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ELEMENTARY CHEMISTRY FOR COAL-MINING STUDENTS

BY

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PREFACE

FOR many years I have delivered both popular and more or less systematic courses of lectures to deputies and other workers in coal mines, students who have little or no knowledge of chemistry but are keenly desirous of learning something of the subject which may be useful to them in their daily occupation. The ordinary text-book of chemistry does not meet their requirements, for it contains much that it is unnecessary for them to study, and much that it is desirable for them to know is not to be found in it.

The present work has been prepared with the object of meeting the wants of these as well as of other students of coalmining. It is really a compilation of those parts of chemistry, pure and applied, that are cognate to the coal-mining industry, and does not pretend to be a text-book of chemistry.

Its arrangement is based on the plan I have adopted in my lectures, namely, to divide the subject into two parts. The first part includes the description of those elements that enter into the composition of coal, among the compounds of which are found all the gases and most of the principal substances met with in coal mines. In this part a certain amount of necessary chemical theory is introduced. The first nine chapters are devoted to this part and in them special attention has been given to such subjects as irrespirable and extinctive atmospheres, the occurrence and detection of poisonous gases and their action on the animal system, the safety lamp and its use in the detection of fire-damp, the hygrometer and its use. The second part is included in the next four chapters and treats of the chemistry of coal and coke, the coking process, by-products and their recovery, explosives, explosions of gases and coal dust.

The ordinary worker underground will probably find it sufficient to confine his studies to the early chapters, but it is hoped that the colliery official and mining pupil may find it profitable to extend their reading to the more advanced subjects

PREFACE

dealt with in the later chapters, which are written specially for them.

In compiling a book of this kind its author must necessarily make use of works which treat of special branches of the subject, and I beg to acknowledge my indebtedness for the information I have obtained from "The Detection of Gases and Inflammable Vapours," by Clowes and Redwood ; "Investigations of Mine Air," by Le Neve Foster and Haldane; "Explosions in Coal Mines," by W. N. and J. B. Atkinson; and "Dictionary of Applied Chemistry," edited by Sir Edward Thorpe. I have made free use of the Transactions of the Institution of Mining Engineers, as well as those of the Midland Institute of Mining, Civil, and Mechanical Engineers, and the Midland Counties Institution of Engineers, and I am indebted to the Council of the Institution of Mining Engineers for the use of diagrams 63, 65, 66, 67, 85, and 86; to Messrs. J. and A. Churchill for the block for Fig. 70, from "Chemical Technology," vol. ii.; Groves and Thorpe, "Lighting"; and to Mr. Henry Davis of Derby for offering me the use of the hygrometric tables given in Appendix V., and of blocks for Figs. 27, 59, 60, 75, and 76. I have to thank Messrs. Crosby, Lockwood & Co. for permission to reproduce the tables on pp. 50, 51, and 151; Messrs. W. N. and J. B. Atkinson for the reproduction of the plans of the Whitehaven and Trimdon Grange explosions, and the Controller of H. M. Stationery Office for the plan of the Altofts explosion. I am also indebted to Mr. W. E. Garforth for permission to give an abridged account of his experiments on coal dust explosions. I have to thank Mr. W. T. Thornhill, who has been most assiduous in reading the proof sheets, and lastly to acknowledge the very valuable assistance I have received from my wife.

L. T. O'S.

SHEFFIELD, 1910.

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ELEMENTARY CHEMISTRY FOR COAL-MINING STUDENTS

CHAPTER I

INTRODUCTION

It has been recognised for many years that some knowledge of chemistry is necessary for those who are engaged in the perilous occupation of coal mining. The miner is surrounded with many dangers which, in a large number of cases, are either closely associated with the chemical properties of bodies met with in the mine, or are the result of certain chemical phenomena.

Although this may be said to be true of all callings in life, yet in the miner's case he is often placed in a situation where escape is difficult and where prompt action is necessary to avoid disaster. A knowledge, therefore, of chemistry, the science which deals with the composition and properties of all kinds of matter, ought to enable the student to foresee the danger and so prevent its occurrence; or if brought face to face with such a danger, to act in a manner which will either avert disaster or confine it to the smallest possible limits.

Whilst it is unnecessary for the mining student to make a complete study of chemical science to understand and realise the causes of the dangers arising from chemical phenomena, it is essential that he should be acquainted with some fundamental chemical principles if he is in any way to profit by a study of those parts of the science which are cognate to his calling.

Whether chemistry be studied as a whole, or merely in part, it is chemistry, and being such is founded on certain fundamental principles and facts which must be known before any progress can be made. The student is therefore recommended to carefully study this chapter, in which are explained a few of those principles.

CHEMISTRY FOR COAL-MINING STUDENTS

It has been said that chemistry deals with the composition and properties of all kinds of matter. The *properties* of any substance are certain characteristics by which it can be readily recognised, and these properties often involve changes in the bodies. For example, water, if cooled to a certain temperature, is converted into a solid, ice; or, if heated to another temperature, into an invisible vapour called steam. The property of water to freeze at one temperature consists in a change from liquid to solid; whilst its property to boil at another temperature consists in a change from liquid to vapour. A piece of bright iron exposed to the air in course of time becomes covered with a brown powder called rust, and if exposed to the air sufficiently long will be completely converted into this brown powder.

The property of iron to rust when exposed to the air consists in the change of the bright grey metallic iron into a brown powder. Again, a soft iron bar placed in contact with some iron nails has no tendency to attract them; but when a current of electricity is passed round the iron it will at once attract the iron nails, which will cling to it as long as the electric current flows round it, but will fall away when the current ceases. This property of soft iron is the result of a peculiar change produced by the action of an electric current.

Another example of a change is one that is brought about when a current of electricity passes through water. Bubbles of gas at once appear. This gas can be collected, and continues to be evolved only whilst the current of electricity passes through the water. A certain change is produced in the water by the electric current, which consists in the production of an invisible gas.

Physical and Chemical Change.—Let us examine these changes more carefully. It has been pointed out that liquid water is converted into solid ice by cooling, and into a vapour by heating. If these processes be reversed and the ice be heated and the steam be cooled both become water again. It is also easy to show that the weight of the ice or steam is exactly the same as that of the water from which they have been produced; and further, that ice, water, and steam, though different in appearance, are chemically the same substance in the solid, liquid, and gaseous form. The change of water into ice or steam does not involve a change in composition, only a change in state. Compare this change with that produced by a current of electricity on water. In this case an invisible gas is produced, and so far it is like steam; but if this gas be cooled it is not converted into water, which would be the case if it were steam, and a closer examination would show that two gases, very different from one another and from water, have been produced, one of which will burn and the other ignite a red-hot chip of wood. A still closer examination would show that some of the water has actually been converted into these two gases; or, in other words, some of the water has been destroyed and something new produced. The change which is here brought about in the water results in the formation of new substances the compositions of which differ from those of water. Again, if we examine the rusting of iron, we find that rust in no way resembles iron. Rust is a soft brown powder. Iron is a hard grey metallic body. Moreover, the weight of the rust is greater than the weight of the iron from which it is produced. Notwithstanding that the rust is produced from iron a careful chemical examination will show that the composition of rust is quite different from that of iron.

No alteration in the composition of an iron bar takes place when it is encircled by a current of electricity, though a certain change takes place which enables it to attract nails. The bar remains iron whether it is able to attract the nails or not, and whatever change has taken place is not a change in composition. It is evident from this examination that bodies can undergo two kinds of change: one which does not involve an alteration in the composition of the body, and another which does.

The first is called a physical change; the second, a chemical change.

Definition of Physical Change : A physical change is a change which does not affect the composition of a body.

Definition of Chemical Change : A chemical change is a change which does affect the composition of a body, new bodies with new properties being produced.

Chemical changes are continually occurring in the commonest operations of our daily life. They always result in the conversion of the bodies taking part in the change into something quite different. In some cases a single body is changed, but in many others more than one body takes part in the change. Although this is not always evident, it is generally possible to show that such is the case.

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Take the example of a burning candle (Fig. 1). It is a matter of everyday experience that a candle is changed by





FIG. 1.

burning because it disappears from our sight, although it is not so evident that the air is also changed. But place a burning candle under a glass bell jar so that the supply of fresh air is cut off, and in a few minutes the candle flame will gradually become smaller and finally go out. If. however, before it actually goes out, the jar be raised and fresh air allowed access to the flame it will burn brightly again. This shows that fresh air must be supplied to a candle flame if it is to continue to burn. It is possible to go further and show that the air is changed by the burning. Take a glass jar, pour in some clear lime water. and shake it with the air in the jar. The lime water remains guite clear and unchanged. Remove the lime water from the jar and place the

jar over a burning candle. When the candle is extinguished, shake the burnt air up with the quantity of lime water originally

used, which will become milky. It is evident that, firstly, air is necessary in order that a candle may burn; and, secondly, that during the burning the air changes as well as the candle. We have here at least two bodies taking part in the change, which, acting together, produce new bodies with properties different from those of either the air or the candle. The same applies to burning coals. We could not have a coal fire without air to burn the coals any more than without coals to burn in



FIG. 2.

the air. A change, exactly similar to the change produced by the burning of a candle, occurs when animals breathe in the air. If an apparatus be arranged, as in Fig. 2, so that air drawn into the lungs can be made to bubble through lime water in the flask, A, whilst air expelled from the lungs bubbles through lime water in flask, B, it will be found that whilst the air drawn into the lungs has no effect on the lime water, the air which is expelled from the lungs rapidly turns the lime water milky. The air which is expelled from the lungs must be different from that which enters the lungs, because lime water is affected differently by it. A chemical change has taken place within the lungs which is evidently similar to the change which occurs in the air when a candle burns, because the burnt air and the air expelled from the lungs behave in a similar manner towards lime water.

The rusting of iron is a similar chemical change to the burning of a candle. For rusting of iron to take place under ordinary conditions, air is necessary, and if air be excluded from a piece of bright iron it will never rust.

Indestructibility of Matter.—In studying chemical changes it is necessary to consider not only the kind of bodies that take part in, and are produced by, a chemical change, but also the actual weights of these substances. For instance, it has been mentioned that when iron rusts, the weight of rust produced is greater than that of the iron from which it is produced, hence in the process of rusting something has been added to the iron. Then, again, take the case of passing a current of electricity through water. Careful weighing of the water before and after would show that after the current had been passing through for some hours the water had lost weight, and therefore some had been lost. It would be equally possible to show that the weight of the two gases produced was equal to the weight of the water lost.

Again, take a burning candle; because it disappears from our sight we know its weight diminishes, but if we collect the bodies formed by its burning we can show they weigh more than the candle from which they were produced. This may be easily shown as follows (Fig. 3):—



FIG. 3.

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An ordinary lamp shade, A, is fitted at the bottom with a cork, B, perforated with a number of holes, and at the top with a cork perforated with a single hole, through which a piece of bent tubing is passed, serving to connect the lamp shade with a U-tube, C. This tube is filled with a substance called caustic soda. The whole of the apparatus is carefully weighed on the balance, D. The candle is removed from the lamp shade, lighted and replaced. In order to supply the candle with air necessary for its combustion the U-tube is connected with a bottle, E, full of water. On allowing the water to run out of the bottle air will be drawn through the apparatus, and as the air can only enter through the holes in the perforated cork, B, it is burnt as it passes the candle flame. It then passes upward and through the U-tube, where the caustic soda retains the bodies formed by the burning of the candle with the air, and any unburnt air passes into the bottle. E.

When the bottle is emptied, the current of air ceases and the candle goes out. On reweighing the apparatus it will be found to have increased in weight. It is evident that the candle weighs less after burning than before, hence the bodies produced by burning must exceed in weight the part of the candle that has been burnt. We have already seen that the air takes part in the burning, and though apparently we have actually increased the weight of matter produced by the burning, we must remember we have not taken any account of the weight of the air. Supposing we had done this by weighing the quantity of air used before and after burning, we should have found that it had lost a weight exactly equal to the increase sustained by the apparatus. Therefore, when the weight of the candle and air is taken into account, there is really neither gain nor loss. From this is learnt that when a chemical change takes place the sum of the weights of the bodies that take part in the change is exactly equal to the sum of the weights of the bodies produced by the change.

