the reddish-brown aqueous solution is evaporated to dryness so that the methyl alcohol can be recovered. The crude calcium or sodium acetate is then distilled with dilute hydrochloric acid. The resulting liquid contains about 50 per cent. of acetic acid. This can be further purified by repeating the treatment. If anhydrous sodium acetate be distilled with concentrated sulphuric acid, a distillate can be obtained which crystallizes on cooling. This is the so-called *glacial acetic acid.*

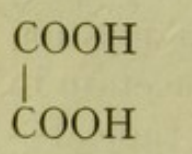
Vinegar.—If dilute solutions of alcohol—*e.g.* wine, cider, beer, etc.—be exposed to air, a curious "acetous" fermentation occurs, and the alcohol is oxidized to acetic acid. The resulting liquid is vinegar, which contains 3–10 per cent. of acetic acid. The fermentation is produced by a minute organism, the so-called **vinegar ferment** (*Mycoderma aceti*). To accelerate the action, the alcoholic liquid is allowed to slowly trickle down a column of wood shavings previously "sown" with the required ferment. If "deteriorated" wines be employed, *wine vinegar* results; and if the alcoholic liquid derived from malted grain (p. 648) be employed, *malt vinegar* results. Vinegar made from the acetic acid derived from wood is called *wood vinegar.*

The properties of acetic acid.—Commercial acetic acid is a colourless aqueous solution containing about 30 per cent. of the anhydrous acid, CH_3COOH. It has a pungent odour and a characteristic "sharp" taste. It is not charred when mixed with concentrated sulphuric acid. The prolonged action of chlorine in sunlight furnishes **mono-, di-, and tri-chloracetic acids**—$CH_2Cl.COOH$, $CHCl_2.COOH$, $CCl_3.COOH$. Acetic acid

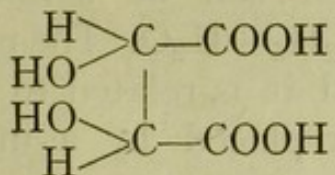
is monobasic, and combines with bases forming **acetates.** Most of the acetates are soluble in water. **Sodium acetate,** CH_3COONa, crystallizes from a solution of sodium carbonate in acetic acid with the equivalent of 3 molecules of water of crystallization. **Barium acetate,** $(CH_3COO)_2Ba$; **lead acetate,** $(CH_3COO)_2Pb$, or *sugar of lead ;* **copper acetate,** $(CH_3COO)_2Cu$, are obtained by treating the respective carbonates with acetic acid. *Verdigris* is a basic copper acetate formed by the action of acetic acid on copper in the presence of air. Acetic acid and the acetates are used in the preparation of dyestuffs, medicines, etc.

Silver acetate precipitates when silver nitrate is added to a solution of sodium acetate. Silver is not reduced even after prolonged boiling. Under similar conditions **silver formate** would be reduced to metallic silver. Like the thiocyanates, acetates give a deep red coloration when treated with ferric chloride, but, unlike the coloration with the thiocyanates, the red colour persists when treated with mercuric chloride.

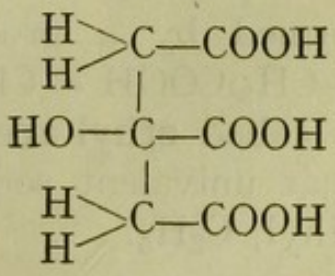
There are three organic acids—oxalic, tartaric, and citric acids—often used in analytical and other work. They do not belong to the same homologous series as acetic and formic acids, although they are fundamentally related to the corresponding hydrocarbons. The organic chemist tells us that their graphic formulæ are—



Oxalic acid (dibasic).



Tartaric acid (dibasic).



Citric acid (tribasic).

Oxalic acid occurs as a potassium or calcium salt in wood sorrel, in rhubarb and many other plants. It is produced during the oxidation of many organic substances—sugar, sawdust, starch, etc.—say by the action of nitric acid. The acid is dibasic with a composition corresponding with $H_2C_2O_4$, or $(COOH)_2$. **Calcium oxalate** is not very soluble in water, and hence oxalic acid or a soluble oxalate is used as a test for

calcium salts, since a white precipitate of calcium oxalate separates when the solutions are mixed. Oxalic acid gives a mixture of carbon mono- and di-oxide when heated with sulphuric acid. The crystals of the acid have the composition $(COOH)_2.2H_2O$.