This perhaps may be made clearer by another experiment (Fig. 4). Take a flask, A, which can be closed with a cork carrying two wires, the ends of which are joined by a piece of platinum wire coiled round a piece of guncotton. Securely wire the cork in the neck of the flask and carefully weigh the flask. On removing the flask from the balance and connecting the wires with a battery, the platinum wire will become red hot and ignite the guncotton, which will be converted into gases. Replace the flask on the balance and its weight will be found to be

unaltered. This experiment differs from the candle experiment because the guncotton and air were weighed both before and after burning, whereas in the case of the candle the air was not weighed. It will be seen, therefore, that when account is taken of the weight of all bodies taking part in the change and all bodies produced by the change the total weight is unaltered.



Though chemical change causes a change in the composition of bodies, and results in the formation of new bodies, it does not result in any loss or gain in the weight of matter, and it is an axiom that the sum of the weights of bodies taking part in any chemical change is exactly equal to the sum of the weights of bodies produced by the change. This is what is understood by the Indestructibility of Matter.

There are various kinds of chemical changes.

1. There is a change in which two or more bodies combine together, producing a new body. This is a synthetical change, or *synthesis*, when bodies enter into chemical combination. An example of this kind of change is the rusting of iron. Here two bodies combine together and produce one new one.

2. The change may result in the conversion of one body into two or more new substances. This is an analytical change, or *analysis*, when a body is said to undergo chemical decomposition. The passing of a current of electricity through water results in an analytical change; the water is decomposed and resolved into two new substances.

3. A third kind of change may take place through the mutual interaction of two or more bodies which results in the production of two or more new substances. This change has been described as a double decomposition; it is partly analytical, inasmuch as it involves, in most cases, the decomposition of the bodies which take part in the change, and partly synthetical, as it results in the formation of new bodies by new combinations of the decomposed parts. When we subject bodies to analytical changes we find that bodies can be grouped into—

- (1) Those that cannot be decomposed by any means that, at present, are at our disposal—*Elements*.
- (2) Those that can be decomposed—Compounds and Mixtures.

Elements.—All bodies which cannot be resolved into two substances having properties differing from those they themselves possess are called elements. They are simple substances from which all other kinds of matter which constitute the earth's crust are formed. There are eighty-one elements known at the present time, and a list of these is given in Appendix I. Although there is so large a number of elements, many of them are very rare. It is quite unnecessary for the coal-mining student to make himself acquainted with all the elements, as the chief substances with which he is concerned do not involve a knowledge of more than five—namely, carbon, hydrogen, oxygen, nitrogen, and sulphur. It is chiefly, therefore, with these that the present volume deals.

The second class of bodies, namely, those which can be resolved into simpler bodies, may be grouped under two heads compounds and mixtures.

The majority of substances which constitute the earth's crust are compounds or mixtures.

Compounds.—A compound is composed of two or more elements so united together that the elements lose their identity. The properties of a compound differ entirely from those of its constituent elements, and a compound can only be resolved into its constituents by chemical means, that is, by bringing about a chemical change.

In the early part of this chapter two compounds have been mentioned: iron rust and water. The former is composed of two elements, the grey metal iron and the invisible gas oxygen. Examine rust, it is a brown, non-cohesive powder, bearing no resemblance to iron or oxygen, and no ordinary method of examination would enable us to discover that iron or oxygen enters into its composition. It may, however, be subjected to certain chemical processes which show us that it contains both iron and oxygen. In carrying out these processes we bring about a chemical change which destroys the rust and resolves it into its constituent elements. Again, examine water, which is a compound derived from two gases, oxygen and hydrogen. By any ordinary method you will fail to trace the existence of these gases in its composition. There appears no connection between the properties of the liquid and those of its constituents, yet we have seen that a current of electricity will resolve the water into these two gases, the elements from which it is produced; and this rending asunder of water by the electric current is a chemical change which resolves it into its elements, thereby destroying the compound.

Many of the substances with which the mining student becomes familiar in following his occupation are compounds, such as :---

| Carbon dioxie | de, . | | | composed of | of carbon | and oxygen. |
|---------------|---------|-----|---|-------------|-----------|----------------|
| Carbon mono | xide, | | | | ,, | ,, |
| Marsh gas, . | | | | 22 | 33 | hydrogen. |
| Sulphuretted | hydroge | en, | | | sulphur | and hydrogen. |
| Iron pyrites, | | | | | iron and | l sulphur. |
| Gypsum or | calciu | m |) | | (calcium | , sulphur, and |
| sulphate, | | | Ì | >> | (oxyg | en. |

There is one very important property of all compounds, namely, that their composition by weight is constant, by which is meant that if several samples of any one compound are obtained from different sources, and other samples of the same compound prepared by different methods, and the weight of each constituent element determined in the same weight of each sample, those weights will always be the same.

> 11.11 parts by weight of hydrogen, and 88.89 ,, ,, oxygen.

Similarly, in 100 parts by weight of carbon dioxide there are :---

27.27 parts by weight of carbon, and 72.73 ,, ,, oxygen.

In 100 parts by weight of carbon monoxide there are :--

42.85 parts by weight of carbon, and 57.15 ,, ,, oxygen. 100 parts by weight of marsh gas contain :---

25 parts by weight of hydrogen, and 75 ,, ,, carbon.

Sulphuretted hydrogen contains in 100 parts by weight :---

5.88 parts by weight of hydrogen, and 94.12 ,, ,, sulphur.

An extensive examination of a very large number of compounds has proved this fact conclusively. On this fixity of the composition of compounds is founded the first great law of chemical combination : the law of definite proportions, namely, that Chemical combination takes place between definite masses of the elements to form compounds.

Mixtures.—The second group of bodies capable of being resolved into two or more constituents are mixtures. The constituents of a mixture may be either elements or compounds; there is no chemical combination between the constituents, each preserves its identity, and their particles lie side by side in more or less intimate contact. Take, for example, a mixture of sand and sugar; if you cannot distinguish the particles of sand from those of the sugar by the naked eye, you will be easily able to do so with the aid of a microscope. The same will be the case if you mix some iron filings and sulphur. Examine a piece of coarse-grained granite and you will easily see that it is composed of different substances, the particles of which lie closely together.

These illustrations of mixtures will serve to show what is meant by saying that in a mixture the constituents preserve their identity and are not chemically combined. Seeing that the constituents of the mixture remain unchanged it is natural that the properties of the mixture resemble those of its constituents. At the same time a mixture can generally be resolved into its constituents by mechanical means, by which is understood means which do not involve the destruction of the constituents by chemical change. For instance, take the mixture of sand and sugar. The separation of these two substances is easily effected by throwing the mixture into water, when the sugar dissolves, and the sand, being insoluble, sinks to the bottom. If a magnet be run through the mixture of iron filings and sulphur, the iron filings will adhere to the magnet whilst the sulphur remains unaffected. If the granite be broken into pieces it is easy to pick out the different constituents and separate it into at least three different substances.

Finally, the composition of a mixture is not necessarily a definite one; substances, as a rule, may be mixed together in any proportion by weight, though examples are known where the proportion in which the constituents are mixed is nearly, if not absolutely, constant.

Examples of mixtures are : the air, black-damp, after-damp, explosives such as gunpowder, ammonium nitrate explosives, and others.

Summary.—Before proceeding further with the subject let us summarise what we have learnt.

1. Bodies can undergo two kinds of changes :---

- (a) Physical change, which does not affect the composition of a body.
- (b) Chemical change, which does affect the composition of a body, new bodies with new properties being produced.

2. There is no change in the total weight of matter when chemical change takes place. The sum of the weights of the bodies taking part in the change is equal to the sum of the weights of the bodies produced by the change.

3. Matter may be divided into three classes of substances :---

- (a) Elements, which cannot be resolved into simpler substances by any means at present at our disposal.
- (b) Compounds, composed of two or more elements united together in fixed proportions by weight. The properties of a compound differ entirely from those of its constituent elements, into which it can be resolved by chemical means only.
- (c) Mixtures, composed of two or more elements or compounds intimately mixed together without chemical combination. The properties of the mixture usually resemble those of its constituents, into which it can generally be resolved by mechanical means. The constituents of a mixture are not necessarily present in any fixed or definite proportion by weight.

4. The law of definite proportion : Chemical combination takes place between definite masses of elements.

Combining Weights .- If the student has grasped the meaning

of these fundamental facts it is now necessary to go a step further and study more closely the composition of the bodies called compounds.

It has already been stated that the composition by weight of every chemical compound is fixed and unalterable. If we examine the numbers representing the percentage composition of any compound we find that in every case they bear to one another a very simple relation, though in some cases this is at first sight not evident.

Let us take the compounds mentioned on pages 9 and 10:— The percentage composition of water is hydrogen 11:11, and oxygen 88:89, which numbers are in the proportion of 1 to 8.

| 11.11 | 1 | | Hydrogen. |
|-------|--------------------|--|-----------|
| 88.89 | $\overline{8}$ | | Oxygen. |

In the case of carbon dioxide the percentage composition is: carbon, $27 \cdot 27$; oxygen, $72 \cdot 73$. Divide each of these numbers by 9.9, and the proportion will become 3 to 8.

| 27.27 | 3 | | Carbon. |
|-------|--------------------|---|---------|
| 72.73 | $\overline{8}$ | _ | Oxygen. |

Carbon monoxide has the percentage composition: carbon, 42.85; oxygen, 57.15. Divide each of these by 14.28, and the relation becomes 3 to 4.

| 42.85 | 3 | | Carbon. |
|-------|--------------------|---|---------|
| 57.15 | $\overline{4}$ | - | Oxygen. |

The numbers representing the percentage composition of marsh gas are: hydrogen, 25; carbon, 75, which are in the proportion of 1 to 3.

| 25 | 1 | Hydrogen. |
|----|--------------------|---------------|
| 75 | $\overline{3}$ | Carbon. |

Lastly, in 100 parts of sulphuretted hydrogen there are: hydrogen, 5.88, and sulphur, 94.12, and these numbers are in the proportion of 1 to 16.

$$\frac{5\cdot88}{94\cdot12} = \frac{1}{16} = \frac{\text{Hydrogen.}}{\text{Sulphur.}}$$

Let us collect these results :---

| In | water | | Hydrogen | : oxygen | =1: | 8 |
|----|------------------|--------|----------|------------|-------|----|
| ,, | carbon dioxide . | | Carbon | : oxygen | =3: | 8 |
| ,, | carbon monoxide | э. | Carbon | : oxygen | = 3 : | 4 |
| ,, | marsh gas . | | Carbon | : hydrogen | = 3 : | 1 |
| " | sulphuretted hyd | lrogen | Hydrogen | : sulphur | =1: | 16 |

It will be seen that in the above examples the relations between the weights of the elements forming these compounds can be expressed by very simple numerical ratios. But what is here shown to be true in a few instances has been proved to be true in an exceedingly large number of compounds; and having found it to be true in the case of every compound that has been examined, without exception, we are justified in assuming, provided the number of cases examined is sufficiently large, that it will be true in the case of all compounds whether already known or to be discovered later. Consequently the general assertion may be made: That the weights in which elements combine together to form compounds bear a simple relation to one another.

Having arrived at this fundamental principle concerning the relative weights of elements combining together, let us examine the numbers that represent the relative weight of any one element in different compounds.

Take, for example, oxygen; in water we find 8, in carbon dioxide 8, and in carbon monoxide 4.

The relation between 4 and 8 is a very simple one, and if we examine a very large number of oxygen compounds we always find that the relative weight of that element can be expressed by some number which is a multiple or sub-multiple of 4, namely, 2, 4, 8, 16, 32, &c.

Similarly with carbon. In the examples given in the table we see that in each case the relative number is 3, and whatever compound of carbon we examine its relative weight can be expressed as some multiple of 3, namely, 3, 6, 9, 12, 18, &c.

In the case of hydrogen the relative weight is always some multiple of 1.

If we examine a large number of compounds containing oxygen, we shall find that we often have to represent the relative weight of that element present in many compounds by some multiple of 8, and experience has shown that the number 16 is the most convenient number to use. Similarly in the case of carbon, 12 is much more convenient than 3. Treating all the elements in this way, we find that for every element a certain number can be selected such that the proportion by weight in which that element enters into combination with others can be represented by it or some simple multiple of it.

Thus, for oxygen we get 16, for carbon 12, for hydrogen 1, for sulphur 32, for nitrogen 14, &c.

These numbers are called the *combining weights* of the elements, and if we adopt these numbers to represent the smallest relative weight of each element that can enter into combination, then the numbers representing the proportional composition of the compounds already mentioned are :--

| Water | Hydrogen : oxygen | 2:16=1: | 8 |
|-----------------------|--------------------|------------|----|
| Carbon dioxide | Carbon : oxygen | 12:32=3: | 8 |
| Carbon monoxide . | Carbon : oxygen | 12:16=3: | 4 |
| Marsh gas | Carbon : hydrogen | 12: 4 = 3: | 1 |
| Sulphuretted hydrogen | Hydrogen : sulphur | 2:32=1: | 16 |

Law of Multiple Proportion .- By expressing the relative weights of elements present in compounds in this way, instead of by the percentage composition, another interesting fact is revealed. Take the two compounds of carbon and oxygen: in carbon dioxide, carbon to oxygen = 12:32, and in carbon monoxide, carbon to oxygen = 12:16; and we see that the proportion of oxygen to carbon in the former is double that in the latter. In another example we have the two compounds of carbon and hydrogen, marsh gas, or light carburetted hydrogen, and ethylene, or heavy carburetted hydrogen. The percentage composition of the former is: carbon 75, hydrogen 25; whilst that of the latter is: carbon 85.72, and hydrogen 14.28. These numbers do not at first sight express any simple relations between the weights of carbon and hydrogen in the two compounds; but we have already seen that we can express the relation between carbon and hydrogen in marsh gas by the numbers 12:4. Adopting the same plan for ethylene, we find that the relation of 85.72:14.28 can be also expressed by the numbers 24:4; and again we see that the proportion of carbon to hydrogen present in ethylene is twice that present in marsh gas. A very large number of similar

INTRODUCTION

examples could be given to illustrate this fact, and as a result we are enabled to formulate another fundamental law of chemical combination, the Law of Multiple Proportion, namely :---

That when two elements, A and B, combine together in more than one proportion by weight, the relative weights of B that combine with a fixed weight of A bear a simple ratio to one another.

| Carbon Dioxide. A, Carbon, 12 B, Oxygen, 32 | Carbon Monoxide. Carbon, 12 Oxygen, 16 | Relation between weights of B. 2:1 |
|---|--|---------------------------------------|
| Marsh Gas. A, Hydrogen, 4 B, Carbon, 12 | Ethylene. Hydrogen, 4) Carbon, 24) | Relation between weights of B. 1:2 |

The student has now reached a second stage in his introductory study of chemistry, and he should understand that every statement made is a statement of fact and not of theory. Further, that when we find the same fact is proved to be true in the majority of cases examined, we state that fact in general language and call it a law. A law in science, then, is a statement of fact which has proved to be generally true for all cases to which it can be applied.

The laws of chemical combination are examples of such scientific laws. They are :---

1. The law of definite proportions.

Chemical combination takes place between definite masses of the elements to form compounds.

2. The relative weights of elements entering into combination with one another can be expressed by simple numbers, called the combining weights.

3. The law of multiple proportions, when two elements, A and B, combine together in more than one proportion by weight, the relative weights of B, which combine with the same weight of A, bear a simple relation to one another.

Symbols and Formulæ.—We have seen that we can represent the relative weights in which elements combine together by simple numbers, and we further represent these numbers by what are known as *symbols*. For each element there is a separate symbol, generally the initial or two first letters of the English or Latin name.

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The symbols of the elements already chiefly mentioned are :---

| Carbon | | | С. |
|----------|--|--|----|
| Hydrogen | | | H. |
| Oxygen | | | 0. |
| Nitrogen | | | N. |
| Sulphur | | | S. |

It is to be distinctly understood that these symbols are not merely a chemical shorthand, but each represents the combining weight of its element, thus :—

C stands for 12 parts by weight of carbon.

| \mathbf{H} | ,, | 1 | ,, | 22 | hydrogen. |
|--------------|-----|----|----|----|-----------|
| 0 | ,, | 16 | ,, | ,, | oxygen. |
| Ν | ,, | 14 | >> | 33 | nitrogen. |
| \mathbf{S} | ,,, | 32 | >> | >> | sulphur. |

This being the case, it is easy to see how we can express at once the formula of a compound. For instance, take carbon dioxide, in which the proportion between the weights of carbon and oxygen is as 12 to 32. C equals 12 parts by weight of carbon, and O equals 16 parts by weight of oxygen, therefore 32 parts by weight of oxygen will be O+O=20, which is often written O_2 , so that the formula for carbon dioxide becomes CO_2 . Similarly the proportion of carbon to oxygen in carbon monoxide being 12:16 the formula becomes CO. In the case of water the proportion of hydrogen to oxygen is 2:16; now H represents 1 part by weight of hydrogen, so 2 parts by weight of hydrogen are represented by 2H or H₂, and as O is 16 parts by weight of oxygen the formula for water becomes H₂O. Thus every compound can be represented by a formula which is not merely a shorthand sign for its name, but, like the symbols of the elements, has a definite numerical value which shows—

1. The relative weights of the elements combining together.

2. The relative weight of the compound produced by their combination. Thus CO_2 represents that 44 parts by weight of carbon dioxide are composed of 12 parts by weight of carbon and 32 parts by weight of oxygen, and CO that 28 parts by weight of carbon monoxide are formed from 12 parts by weight of carbon and 16 parts by weight of oxygen, whilst H_2O

represents 18 parts by weight of water, composed of 2 parts by weight of hydrogen and 16 parts by weight of oxygen.

If the student has carefully studied the foregoing pages, he will remember that chemical combination takes place between definite masses of substances, and that the sum of the weights of bodies taking part in any chemical change is equal to the sum of the weights of the bodies produced by the change.

Chemical Equations.—Having given a numerical value to the symbols of elements and the formulæ of compounds, we can use these to represent a chemical change. This is done in the form of what is called a chemical equation, in which the symbols representing the relative weights of the bodies taking part in the change are written down and connected by the sign of addition (+), and similarly the symbols representing the relative weights of bodies produced by the change, whilst the two sets of symbols are connected by the sign of equality (=). The sign of addition in a chemical equation does not mean "added to" but rather "combined with." For instance, the formation of water from hydrogen and oxygen is written thus, $H_2 + O = H_2O$, whilst the decomposition of water into hydrogen and oxygen is written $H_2O = H_2 + O$. To express such equations in words we should say of the first—

| 2 | parts | by | weight of hyd | rogen | combine with |
|----------|-------|----|-------------------|-------|--------------|
| | | | H_2 | | + |
| 16 | parts | by | weight of oxy | gen | and produce |
| | | | 0 | | |
| 18 | parts | by | weight of wat | er. | |
| | | | H ₂ O. | | |
| | _ | | | | |

And of the second—

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| 18 | parts | by | weight of water | produce on | decomposition |
|----------|-------|----|--------------------|------------|---------------|
| | - | | H ₂ O | = | |
| 2 | parts | by | weight of hydrogen | and | |
| | - | • | H ₂ | + | |
| 16 | parts | by | weight of oxygen. | | |
| | - | Ť | 0. | | |

The student should specially note the meaning of the signs + and =. In only one sense can the sign of equality be taken in its algebraic signification, namely, to represent that the sum of the weights of bodies taking part in a chemical

change is equal to the sum of the weights of the bodies produced by the change. Most chemical changes can be represented by equations, and these equations represent :---

1. The relative weights of substances taking part in the change.

2. The relative weights of substances produced by the change.

3. That the sum of the weights of substances taking part in the change is equal to the sum of the weights of substances produced by the change.

CHAPTER II

THE AIR OR ATMOSPHERE

THE atmosphere or gaseous envelope which surrounds the solid portion of the earth's crust is called the Air. It is an example of the class of bodies described as mixtures.

The following experiment will show that the air is not a simple gas. A bell jar, A (Fig. 5), is placed over a stand, B, in a



Before burning.



After burning.

trough, C, containing water. A small quantity of red phosphorus is placed on the stand, and it is noticed that the level of the water inside and outside the bell jar is the same. The phosphorus is ignited and allowed to burn in the air contained in the closed bell jar. A large quantity of white fumes is produced, and eventually the phosphorus ceases to burn. After a time the white fumes become dissolved in the water, and a large quantity of a transparent gas remains in the upper part of the bell jar. But it will be noticed that the level of the water inside the bell jar is considerably higher than that of the water outside ; a certain quantity of the air has disappeared during the combustion, and the volume it occupied is now filled with water. If water be now poured into the trough until the level of the water outside the bell jar is brought up to the same level as that

FIG. 5.

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inside, and after removing the stopper a lighted taper be plunged into the bell jar the taper will be extinguished. This shows that only a portion of the air takes part in the combustion of phosphorus, whilst a considerable residue of gas is left behind which is not air, inasmuch as it will not support combustion. Air, then, is not a simple body, but consists of at least two parts, one of which supports combustion and the other does not.

Very careful investigation has shown that the portion of the air which supports the combustion of the phosphorus is oxygen, whilst the inactive residue contains two gases, nitrogen and argon. These three gases form the greater part of our atmosphere; but others, namely, carbon dioxide, ammonia, nitric acid, and aqueous vapour, are present in relatively very small quantities.

The constituents of the air are not in a state of chemical combination, consequently it is a mixture and not a compound; therefore its properties must resemble those of its constituents, and, if the properties of its constituents be studied, something will be learnt of the properties of air. It is natural to suppose that the properties of the mixture will be chiefly determined by those of the gases present in the largest quantities. These are oxygen and nitrogen.

Oxygen. Symbol O. Atomic weight, 16.

Oxygen was discovered in 1774 by Joseph Priestley, who heated red oxide of mercury (mercuric oxide), HgO, and obtained



FIG. 6.

a gas which would ignite a glowing chip of wood (Fig. 6). The experiment can easily be repeated by heating mercuric oxide in a test tube, when a chemical change takes place; globules of mercury collect on the cool part of the tube and oxygen gas is set free, so that a glowing chip bursts into flame when plunged into the test tube.

The decomposition of mercuric oxide is expressed by the equation HgO = Hg + O. The yield of oxygen given by mercuric

oxide is very small. Oxygen, however, enters into the composition of many other substances, some of which when heated yield very large quantities of the gas, and may be used for its preparation. Amongst these substances is potassium chlorate $KClO_3$, a white crystalline body composed of potas-
sium, chlorine, and oxygen. When heated it melts, and gives off oxygen in large quantities; eventually a white substance remains, called potassium chloride, KCl, a compound of potassium and chlorine only—

$$KClO_3 = KCl + O_3$$
.

The decomposition of potassium chlorate is not so simple as the above equation would appear to show. It really takes place in different stages when intermediate compounds containing oxygen are formed; but on prolonged heating these compounds decompose, so that when the decomposition is complete only potassium chloride remains.

The production of oxygen from potassium chlorate is easily shown by heating it in a test tube in a similar manner to that described in the case of mercuric oxide.

To prepare oxygen from potassium chlorate alone requires prolonged heating at high temperature, and the oxygen is evolved somewhat slowly; if, however, a small quantity of manganese dioxide, MnO_2 , be mixed with the potassium chlorate the gas is much more readily evolved at a considerably lower temperature. This method is usually adopted for the preparation of large quantities of oxygen. The apparatus shown in Fig. 7 may be used for this purpose.



FIG. 7.

Physical Properties.—Oxygen is a colourless, odourless, tasteless gas, slightly heavier than air, its specific gravity being 1.1056. It is slightly soluble in water, and by the combined action of cold and pressure can be condensed to a liquid.

Chemical Properties.—It combines chemically with most of the elements, and all bodies which burn in air burn more brightly in oxygen. A glowing chip plunged into a jar of

oxygen gas at once inflames. When a candle burns in air it has been shown to produce a gas which turns lime water milky.



A lighted candle introduced into a jar of oxygen (Fig. 8) will burn with increased brilliance, and the gas which remains after the burning has taken place will turn lime water milky.