Tartaric acid occurs in the juice of many fruits—grape, pineapple, mulberry—either free, or as the potassium or calcium salt. The analysis and other properties of tartaric acid correspond with the empirical formula $C_4H_6O_6$. The acid is dibasic. **Potassium tartrate** has the composition $K_2C_4H_4O_6$; **potassium acid tartrate,** also called *cream of tartar*, has $KHC_4H_4O_6$. A crude form of this salt is deposited in wine casks and called *argol* or *tartar of wine*. *Rochelle salt* is a **potassium sodium tartrate,** $KNaC_4H_4O_6$. **Potassium antimonyl tartrate,** or *tartar emetic*, has $K(SbO)(C_4H_4O_6)_2.H_2O$.

Citric acid occurs in many fruits—orange, lemon, gooseberry, currant, etc. The acid is tribasic and the crystals have the composition $H_3C_6H_5O_7.H_2O$. Magnesium and iron citrates are used medicinally.

Esters.—When ethyl alcohol is warmed with acetic acid and sulphuric acid, one of the products of the action is a volatile liquid with a pleasant fruit-like odour. The analysis, vapour density, etc., indicate that the compound has a composition corresponding with the formula $CH_3.COOC_2H_4$, and that it is formed by a process which can be symbolized: $C_2H_5OH + CH_3.COOH = CH_3.COOC_2H_5 + H_2O$. The product in question is called **ethyl acetate,** and it is related to sodium acetate in that univalent sodium is replaced by a univalent radical—ethyl, C_2H_5.

$CH_3.COOH$	$CH_3.COONa$	$CH_3.COOC_2H_5$
Acetic acid.	Sodium acetate.	Ethyl acetate.

Ethyl acetate is one member of a large group of similar compounds called **esters.** The esters can be regarded as salts of organic acids, with organic radicles in place of the basic elements—Na, K, Ba, Pb, etc.—of ordinary **salts.** The odour of ethyl acetate is so characteristic that the reaction under discussion can be used as a **test for acetic acid or for ethyl**

alcohol. Some of the esters are used as cheap flavouring extracts and perfumes: *e.g.* **ethyl butyrate**—derived from butyric acid—has a smell and taste resembling pine-apples; **amyl acetate** similarly has the fruity smell of Jargonelle pears; **amyl valerate**, apples; etc.

§ 8. Soaps.

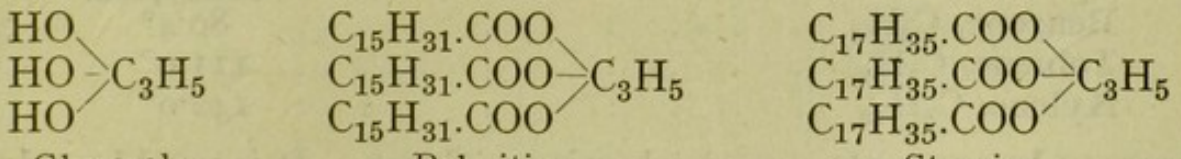
Descending the homologous series of the so-called fatty acids

		Boiling point.
Formic acid	$H.COOH$	100°
Acetic acid	$CH_3.COOH$	119°
Propionic acid	$C_2H_5.COOH$	140°
Butyric acid	$C_3H_7.COOH$	163°
Valeric acid	$C_4H_9.COOH$	185°

we come, in the same homologous series, to

		Melting point.
Palmitic acid	$C_{15}H_{31}.COOH$	62·0°
Margaric acid	$C_{16}H_{33}.COOH$	59·9°
Stearic acid	$C_{17}H_{35}.COOH$	69·2°

The esters of the three last-named acids with the trihydric alcohol glycerol, $C_3H_5(OH)_3$—stearin and palmitin—are found in many natural fats, thus, **stearin** is found in tallow, etc.; **palmitin** in palm-oil, etc. Olive oil contains a similar substance, **olein,** which is similarly derived from **oleic acid,** $C_{17}H_{33}.COOH$, an acid related with stearic acid in the same sense that ethane, C_2H_6, is related to ethylene, C_2H_4. *Beef and mutton fats* are mixtures of these substances with stearin predominating; in *lard*, palmitin and olein predominate; *butter* contains all three substances along with glycerolic esters of butyric and other acids. Hence, the acids in the same homologous series as those just indicated are often called **fatty acids.**



Glycerol. Palmitin. Stearin.