It is evident that whether a candle burns in air or oxygen the same gas is formed.

Charcoal, a form of the element carbon, will burn in air, but only with a glow. If a piece of glowing charcoal be plunged into a jar of oxygen (Fig. 9), it will burn with much greater activity, $C + O_2 = CO_2$.

If lime water be added to the gas in which the charcoal has burnt, the lime water is turned milky.

The same gas must be formed whether carbon or a candle burns in oxygen. This gas is carbon dioxide. The wax of which the candle is made contains carbon, and the

carbon dioxide formed when a candle burns in air or oxygen is produced by the union of the carbon in the wax with oxygen. In the same way carbon dioxide is formed when any body containing carbon, such as coal, wood, paper, &c., burns in air or oxygen.

Sulphur readily takes fire in air and burns with a pale blue flame, producing a gas with a suffocating

odour, which is noticed in the neighbourhood of any spoil heap that is on fire. If a piece of







FIG. 10.

burning sulphur is plunged into oxygen it burns with increased brilliancy, and the same suffocating odour will be noticed. This is due to the formation of a gas called sulphur dioxide, $S + O_2 = SO_2$.

If we add blue litmus ¹ solution to the jar in which sulphur has been burnt it will be turned red (Fig. 10). Just as any body

containing carbon forms carbon dioxide when burnt in air or oxygen, so any body containing sulphur produces sulphur dioxide when burnt in air or oxygen. Coal contains sulphur, and sulphur dioxide is always produced when coal burns in the

¹ Litmus is a blue vegetable colouring matter formed from a lichen. The blue colour is turned to red by acids, but is restored by alkalis.

air. In a spoil heap there is generally a large quantity of iron pyrites, which contains sulphur in its composition. When a spoil heap takes fire the sulphur in the pyrites burns, forming sulphur dioxide.

We have seen how phosphorus burns in air, producing copious white fumes. It burns in oxygen with far greater brilliancy, and forms similar white fumes. These fumes consist of phosphorus pentoxide, $P_2 + O_5 = P_2O_5$, which if brought into contact with blue litmus solution instantly turns it red.

The element hydrogen burns in air or oxygen, forming water or hydrogen monoxide, $H_2 + O = H_2O$, and water is formed when any body containing hydrogen burns in air or oxygen. Coal and the wax of the candle contain hydrogen as well as carbon, so that when coal or a candle burns in air or oxygen, water is formed as well as carbon dioxide.

These experiments serve to show that the processes of combustion in air and oxygen are similar chemical changes, and, at all events in the cases mentioned, the same products are formed.

There are many substances which either do not burn readily or do not burn at all in air, but which will easily burn in oxygen. For instance, iron can be made to burn with great brilliance in oxygen, and the diamond, which will not burn in air, can be burnt in oxygen if heated at a very high temperature.

Oxides.— Whenever an *element* combines with oxygen the compound produced is called an oxide, thus—

Carbon produces carbon dioxide, CO₂.

Sulphur produces sulphur dioxide, SO_2 .

Phosphorus produces phosphorus pentoxide, P_2O_5 .

Hydrogen produces hydrogen monoxide (water), H₂O.

The oxides are a very numerous and important class of compounds. Many of them are found in the earth's crust, and constitute valuable ores, from which metals are extracted; amongst these are oxides of iron, manganese, copper, tin, &c., whilst water, the most widely distributed of all oxides, is hydrogen monoxide.

Distribution of Oxygen.—Oxygen is very widely distributed in nature; 23 per cent. of the weight of air, or slightly more than one-fifth of its volume, is composed of oxygen, whilst it forms eight-ninths of the weight of water, and 48 per

cent. of the weight of the solid part of the earth's crust. It also enters largely into the composition of all animal and vegetable matter.

Nitrogen. Symbol N. Atomic Weight 14.

The gas which remains after the burning of phosphorus in air (see p. 19) is composed of nitrogen mixed with a small quantity of argon. It was discovered in 1772 by Rutherford.

It can be prepared from air by burning out the oxygen, but when produced by this method it is always mixed with argon.

One method of burning the oxygen out of the air by means of phosphorus has been described. A more convenient way is to pass air over red-hot copper.

Copper turnings are placed in a tube, A (Fig. 11), and heated in a gas furnace, B, to a bright red heat; air contained in the gas-holder, C, is then slowly passed through the tube. The copper combines with the oxygen, forming copper oxide, CuO, Cu + O = CuO, whilst the nitrogen escapes, and may be collected over water, as shown in the illustration.



FIG. 11.

Another method of preparing nitrogen is to heat a solution of ammonium nitrite, $NH_4NO_2 = N_2 + 2H_2O$. As this salt is difficult to prepare, a mixture of ammonium chloride and potassium nitrite may be used instead—

$$\mathrm{KNO}_{2} + \mathrm{NH}_{4}\mathrm{Cl} = \mathrm{KCl} + \mathrm{N}_{2} + 2\mathrm{H}_{2}\mathrm{O}.$$

The gas prepared in this way is free from argon.

Physical Properties.—Nitrogen is a colourless, odourless, tasteless gas. It is slightly lighter than air, its specific gravity

being 0.9713. It is more sparingly soluble in water than oxygen, and is condensed to a liquid by intense cold and high pressure.

Chemical Properties.—The chemical properties of nitrogen are much less active than those of oxygen. It is incombustible, and does not support the combustion of bodies that burn in air. A burning taper is extinguished in the pure gas. It is nonpoisonous, but it cannot be breathed in a pure state because of the absence of oxygen. When mixed with small quantities of oxygen it can be breathed without any effect on the animal system. It does not turn lime water milky.

Nitrogen is chemically a comparatively inert gas. It does not readily combine directly with other elements, though a few elements heated at a high temperature in a stream of nitrogen gas do combine with it.

Nitrogen is widely distributed in nature. The gas itself composes about 78 per cent. of the volume of air, or about 76 per cent. by weight. Coal contains from 1 to 2 per cent. of nitrogen, and it is found in the minerals saltpetre (potassium nitrate), and Chili saltpetre (sodium nitrate). It is also a constituent of all vegetable and animal matter.

Although nitrogen itself is a somewhat inert body, it forms some very important compounds with other elements. Amongst these are ammonia and nitric acid, both of which are of importance to the mining student, the former because it is one of the by-products recovered during the coking of coal, and the latter because it is largely used in the manufacture of explosives.

Ammonia. Symbol NH₈. M.W.* 17.

Ammonia was discovered in 1774 by Priestley. It is a compound of nitrogen and hydrogen, and is produced in nature when the nitrogenous constituents of animal and vegetable matter decompose.

It can be formed by the direct union of nitrogen and hydrogen, though this is rather difficult to accomplish. It is most readily obtained by heating any ammonium compound with lime. The compound generally used is ammonium chloride, NH_4Cl , when ammonia is set free and water and calcium chloride, $CaCl_2$, simultaneously formed.

$$2\mathbf{NH}_{4}\mathbf{Cl} + \mathbf{CaO} = 2\mathbf{NH}_{3} + \mathbf{H}_{2}\mathbf{O} + \mathbf{CaCl}_{2}.$$

M.W. = Molecular weight.

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The apparatus for the preparation of the gas is shown in Fig. 12. A is a flask containing a mixture of finely powdered



ammonium chloride and lime, whilst the tower, B, contains quicklime for drying the gas, which is afterwards conducted into the inverted and dry gas jar, C. This method of collecting the gas is rendered necessary by its extreme solubility in water.

The chief source of ammonia is coal, from which about 0.2 to 0.4 per cent. of its weight of ammonia is obtained when it is distilled in the gas retort or by-product coke oven.

Physical Properties .--- It is a colourless gas, with a powerfully pungent odour. It is lighter than air; its specific gravity is 0.586. It is easily condensed to a liquid by cooling at a temperature of -40° C., or by subjecting the gas to a pressure of 8.5 atmospheres at 20° C. Large quantities of liquid ammonia are used in the manufacture of ice, and in the freezing process for sinking through wet ground. It is exceedingly soluble in water.



FIG. 13.

Under atmospheric pressure water will dissolve-

| \mathbf{At} | 0° | С. | 1149 | times | its volume | of ammonia. |
|---------------|--------------|---------------|------|-------|------------|-------------|
| At | 10° | $\mathbf{C}.$ | 891 | ,, | ,, | ,, |
| \mathbf{At} | 20° | C. | 529 | ,, | ,, | " |
| \mathbf{At} | 100° | $\mathbf{C}.$ | 97 | ,, | ,, | ,,, |

The solution possesses the pungent odour of the gas, and is known as ammonia, or sometimes as spirits of hartshorn. Its solubility in water can be shown by placing a vessel, A (Fig. 13), filled with the gas, over water, when the liquid will be drawn into A through the tube, B, owing to the rapidity with which the gas is dissolved.

Chemical Properties.—Ammonia will not burn if a light is brought to it in the air, but if oxygen be passed through a solution of ammonia contained in a flask the mixture of ammonia and oxygen can be ignited, when nitrogen and water are formed—

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

It turns red litmus solution blue, and is said to have an alkaline reaction. It does not support combustion, and cannot be breathed. It readily unites with acids to form bodies called ammonium salts. Thus with hydrochloric acid it forms ammonium chloride, NH_4Cl —

$$NH_3 + HCl = NH_4Cl.$$

With sulphuric acid it readily combines and forms ammonium sulphate, $(NH_4)_2SO_4$ —

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

Large quantities of this salt are made in the recovery of by-products from coke-oven gases, when, after the ammonia has been recovered, it is converted into ammonium sulphate by passing the gas into sulphuric acid.

Ammonium nitrate, NH_4NO_3 , is formed by the combination of ammonia with nitric acid—

 $\rm NH_3 + HNO_3 = NH_4NO_3$,

a salt which is largely used in the manufacture of explosives.

Nitric Acid. Symbol HNO₃. M.W. 63.

Nitric acid is a compound of hydrogen, nitrogen, and oxygen. It is a liquid obtained by distilling potassium nitrate, KNO_3 , or sodium nitrate, $NaNO_3$, with sulphuric acid.

If potassium nitrate is used the reaction takes place as follows: 2KNO + H SO 2KNO + K SO

$$2\mathrm{KNO}_3 + \mathrm{H}_2\mathrm{SO}_4 = 2\mathrm{HNO}_3 + \mathrm{K}_2\mathrm{SO}_4.$$

When sodium nitrate is used the reaction is expressed as follows: $-2NaNO_{2} + H_{2}SO_{4} = 2HNO_{2} + Na_{2}SO_{4}$.

The apparatus for preparing it on a small scale is shown in Fig. 14.

Physical Properties.—It is a colourless liquid which fumes strongly in the air and has a specific gravity of 1.53 at 5° C.

It readily mixes with water in all proportions. It boils at 86° C., but decomposition begins below this temperature.

Chemical Properties.—It turns blue litmus red. It is a powerful acid which rapidly attacks and destroys animal and



FIG. 14.

vegetable matter. Dropped on to the skin it stains it yellow, and eventually produces a sore which generally heals with difficulty. It destroys the colour of many colouring matters, and dissolves most metals, forming salts called nitrates.

The following are some of the nitrates :---

| Potassium nitrate | | KNO ₈ . |
|-------------------|-----|-----------------------|
| Sodium nitrate . | | $NaNO_{2}$. |
| Barium nitrate . | • 、 | Ba(NO ₂). |
| Ammonium nitrate | | $(NH_4)NO_3$ |

Nitric acid and the nitrates contain large quantities of oxygen, which they readily part with to bodies capable of uniting with it.

If a piece of charcoal be dropped on to melted potassium nitrate it will at once take fire and burn in the oxygen supplied by the nitrate. On account of this property the above nitrates are used to supply oxygen necessary for the proper combustion of the combustible bodies used in the manufacture of explosives. Nitric acid also interacts with certain compounds of carbon and forms what are known as nitro-compounds, many of which are explosive, and are largely used in the manufacture of blasting explosives. Thus with glycerol (glycerin) it forms nitroglycerol (nitroglycerin), which is a powerful explosive used in the manufacture of dynamite, kynite, &c., whilst guncotton or nitrocellulose is prepared by the action of nitric acid on cotton or cellulose. With benzene it forms dinitro-benzene, and with naphthalene, dinitro-naphthalene and trinitro-naphthalene, which are used in the manufacture of many of the so-called ammonium nitrate explosives.

Acids, Bases, and Salts.—In nitric acid and ammonia we have examples of bodies which belong to two great groups, namely, *acids* and *bases*. Nitric acid belongs to the first and ammonia to the second group. Associated with these is a third group, embracing a large number of substances called *salts*.

Acids .- An acid may be defined by its properties.

Firstly, acids are compounds which contain hydrogen that can be replaced by its equivalent of a metal.

Secondly, acids interact with bases to form salts.

Thirdly, most acids turn blue litmus red.

Fourthly, many acids have a sour taste.

The first property is possessed by all acids, though it alone is not sufficient to define an acid, as there are compounds, containing hydrogen that can be replaced by a metal, which are not acids; but if this property be combined with the second, the body must be an acid. The third and fourth properties are possessed by many, but not by all acids.

Among the commoner acids are :---

| Hydrochloric acid | | HCl (spirits of salts). |
|-------------------|--|---------------------------------|
| Sulphuric acid | | $H_{2}SO_{4}$ (oil of vitriol). |
| Nitric acid . | | HNO_3 (aqua fortis). |
| Acetic acid . | | $C_{2}H_{4}O_{2}$ (vinegar). |

Many so-called acids are not acids, because they contain no hydrogen. The so-called carbonic acid, CO_2 , is carbon dioxide, and is not an acid. Again, sulphur dioxide, SO_2 , is often called sulphurous acid, but it is an oxide and not an acid; an acid must contain hydrogen.

Bases.—A base is generally a compound of a metal with oxygen (an oxide), or of a metal with hydrogen and oxygen (a

hydroxide), which will interact with an acid to form a salt and water. The following are examples of bases :----

Oxides. Sodium oxide, Na_2O . Potassium oxide, K_2O . Calcium oxide (lime), CaO. Lead oxide, PbO. Zinc oxide, ZnO. Copper oxide, CuO. Bismuth oxide, Bi_2O_8 . &c.

Hydroxides.

Sodium hydroxide, NaHO. Potassium hydroxide, KHO. Calcium hydroxide, Ca(HO)₂. Lead hydroxide, Pb(HO)₂. Zinc hydroxide, Zn(HO)₂. Copper hydroxide, Cu(HO)₂. Bismuth hydroxide, Bi(HO)₃. &c.

Some of these bases are soluble in water, and those that are soluble have the property of turning red litmus blue. They are said to have an alkaline reaction, and are often called alkalis. Amongst the bases mentioned, sodium oxide, potassium oxide, and calcium oxide are soluble in water and act in this way. Now, if we take ammonia, NH_a , we see it is not an oxide, and yet it has been called a base. Properly speaking, it is not a base according to the definition given, but in many respects it acts like a base, and hence it is often included amongst the bases.

Firstly, it combines directly with acids to form salts, called *ammonium* salts. With hydrochloric acid it forms ammonium chloride, $NH_3 + HCl = NH_4Cl$; with sulphuric acid it combines to form ammonium sulphate, $2NH_3 + H_2SO_4 = (NH_4)_2SO_4$; and with nitric acid ammonium nitrate is formed, $NH_8 + HNO_8 = NH_4NO_8$.

Secondly, it is very soluble in water, and its solution turns red litmus blue. Its solution in water acts on the salts of other metals in a similar manner to solutions of potassium and sodium hydroxides, on which account the solution is often called ammonium hydroxide, and is given the formula, NH_4HO . For these reasons ammonia is classed amongst the bases.

Salts.—With regard to the third class of bodies, they are formed—

- (1) By the interaction of metals with acids, when the hydrogen of the acid is replaced by the metal.
- (2) By the interaction of an acid with a base, when the metal of the base replaces the hydrogen of the acid, which in its turn combines with the oxygen of the base to form water.

A salt may therefore be defined as an acid in which the hydrogen has been replaced by its equivalent of a metal.

To understand this statement more clearly, let us examine these bodies, acids, bases, and salts, more closely. All acids contain hydrogen, and if we treat any one of them with a metal the hydrogen will be replaced by the metal. Pour some hydrochloric acid on to some tin—tin chloride, $SnCl_2$, is formed, and hydrogen set free, $Sn + 2HCl = SnCl_2 + H_2$; or treat zinc with sulphuric acid, and zinc sulphate, $ZnSO_4$, is formed, $Zn + H_2SO_4 = ZnSO_4 + H_2$; or if we mix the acids with bases, the metal of the base replaces the hydrogen of the acid, and water is simultaneously formed. Pour some nitric acid on to lead oxide, and lead nitrate, $Pb(NO_3)_2$, and water are at once formed, $PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$. Mix a solution of sodium hydroxide with acetic acid, and sodium acetate, $NaC_2H_3O_2$, and water are the result, $NaHO + HC_2H_3O_2 = NaC_2H_3O_2 + H_2O$.

We see that when hydrochloric acid interacts with tin, tin chloride is formed, and that zinc and sulphuric acid give zinc sulphate; whilst from lead oxide and nitric acid lead nitrate is formed, and sodium acetate is produced when sodium hydroxide interacts with acetic acid. These bodies, tin chloride, zinc sulphate, lead nitrate, and sodium acetate, are salts respectively of hydrochloric, sulphuric, nitric, and acetic acid.

Comparing the formula of hydrochloric acid with that of tin chloride, we see that the formula for hydrochloric acid is HCl, and that of tin chloride $SnCl_2$; and if we take a quantity of acid representing twice that amount, we shall have HCl + HClor 2HCl; by removing the two hydrogen atoms and putting one atom of tin (Sn) in their place we get $SnCl_2$, or tin chloride. This may be graphically expressed thus—

$$\binom{\text{ClH}}{\text{ClH}} + \text{Sn} = \binom{\text{Cl}}{\text{Cl}} \text{Sn} + \frac{\text{H}}{\text{H}}$$

Similarly the formula for sulphuric acid is H_2SO_4 , and if the H_2 be taken away and one atom of zinc (Zn) substituted, zinc sulphate is obtained—

$$SO_4 \begin{cases} H \\ H \end{cases} + Zn = SO_4 Zn + \begin{cases} H \\ H \end{cases}$$

Lead nitrate may be considered as being formed in the same

way from lead oxide and nitric acid. Here the atom of lead (Pb) replaces the hydrogen atoms in 2HNO_3 —

Let us take the last example. Acetic acid has the formula, $C_2H_4O_2$; of the four atoms of hydrogen it contains only one can be replaced by a metal, and to show this we may write its formula, $HC_2H_3O_2$. Sodium acetate is formed from it by the replacement of that single hydrogen atom by a single atom of sodium, thus:—

$$HC_{2}H_{3}O_{2} + \frac{Na}{H}O = NaC_{2}H_{3}O_{2} + \frac{H}{H}O$$

These examples show clearly the similarity between the composition of each acid and its salts, and what is meant by saying a salt may be considered as an acid in which the hydrogen is replaced by a metal.

The salts formed from hydrochloric acid are all called chlorides, those from sulphuric acid, sulphates, those from nitric acid, nitrates, and those from acetic acid, acetates.

Some acids are capable of forming two classes of salts when treated with the bases of certain metals, such as potassium or sodium. Sulphuric acid, H_2SO_4 , is an instance of these acids. If 112 parts by weight of potassium hydroxide and 80 parts by weight of sodium hydroxide respectively interact with 98 parts by weight of sulphuric acid, potassium sulphate and sodium sulphate are formed.

If only half the quantities of potassium hydroxide and sodium hydroxide be used, then new salts are formed which are represented by the formulæ, $\rm KHSO_4$ and $\rm NaHSO_4$ respectively, and are known as potassium hydrogen sulphate and sodium hydrogen sulphate—

$$\begin{array}{c} H_2 SO_4 + KHO = KHSO_4 + H_2O \\ 98 & 56 & 136 & 18 \\ H_2 SO_4 + NaHO = NaHSO_4 + H_2O \\ 98 & 40 & 120 & 18 \end{array}$$

THE AIR OR ATMOSPHERE

and if we take either of these bodies, $\rm KHSO_4$ or $\rm NaHSO_4$, and treat them with the other half of the bases we shall get respectively potassium sulphate and sodium sulphate formed—

$$\begin{array}{c} \mathrm{KHSO_4} + \mathrm{KHO} = \mathrm{K_2SO_4} + \mathrm{H_2O} \\ 136 & 56 & 174 & 18 \\ \mathrm{NaHSO_4} + \mathrm{NaHO} = \mathrm{Na_2SO_4} + \mathrm{H_2O} \\ 120 & 40 & 142 & 18 \end{array}$$

The substances, KHSO_4 and NaHSO_4 , are both salts and acids. Salts, because a metal has replaced part of the acid hydrogen, and acids, because they still contain hydrogen that can be replaced by a metal. They are therefore called acid salts. An acid salt is a salt in which only a portion of the hydrogen of the acid is replaced by its equivalent of a metal.

Not only can we convert potassium hydrogen sulphate into potassium sulphate by treatment with potassium hydroxide, but if we treat it with sodium hydroxide instead of potassium hydroxide we get a salt containing both potassium and sodium, namely, potassium sodium sulphate—

$$KHSO_4 + NaHO = KNaSO_4 + H_9O_1$$

or by taking sodium hydrogen sulphate and treating it with potassium hydroxide we get the same result—

 $NaHSO_4 + KHO = KNaSO_4 + H_9O.$

Salts of this kind are called double salts.

Argon. Symbol A. Atomic Weight, 39.5.

The third gas of importance in the atmosphere is argon, which was discovered in 1895 by Lord Rayleigh and Sir W. Ramsay. The former showed that nitrogen prepared from the air was slightly heavier than the same gas prepared from one of its compounds, say ammonia, which led the latter to suggest the presence of some foreign gas in the atmospheric nitrogen. In conjunction the two investigators succeeded in isolating the gas, to which the name argon was given. It is a colourless, tasteless, odourless gas, having a specific gravity of 1.3821, and it is more soluble in water than either nitrogen or oxygen.

Its chemical properties are negative; up to the present all attempts to bring about combination between it and the other

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elements have been unsuccessful, though it is said to interact with benzene when electric sparks are passed through a mixture of the gas with benzene vapours.

It does not take any part in the chemical properties of the atmosphere, but serves with the nitrogen to dilute oxygen.

Other Gases present in the Atmosphere.

It has already been mentioned that, in addition to oxygen, nitrogen, and argon, there are relatively small quantities of carbon dioxide, ammonia, nitric acid, and aqueous vapour present in all natural air.

Carbon Dioxide.—Of these gases carbon dioxide is the most important. This gas escapes into the atmosphere from the surface of all natural waters and from the soil, where it is produced by the decomposition of animal, vegetable, and other organic matters. It is a product of the respiration of all airbreathing animals and of the combustion of all bodies that contain carbon, such as wood, oil, candles, coal, &c. The purest air contains this gas in small quantities, but where animals congregate and where much combustion is carried on the quantity present increases, and in closed places where the ventilation is imperfect, very often comparatively large quantities are found.

The quantity of carbon dioxide in pure natural air may be taken to be about 2.5 to 3 volumes in 10,000 or 0.025 to 0.03per cent. by volume, and so long as the quantity does not exceed this amount, carbon dioxide may be considered as a normal constituent of air, but any excess of this gas is generally regarded as an impurity. In towns the quantity generally increases to 0.035 to 0.04 per cent. and in confined spaces where there is much animal life the quantity is often very much higher.

Owing to the ease with which this gas can be estimated, it is often used as a standard for determining the purity of the air.

Ammonia.—Ammonia is present in small quantities in the air owing to the decomposition of organic matter containing nitrogen. It exists partly as ammonium carbonate and partly as ammonium nitrate. A piece of pipe-clay heated to redness and exposed for a few days to the air will yield a perceptible quantity of ammonia on being reheated. The quantity present is very variable, the recorded results showing from 0.1 to 135 volumes of ammonia in 1,000,000 volumes of air.