When these fats are boiled with an alkali, sodium hydroxide or sodium carbonate, they are hydrolyzed, the sodium salts of the

respective acids and glycerol are formed. The process of decomposition is called **saponification.** In symbols :

$$(C_{17}H_{35}COO)_3C_3H_5 + 3NaOH \rightleftharpoons 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

Stearin. Sodium stearate. Glycerol.

If the fats be treated with hot steam or dilute sulphuric acid, glycerol, and the corresponding acid are formed. Ordinary **hard soap** is mainly a mixture of the sodium salts of these acids—sodium palmitate, sodium stearate, and sodium oleate ; while ordinary **soft soap** is a similar mixture of the potassium salts of these acids.

The sodium and potassium soaps are readily soluble in water, while the corresponding calcium and magnesium soaps are but very sparingly soluble—pp. 210 and 211. The soap in aqueous solution is partially hydrolyzed into the corresponding acids and the alkali hydroxide, the latter attacks grease and removes it from fabrics, etc., in a soluble condition. Soap also attacks paraffin oils not attacked by the alkali hydroxides. Hence it is inferred that the cleansing properties of the soaps is a two-fold action.

To summarize, the fats are esters which can be hydrolyzed by steam or dilute acids to form glycerol and the corresponding fatty acids, and converted by alkalies into glycerol and soap. The glycerol of commerce is thus a by-product in the manufacture of soap.

§ 9. Benzene and its Derivatives.

Benzene, or benzol, is a colourless liquid obtained as a by-product in the distillation of coal tar. It is the first member of a homologous series of hydrocarbons which runs :

	Boiling point.
Benzene, C_6H_6	80·4°
Toluene, C_7H_8	111·0°
Xylene, C_8H_{10}	142·0°

Benzene burns with a smoky luminous flame. It is used largely as a solvent for fats, oils, resins, sulphur, rubber, etc. When treated with nitric acid, it forms a yellow liquid which has the

smell of bitter almonds. Analysis and vapour density determinations correspond with the formula $C_6H_5NO_2$, and the product is called **nitrobenzene.** When nitrobenzene is reduced by nascent hydrogen, it furnishes an oily liquid called **aniline,** which has a composition corresponding with $C_6H_5.NH_2$. It is largely used in the manufacture of **aniline dyes.** The chemistry of aniline is extensive.

The so-called **carbolic acid** is a by-product of the distillation of coal-tar. It can be regarded as an alcoholic derivative of benzene, in the same sense that methyl alcohol is a derivative of methane. The anhydrous compound has a composition corresponding with C_6H_5OH, and it is called **phenol**, or **phenyl alcohol.** The aqueous solution of phenol is called carbolic acid, because it behaves in some respects like an acid : (1) It reddens blue litmus ; (2) it reacts with sodium hydroxide, forming a derivative $C_6H_5.ONa$—**sodium phenylate**—soluble in water ; (3) the aqueous solution also conducts electricity like weak acids do. The phenylic alcohols thus form a distinctive class with properties distinguishing them sharply from those of the methylic series of alcohols. The explanation of the acidic properties of the phenols in terms of the ionic theory is still in the controversial stage.

There are several other homologous series of hydrocarbons besides those just indicated. **Turpentine,** for example, $C_{10}H_{16}$, is the sixth member of a series beginning with C_5H_8, **valylene ;** and **naphthalene,** $C_{10}H_8$, and **anthracene,** $C_{14}H_{10}$, are obtained as by-products from coal tar. Both naphthalene and anthracene are white solids. The former is used as a substitute for camphor under the name " moth balls." Naphthalene is used in the manufacture of *indigo* dye, and anthracene in the manufacture of *alizarine* dye, in imitation of the Turkey red dye formerly extracted as a colouring principle from madder root.

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