Nitric Acid.—Nitric acid is present in such small quantities that it is only possible to detect it in rain water. It is probably formed by the oxidation of ammonia, and the quantity present is said to increase during a thunderstorm.

Ozone.—Ozone is said to be present in pure air, but it is more than probable that the so-called ozone is hydrogen dioxide, the presence of which in the air was established in 1863.

Aqueous Vapour.—Aqueous vapour is always present owing to the evaporation that continually takes place from the surfaces of all waters exposed to the air. The quantity present is variable and depends on the temperature. For every temperature there is a maximum amount of water vapour which the air can contain without condensation of the vapour to liquid; when at any temperature the air contains that maximum quantity it is said to be saturated at that temperature. The higher the temperature the greater the quantity of vapour required to produce saturation.

Under ordinary conditions of temperature the air is not, as a rule, saturated with moisture, and is often described as dry or moist. The dryness or moistness of the atmosphere does not depend on the actual amount of moisture in the air, but on the relation which the actual amount of moisture present bears to the amount required to produce saturation at the given temperature.

The amount of moisture in the air of mines depends on whether the pit is a dry or wet one, and is generally greater in the return air-ways than in the intakes. It is often desirable to know how much moisture the air contains, and this may be ascertained by actually weighing the water that can be absorbed from a measured volume of air, but this requires a trained experimenter and special apparatus. A very common method is to use the wet and dry bulb thermometer known as a hygrometer. This instrument consists of two Fahrenheit thermometers mounted on one frame, the bulb of one being covered with muslin to which is fastened some threads of worsted; these threads dip into a vessel of water placed below the ther-The muslin and worsted are thoroughly wet with mometer. the water and by capillary attraction the muslin is kept continually wet, the bulb of the other thermometer, being uncovered,

remains dry. The accompanying figure shows an instrument designed by Davis & Sons of Derby suitable for use in mines.

If this apparatus be placed in an atmosphere which is saturated with moisture both the thermometers will register



FIG. 15.—Davis's Pit Hygrometer.

the same temperature, but if the atmosphere is not saturated with moisture the wet-bulb thermometer will register a lower temperature than the dry one, because in the unsaturated air evaporation of the water on the muslin which surrounds the wet bulb takes place, and in so doing heat is absorbed which is registered by a fall in the thermometer. The more nearly the air is saturated the less the evaporation that takes place and the smaller the amount of heat absorbed, consequently the smaller the difference between the temperatures registered by the wet and dry bulbs. The actual relation between the difference in the temperatures registered by the two thermometers and the quantity of moisture in the air has been worked out by Professor Glaisher, who has published tables which give the fullest information on the subject. By the kindness of Mr. H. Davis the author is enabled to give abridged tables which are based upon Glaisher's calculations. These, together with instructions for reading the tables, are given in Appendix V. The actual quantity is

generally stated in grains of water per cubic foot of air.

The humidity of the atmosphere, or degree of saturation, is the relation which the quantity of moisture present bears to the quantity required to saturate the air at the temperature of the dry bulb. The relation is generally expressed as a percentage.

The humidity of the atmosphere in mines has an important bearing on the effect of high temperature on the human system.

When a man is working hard the temperature of the body is kept down by evaporation of the sweat. If the atmosphere be hot and dry, evaporation can take place freely and the body temperature can be kept down sufficiently low to prevent danger from heat stroke, but if the atmosphere be hot and moist the evaporation of the sweat does not take place so freely and there is a danger of the body temperature rising. According to Dr. Leonard Hill ¹ it does not matter what the dry bulb temperature is, the power of the body to regulate the body temperature depends on the wet bulb temperature. It is impossible for a man to work hard in an atmosphere where the wet bulb registers 85° F. without suffering from a fairly rapid rise in his body temperature, and consequent danger of heat stroke. This danger becomes greater at temperatures above 85° F. When the wet bulb registers 75° F. it is possible for a man to do hard work without danger of a serious rise in his body temperature.

Sulphur Dioxide.—Wherever coal is burnt sulphur dioxide will be found in the air, as this gas is formed by the union of the sulphur in the coal with the oxygen of the air. In the neighbourhood of a spoil heap that is on fire large quantities of this gas are formed by the combustion of the sulphur derived chiefly from the pyrites which is present in the dirt.

Gases found in the Air of Coal Mines.

Most of the foregoing statements have been made with reference to the air at the surface. The same impurities are or may be found in the air underground, whilst in addition marsh gas (fire-damp) is nearly always present in small quantities, and, under certain conditions, carbon monoxide and sulphuretted hydrogen may be found.

Sources of Impurities in Mine Air.

Carbon Dioxide.—This gas is produced by the burning of lamps and the breathing of animals. It also escapes from natural waters running into the mine and from the face of the coal, in the pores of which large quantities of this gas are often enclosed under very great pressure; it is also produced by the oxidation of the coal at the ordinary temperature of the mine. A certain quantity of this gas will be formed by the action of waters containing sulphuric acid on the calcium carbonate that is often associated with the coal. The amount of carbon dioxide pro-

¹ Trans. Inst. M.E., vol. xxxvi. p. 549.

duced by combustion and respiration is small compared with that produced from the other sources.

The quantity present in the atmosphere of a mine is generally greater than that in the air at the surface, it usually increases the further we go "in-bye" and reaches its maximum in the return air-ways.

Ammonia.—The presence of this gas is particularly noticeable in the neighbourhood of the stables, where it is formed in large quantities by the decomposition of the urine.

Marsh Gas.—Marsh gas, often called fire-damp, is found in the atmosphere of most coal mines, into which it escapes from the coal face and surrounding strata.

Carbon Monoxide.—Carbon monoxide is always found in the neighbourhood of a gob-fire and after an explosion of marsh gas or coal dust, whilst the fumes from some explosives contain appreciable quantities of this gas.

Sulphuretted Hydrogen.—Sulphuretted hydrogen is found in some natural waters, and it is possible it may be carried into the mine by such waters as contain it; it is sometimes associated with the gases escaping from the coal face, and is generally formed when the coal is heating before actually breaking out into a gob-fire. It often forms in the sump water and in waters that accumulate in old workings or behind dams or stoppings. According to some authorities, it is also formed by the action of carbon dioxide and moisture on easily decomposable sulphides. In most mining books it is stated to be formed by the action of water on iron pyrites. This gas, however, is not produced in this way at the temperature of the coal mine.

Sulphur Dioxide.—Sulphur dioxide is formed by the combustion of sulphur in the coal and pyrites, hence small quantities of this irritating gas are found in the atmosphere wherever there is an underground fire.

Composition of Air.

Having learnt what different gases are to be found in the air it is necessary to go a step further and determine how much of each constituent is present. Before analysing air for the purpose of determining its composition it is generally freed from such constituents as carbon dioxide, ammonia, ozone, hydrogen dioxide, &c. The numbers given below refer to air so purified. Air being a gas, its composition may be expressed either by volume or by weight.

Composition by Volume.—Reference has already been made to the fact that when phosphorus burns in a closed volume of air the oxygen combines with the phos-

hor and the volume of air is reduced. Advantage may be taken of this fact to show the quantity of oxygen present in a given volume of air.

A glass tube AB (Fig. 16), closed at one end and open at the other, is divided into five equal parts and a small quantity of phosphorus placed in it; the tube is tightly corked at B, and the phosphorus gently heated till it takes fire, when, by careful shaking, the phosphorus can be made to run down the tube and consume the whole of the oxygen. When the tube has cooled the cork is removed underneath the surface of the water in the cylinder, C, when the water will rise in the tube, AB, and if it be lowered into the cylinder until the level of the water inside and outside the tube is the same, it will be seen that this is the case when the tube is lowered to the first mark from the open end. The volume of the tube now occupied by the water measures the volume of oxygen consumed by the phosphorus, whilst the volume of gas remaining is the volume of nitrogen and argon.

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FIG. 16.

We thus see that about one-fifth of the total volume of air is oxygen and about four-fifths nitrogen and argon. This is only a rough experiment and cannot give accurate results; but, as may be expected, a very large number of careful experiments have been made to determine the exact composition of the atmosphere by volume, and they show that the air contains somewhat more than one-fifth of its volume of oxygen. The composition of the air is not quite the same in all parts of the globe. Bunsen found that the percentage volume of oxygen varies between 20.97 and 20.84, and these numbers have been confirmed by subsequent observers. The quantity of argon

found by Rayleigh and Ramsay is 0.93 per cent., and therefore the quantity of nitrogen varies between 78.07 and 78.23 per cent. For the purpose of ordinary calculations the following may be taken as the composition of the air by volume without introducing any serious error :---

| Oxygen | | | 21 |
|----------|--|---|---------|
| Nitrogen | | | 78 \ 70 |
| Argon | | | 1 / " |
| | | - | |
| | | | 100 |
| | | | |

Composition by Weight.—Very careful determinations of the composition of air by weight give oxygen 23.15 and nitrogen and argon 76.85 in 100 of air, and allowing for the argon present the following will express its composition by weight without introducing any serious error :—

| Oxygen | | | 23.00 |
|----------|--|--|------------|
| Nitrogen | | | 75.75 1 77 |
| Argon . | | | 1.25 / '' |
| - | | | |
| | | | 100.00 |

The Air a Mixture.

The gases present in the air are not in a state of chemical combination, but simply mixed together. The reasons for coming to this conclusion are as follows :---

1. The numbers representing the proportions by weight in which oxygen and nitrogen are present in air do not bear any simple relation to their combining weights, which would be the case if they were combined together.

2. The composition by volume of all gaseous compounds is constant, and slight variations in the composition of air taken from various parts of the globe and at different heights above sea level have been proved. These variations are too great to be attributed to errors in analysis.

3. The oxygen in the air behaves exactly like the pure gas when brought into contact with nitric oxide or pyrogallol.

4. When nitrogen and oxygen are mixed together in the proportion in which they occur in the air no contraction in volume or evolution of heat is observed, and the mixture behaves in every way like air. 5. Oxygen is more soluble in water than nitrogen, and when air is dissolved in water the proportion between the oxygen and nitrogen in the dissolved air is quite different from that in undissolved air. The quantity of each gas dissolved is strictly in accordance with the laws of gas absorption by liquids on the assumption that air is a mixture. The following is the composition of undissolved air and of air dissolved in water below 30° C. :—

| | Air Undissolved in Water. | Air Dissolved in Water. |
|--------------------|------------------------------|----------------------------|
| Oxygen | . 20.96 | 34.92 |
| Nitrogen and argon | . 79.04 | 65.08 |

If air were a compound the composition of dissolved air would be identical with that of undissolved air, unless the compound were decomposed by water, in which case ordinary solution would not occur. The air, however, cannot be decomposed by water, as by far the greater portion of the atmosphere on the earth's surface is in contact with water.

6. By passing electric sparks through the air the oxygen and nitrogen will combine together in the same manner as when sparks are passed through an artificial mixture of the two gases.

Combustion.

In the first chapter it has been shown that air is necessary in order that a candle may burn, and in describing the properties of oxygen it was pointed out that this gas plays a very active part in the burning. It has also been shown that, whether a candle burns in air or oxygen, the same substances are formed. We may therefore conclude that it is oxygen that is the active agent in the air that makes burning possible.

The phenomenon of burning is known also as combustion, and in order that combustion may take place there must be, firstly, two bodies, one called the "combustible body," the other the "supporter of combustion"; secondly, these two bodies must interact chemically; and thirdly, by the interaction heat must be produced.

Combustion or burning then may be defined as a chemical phenomenon which takes place when two bodies interact with generation of heat. It is a perfectly general chemical phenomenon, of which combustion in air is a particular example,

and as long as this is understood it is only necessary for the purposes of the mining student to consider combustion in air.

As already stated, combustion in air is combustion in oxygen; the oxygen is, however, diluted with nitrogen, and hence combustion in air is not as violent as in undiluted oxygen. The nitrogen takes no part whatever in the combustion, therefore oxygen is called the "supporter of combustion," and bodies which burn in the air are the "combustible bodies." The terms "combustible body" and "supporter of combustion," however, are only relative, for it is possible by observing certain conditions to convert the so-called "supporter of combustion" into the "combustible body," and vice versa.

Under ordinary conditions, if we allow a jet of coal gas to issue into the air and apply a light to it, it will burn. Coal gas



FIG. 17.

is the combustible body and oxygen the supporter of combustion. But take a lamp-glass, A (Fig. 17), fitted at the bottom with a cork through which a tube passes; pass coal gas through this tube into the lamp-glass and light the gas as it issues at the top. If oxygen from the gasholder, C, be allowed to issue from the jet, B, and the jet be slowly inserted into the lamp-glass through the flame of coal gas, the oxygen will take fire as it passes

t hrough the gas flame, and on lowering the jet into the coal gas a flame of burning oxygen will be seen to issue from the jet. In this case the coal gas may be said to be the "supporter of combustion," and the oxygen the "combustible body." All that is necessary for combustion is that the bodies capable of chemical interaction shall be brought together under the proper conditions for chemical interaction to take place.

Quick and Slow Combustion.—We have seen in the first chapter that the burning of a candle and the breathing of an animal involve similar chemical changes; both are forms of combustion, but whilst chemically they are similar, they differ in certain respects. The burning of a candle is accompanied by high temperature, and light is given out, whilst in the breathing of an animal the temperature is low and no light is given out. The former is an example of what is known as quick combustion or burning, the latter, of slow combustion or oxidation. In quick combustion the combination with oxygen is rapid, the temperature is very high, and the burning body becomes red-hot and may burn with flame. In slow combustion the combination with oxygen is slow, the body does not become red-hot or burn with flame. In order that quick combustion may take place, the combustible body must first be heated to a certain temperature, called the temperature of ignition.

Temperature of Ignition.—The temperature of ignition is that temperature at which a combustible body must be heated in order that it may combine with oxygen and at the same time give out light. The temperature of ignition varies widely with different substances. Ordinary phosphorus takes fire at 60° C., whilst the vapour of carbon disulphide can be ignited by a glass rod heated at 149° C., or considerably below a red heat. Ether vapour requires a higher temperature, but can be ignited by a glowing cigarette, whilst coal gas can be lighted with a red-hot platinum wire. Marsh gas, however, requires a still higher temperature, and will not take fire in the air below 750° C. Quick combustion, then, is that combustion which takes place above the temperature of ignition when bodies become red-hot or burn with flame.

It is not necessary, however, that a body be heated to its temperature of ignition in order that it may combine with oxygen; many bodies enter into this combination at the ordinary temperatures. A piece of ordinary phosphorus will combine with oxygen at 10° C., but it does not take fire at that temperature. Iron exposed to moist air combines with oxygen and is converted into rust; even coal combines with oxygen at the ordinary temperature. In all these and other similar examples combustion is taking place, but under ordinary circumstances no great rise in temperature can be noticed. In these cases combination with oxygen is slow; it takes place below the temperature of ignition, and is known as slow combustion or oxidation.

Heat of Combustion.—It has been mentioned that when combustion takes place heat is evolved. This evolution of heat is the result of the chemical combination that takes place. The heat is quite distinct from the temperature that results from the combination, and it must be borne in mind that the total

amount of heat produced depends only on the weight of bodies that interact; and so long as the same weight of a substance combines with oxygen the heat produced is the same whether the combustion takes place in a few minutes or takes years to accomplish, but the temperature will be different in the two cases. In the first case the rise in temperature will be very considerable, and in the second hardly appreciable. The heat evolved in this way can be easily measured. In English measures it is expressed either in Thermal Units (T.U.), the number of lbs. of water whose temperature is raised 1° C. by the combustion of 1 lb. of the substance, or in British Thermal Units (B.T.U.), the number of lbs. of water whose temperature is raised 1° F. by the combustion of 1 lb. of the substance. In the decimal system of weights and measures it is expressed in Calories (Cal.), the number of kilogrammes of water whose temperature is raised 1° C. by the combustion of 1 kilogramme of the substance.

The numbers obtained in this way express what is known as the heat of combustion of the substance, or the units of heat produced when a unit weight of any substance combines with oxygen. The following table gives the heats of combustion of certain bodies in Thermal Units, British Thermal Units, and Calories.

| | | | T.U. | B.T.U. | Cal. |
|--|-------------|---|--|---|--|
| Carbon— Charcoal Diamond Graphite Hydrogen. Sulphur | • • • | • | 8,080 7,770 7,811 34,462 2,307 | $14,544 \\13,986 \\14,058 \\62,031 \\4,152$ | 8,080 7,770 7,811 34,462 2,307 |

The heat of combustion of coal is an important property because by its means the value of coal as a fuel is determined.

Whenever combustion takes place a certain quantity of oxygen is consumed and converted into the products of combustion. It might therefore be expected that steady reduction in the amount of oxygen present in the air was continually taking place.

The chief fuels used contain carbon, and most of the oxygen that is burnt is converted into carbon dioxide. For every volume of oxygen consumed in this way an equal volume of carbon dioxide is formed, so that in addition to a reduction of the quantity of oxygen a proportional increase in the carbon dioxide in the air might be expected. Analyses do not reveal any decrease in the quantity of oxygen in air generally, and only a slight increase in the carbon dioxide present in the neighbourhood of towns where a large amount of combustion is going on. It is evident, therefore, that there must be some compensating influence to prevent the gradual decrease in the oxygen in the air. This is found in the action of plants, the green colouring matter of which in presence of bright sunlight decomposes carbon dioxide, liberating free oxygen to regenerate the air, and absorbing the carbon to build up their own structures.

Spontaneous Ignition of Coal.

The spontaneous ignition of coal is the expression generally applied to ignition which takes place in the gob and in coalstacks apparently without any cause. The expression is not a happy one, as it implies that it is a sudden action which takes place without any previous preparation or warning; this, however, is not the case. The ignition is due to a slow and steady process of oxidation.

It has been attributed to various causes :---

- 1. To the oxidation of the pyrites in the coal.
- 2. To the heat produced by friction when the roof settles down.
- 3. To the heat produced by the friction of the air as it travels into the stack or gob.
- 4. To the oxidation of the coal itself.

That coal does undergo oxidation when exposed to the air at the ordinary temperature can be easily shown.

If about 1 lb. of finely crushed coal be placed in a flask, A (Fig. 18), which is closed with a cork to which is fitted a bent tube, in the U-bend of which is mercury so as to allow any alteration of the gaseous pressure inside the flask to be noticed, it will be seen that at first the pressure somewhat increases, then it slowly diminishes, and afterwards slowly increases again. By analysis it can be shown



FIG. 18.

that the increase in pressure first observed is due to the escape of gases from the coal, that the diminution of pressure

is due to absorption of oxygen, and the gradual increase in pressure finally noticed is due to the evolution of carbon dioxide. The oxygen that the coal itself absorbs gradually oxidises the carbon, and produces carbon dioxide, which escapes as gas into the atmosphere. It is also true that the iron pyrites oxidises, but this oxidation requires the presence of moisture, when ferrous sulphate and sulphuric acid are formed—

$$2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2 \text{O} = 2 \text{FeSO}_4 + 2 \text{H}_2 \text{SO}_4.$$

The oxidation of the coal and the pyrites causes the evolution of heat, and at one time the spontaneous ignition of coal was attributed solely to the heat generated by the oxidation of the pyrites. When, however, it was found that some coals which are very susceptible to spontaneous ignition contained less pyrites than others which were not so susceptible, this theory was abandoned, and the ignition was attributed to the oxidation of the bituminous constituents of the coal by the oxygen absorbed. There is little doubt that the oxidation of the substance of the coal plays a very important part in the spontaneous combustion of coal. A few years ago, however, Dr. Haldane and Mr. Meachem 1 revived the old theory that the oxidation of the pyrites was primarily responsible for the ignition. From experiments made by them at the Hamstead Colliery in South Staffordshire, where the "Ten-yard" seam is worked -a seam very susceptible to spontaneous ignition-they concluded that the rise in temperature in the air as it passes from the down-cast shaft to the workings may be accounted for by the oxidation of the pyrites.

When the pyrites oxidises it not only generates heat, but also causes the coal to break up into slack. This tends to promote the oxidation of the coal itself by exposing a larger surface to the air.

Oxidation, then, is the cause of spontaneous combustion in coal, and what takes place in the gob and in the coal-stack is probably as follows :---

Air finds its way slowly into the gob or stack, where it meets with the coal and oxidation both of the coal itself and of the pyrites takes place; heat is then generated. Owing to want of ventilation the heat is not dissipated, but causes a rise of temperature. As more air filters in oxidation continues, and the temperature continues to rise; as the temperature rises the rate of oxidation increases, which causes the heat to be evolved more quickly, and the temperature to rise more rapidly, till eventually the temperature of ignition is reached and the coal takes fire. The temperature of ignition of coal depends on its composition and state of division. Small coal is said to ignite at a temperature of between 176° and 190° C., whilst coal dust has been ignited at a temperature of 140° to 150° C.

It is often noticed that some seams of coal are liable to gob fires, and also to fires in the pillars left to support the roof, whereas the coal itself does not readily undergo spontaneous ignition.

In the gob, dirt, bind, small coal, and pyrites are thrown, and many of the dirts and binds are of the character of shales containing certain quantities of combustible matter which readily oxidise, whilst the coal is generally in the form of slack or dust, which offers a large surface to the action of the air, so that oxidation proceeds more rapidly than when the coal is in the lump, and doubtless this explains why gob fires occur in seams where the coal in the lump does not undergo spontaneous ignition.

A somewhat similar explanation accounts for fires in pillars of coal, for in the case of these pillars the coal gets crushed by the weight of the roof, and air can penetrate into the pillar through the cracks in the crushed coal, and set up oxidation more readily than is possible in the case of uncrushed coal.

With regard to the heat generated by the friction due to the passage of the air and the settling of the roof, it is not likely that sufficient heat can be generated from these causes to produce ignition. In the case of the experiments made by Dr. Haldane and Mr. Meachem, it was calculated that of the total heat generated in the pit only $\frac{1}{10}$ th could possibly be produced by the settling of the strata, and about $\frac{1}{60}$ th by the friction of the air.

It must, however, be remembered that any cause whatever that produces a rise of temperature in the coal tends to promote or increase oxidation, and though friction alone may not actually cause ignition, the heat generated by the friction will increase that produced by oxidation.

The spontaneous ignition of coal is caused by the heat generated by oxidation, assisted by any other causes which produce a rise in temperature of the oxidisable matter in the coal or associated with the coal.

The firing of spoil heaps is caused in the same manner, but in this case the pyrites doubtless plays a great part. It readily oxidises when it becomes moistened by the rain, to which all spoil heaps are exposed. The heat produced by this oxidation causes the distillation of a certain quantity of the sulphur which finds its way to the surface of the heap. As sulphur has a low temperature of ignition it readily takes fire, and once ignited sets fire to the combustible matter in the dirt of which the spoil heap is composed.

Before coal in the gob actually takes fire there are generally warnings, such as the sweating of the walls of the roadways, the appearance of haze in the atmosphere, and the evolution of "gob-stink" or "fire-stink." These are caused by a partial distillation of the coal which takes place before actual ignition occurs. Moisture and other gases are evolved, and amongst the latter is sulphuretted hydrogen, which is one of the characteristic gases present in "gob-stink."

To prevent the spontaneous ignition of coal, the gob or coal-stack should be well ventilated. It has been explained that the ignition is due to the accumulation of heat produced by oxidation, which causes a rise in the temperature up to the temperature of ignition. If the temperature of the coal is kept below the temperature of ignition it will not take fire. The rise in temperature can be prevented if air can be made to pass through the gob or stack in sufficient quantities to carry away the heat as fast as it is produced.

But if the coal is already ignited, the admission of air will only increase the combustion; therefore, in such a case all air should, as far as possible, be excluded by building walls and so enclosing the district that the fire will eventually die out for want of air. When once the district on fire has been enclosed, time must be allowed for the temperature of the mass to fall below its temperature of ignition before admitting air; for so long as the temperature of the mass remains above the temperature of ignition of the combustible materials they will re-ignite as soon as air is admitted. The cooling process will doubtless be very slow, as the heat can only be dissipated by conduction through the surrounding strata. It is impossible to say how long this will take, and it is conceivable that it may take years to cool sufficiently to allow of the safe admission of air.

There are other causes of underground fires besides the oxidation of the combustible matter in the strata, such as $-(\alpha)$ Ignition of coal or timbers by naked lights or by underground furnaces used for purpose of ventilation; (b) an explosion of fire-damp or coal dust; (c) the heat generated by the action of steam or steam-pipes on the coal, strata, or timber; (d) the oxidation of oily waste or similar bodies which may accumulate underground; (e) defects in the electric plant underground, which give rise to sparking or excessive heating of electric For a full account of the various causes of undercables. ground fires, the paper on "Underground Fires," by Professor F. W. Hardwick,¹ should be consulted.

Extinctive and Irrespirable Atmospheres.

It has been explained that a candle flame is extinguished unless continually supplied with fresh air, and the same is true of the flames of all combustible bodies.

An atmosphere may be rendered extinctive by the presence of either an incombustible or a combustible gas.

Incombustible Gases .-- In the case of the presence of an incombustible gas the extinctive action of the atmosphere depends on the reduction in the proportion of the oxygen present rather than on any specific property of the diluting gas.

This is well illustrated by experiments made by Dr. Clowes,² in which he determined—(1) The composition of the residual atmosphere that extinguished a flame which had burnt in the air; (2) the composition of the extinctive atmosphere produced by adding an inert gas, for example, nitrogen. His results are given in the following table, taken from the "Detection and Estimation of Inflammable Gas and Vapour in the Air," by Clowes and Redwood.

¹ Trans. Inst. M.E., vol. xxv. p. 724.

² Proceedings of the Royal Society, vol. lvi.; vol. lxvii. p. 353.

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| 50 | CHEMISTRY | FOR | COAL-MINING | STUDENTS |
|----|-----------|-----|-------------|----------|
|----|-----------|-----|-------------|----------|

| Combustible Substance Burnt. | Percent the I phere i was | age Comp Residual A n which th Extingui | Proportions per cent. of O ₂ ,N ₂ in which Flame is Extinguished when Introduced. | | |
|--|---|--|---|--|--|
| | Oxygen. | Nitrogen. | Carbon Dioxide. | Oxygen. | Nitrogen. |
| Alcohol (absolute) . Alcohol (methylated) . Paraffin, lamp oil . Colza and paraffin . Candle | $ \begin{array}{r} 14 \cdot 9 \\ 15 \cdot 6 \\ 16 \cdot 6 \\ 16 \cdot 4 \\ 15 \cdot 7 \end{array} $ | 80·7 80·25 80·4 80·5 81·1 | 4·35 4·15 3·0 3·1 3·2 | $16.6 \\ 17.2 \\ 16.2 \\ 16.4 \\ 16.4 \\ 16.4$ | 83·4 82·8 83·8 83·6 83·6 83·6 |
| Hydrogen Carbon monoxide Marsh gas Coal gas (Nottingham) | $5.5 \\ 13.35 \\ 15.6 \\ 11.35 $ | $94.5 \\ 74.4 \\ 82.1 \\ 83.75$ | 12.25 2.3 4.9 | 6·3 15·1 17·4 11·3 | 93·7 84·9 82·6 88·7 |

It is seen from these results that in the case of the wick-fed flames of combustible vapours of bodies containing carbon, the flames are extinguished when the proportion of oxygen is reduced to between 15 and 16 per cent., whether the reduction is produced by removing the oxygen by combustion or by dilution with an inert gas, whereas in the case of the flames of gases burning at jets the reduction in the proportion of oxygen required to produce extinction is variable and depends on the gas that is burnt, but in every case there is a close agreement between the proportion of oxygen in the extinctive atmosphere whether that proportion be reduced by combustion or dilution.

This has an important bearing on the quantity of carbon dioxide required to extinguish a candle or oil flame. When the reduction in the oxygen is produced by combustion of carbon, the volume of carbon dioxide formed is equal to the volume of oxygen consumed in its formation, and 1 per cent. increase in carbon dioxide means 1 per cent. decrease in the oxygen. If the fuel contains hydrogen as well as carbon, oxygen is removed by the combustion of hydrogen, and when about 3 to 4 per cent. of carbon dioxide is present the oxygen falls to about 16 per cent. and the atmosphere becomes extinctive. But if the carbon dioxide pours into the atmosphere from some outside source, such as from the strata or from the goaf, it acts as a diluent; and seeing that there are nearly four volumes of nitrogen to one of oxygen in the air, it is evident that to reduce the oxygen by 1 per cent. the nitrogen must be reduced by 4 per cent.; therefore of every volume of carbon dioxide that flows in roughly one-fifth goes to dilute the oxygen and fourfifths to dilute the nitrogen—consequently to render the atmosphere extinctive to a candle or oil flame about 15 per cent. is necessary.

The following table, taken from Clowes and Redwood's "Detection of Inflammable Gas and Vapours," strikingly illustrates this important difference.

Percentage Composition of Atmospheres Extinctive of a Common Oil or Candle Flame.

| | Oxygen. | Nitrogen. | Carbon Dioxide. |
|--|---------|---------------|--------------------|
| 1. Air expired from the lungs (average) | 16.15 | 79.9 | 3.95 |
| 2. Air in which a candle or oll flame had burnt until it | 16.05 | 80.80 | 3.12 |
| 3. Mixture of air and nitrogen . 4 Mixture of air with carbon | 16.04 | 83.6 | |
| dioxide | 18.06 | 67.94 | 14.00 |
| 5. Fresh air for comparison . | 20.9 | 79 .06 | 0.04 |

It is important to notice that carbon dioxide and nitrogen act similarly as diluents, the addition of 15 per cent. of the former and 17 per cent. of the latter being sufficient to produce an extinctive atmosphere, hence carbon dioxide itself has very little specific action in extinguishing flame. In this respect it has been shown by Dr. Haldane that a candle will burn in an atmosphere containing 75 per cent. of carbon dioxide and 25 per cent. of oxygen.

Combustible Gases.—The action of combustible gases in extinguishing a flame is somewhat different from that of

incombustible gases. Before a combustible gas is present in sufficient quantity to reduce the oxygen in the air below 16 per cent. the gas as a rule will take fire. In burning it reduces the oxygen in the neighbourhood of a flame below the quantity necessary to support combustion and the flame is extinguished.

Irrespirable Atmospheres.—An atmosphere may become irrespirable from the presence of gases which exert a poisonous action on the animal system, or from deficiency in oxygen caused by the dilution of the air by gases which have no specific action on men or animals.

At this stage only the effect on the animal system of diluting the oxygen will be considered, whilst the action of specifically poisonous gases will be discussed when describing their properties. The question of the action of want of oxygen on men and animals has been exhaustively discussed in a paper by Dr. Haldane and Dr. Lorrain Smith in the Journal of Pathology and Bacteriology, vol. i. p. 168. From their experiments it appears that when the quantity of oxygen in the air is gradually reduced either by absorption or dilution, the first symptoms appear when the quantity of that gas is reduced to 12 per cent., at which point the respiration becomes perceptibly deeper. At 10 per cent. the respirations are distinctly deeper and the colour of the lips becomes slightly blue. At 8 per cent. little or no distress is felt, but the face assumes a leaden hue, whilst at 5 or 6 per cent. panting occurs together with confusion of mind and loss of power over the limbs, which would probably be followed by death. With 1 or 2 per cent. loss of consciousness occurs in forty or fifty seconds without previous warning and is quickly followed by convulsions and cessation of respiration. Loss of consciousness due to deficiency of oxygen takes place very suddenly and may be produced much more rapidly under exertion than when at rest. Therefore in exploring in atmospheres which have been flooded with diluting gases great care must be exercised, as by rapidly entering such atmospheres the deficiency in oxygen, combined with the exertion, may produce unconsciousness without any warning symptoms.

The extinction of a lamp or candle is usually taken as a sign that the atmosphere is unfit to breathe, but that is not necessarily the case. Air which has once been breathed will extinguish a candle or oil flame, but it can be breathed again for three or four times before the distress due to deficiency in oxygen becomes apparent, whilst an extinctive atmosphere produced by the combustion of a candle or oil flame contains 17 per cent. of oxygen and consequently can be breathed without any marked distress. In these cases the extinction of a flame is no indication that the atmosphere is dangerous to life. On the other hand, where a poisonous gas is present the fact that a candle or lamp continues to burn in the atmosphere is no indication of the purity of the air for respiration.

It is useful in practice to refrain from entering an atmosphere in which a lamp will not burn. And if it be necessary to enter an atmosphere in which a candle will burn but which is suspected to contain poisonous gases, great care should be taken not to proceed too far, and to note any poisonous symptoms.

CHAPTER III

PRESSURE OF A GAS AND ATMOSPHERIC PRESSURE

ALL gases exert a pressure. The molecules of every gas are in a constant state of rapid motion, and the pressure exerted by gases is due to the motion of their particles. The pressure is exerted whether the gas is confined in a vessel or not. It is a property of the gas itself, and is not caused by any external pressure that may be applied to the gas.

When a gas is confined within any vessel its sides are continually bombarded by the gaseous particles, and this bombardment produces a pressure upon them. The pressure thus exerted is equal in all directions, downwards, upwards, and outwards, and is not produced by the actual weight of the gas, but depends on the weight of gas contained in a given volume, that is, upon the density of the gas.

The greater the weight of gas contained in any given volume the larger the number of particles that are confined within the given space, therefore the greater the bombardment and, in consequence, the greater the pressure.

To realise that the pressure and the weight of a gas are not the same, consider a hollow cube, each face of which is 1 square foot, filled with air. The volume of air is 1 cubic foot, and if its temperature is 0° C. and its pressure 30 inches of mercury, its weight is 0807 lbs., but the actual pressure exerted by the gas on every square inch of surface of the cube is 14.7 lbs., or 2086.8 lbs. on each face of the cube.

A gas and its pressure may be compared with a spring. The pressure exerted by a spring does not depend on its weight. It exerts its pressure by trying to extend itself after it has been coiled up, and the more closely it is coiled up the greater the pressure it exerts. Similarly a gas exerts a pressure independent of its weight, due to the bombardment by its moving particles of bodies in contact with it. The more closely its particles are packed together, i.e. the greater its density, the greater the bombardment becomes and the greater the pressure exerted.

The characteristics of the pressure of a gas are :---

1. It is equal in all directions.

2. It is equally distributed over the surfaces of all bodies with which the gas is in contact.

3. Any change in pressure is instantly communicated throughout the mass of the gas without any loss.

4. If two gases of unequal pressure be brought in contact with one another, their pressures immediately become equalised.

The atmosphere exerts a pressure not because it is the atmosphere, but because it is a gas and possesses this property in common with all gases. The atmosphere may be used to show the downward and upward pressure of a gas.

A cylinder, A (Fig. 19), open at both ends, has one end closed with a sheet of india-rubber, B, and is placed on the plate of an

air-pump, C. On exhausting the air from the cylinder, the sheet of india-rubber is gradually pressed down into the cylinder, forming a cup, by the external atmospheric pressure, which now exceeds the pressure of the air inside the cylinder. On allowing air to re-enter the cylinder, the sheet of india-



rubber forms a horizontal surface as soon as the pressure of the air inside the cylinder has become equal to the pressure of the air outside.

The upward pressure can be shown by fitting a funnel, A,



into the flask, B, by means of a well-fitting cork (Fig. 20). If water be now poured into the funnel, only a few drops will enter the flask so long as the cork fits tightly, because the upward pressure of the air in the flask balances the downward pressure of the water in the funnel; but loosen the cork so that the air in the flask can escape, and the water will at once run out of the funnel.

The atmospheric pressure plays a very important FIG. 20. part in mining operations, because, on account of its great magnitude, it gives a certain amount of support to the roof

and sides of the workings and roadways in a mine, and it also influences the escape of gases from the wastes and goaves into the mine's atmosphere.

But the pressure of the atmosphere is variable; it changes from day to day and hour to hour owing to the meteorological changes. At times great reductions in the atmospheric pressure occur, which are accompanied by falls of roof and the escape of fire-damp and black-damp into the workings. It is necessary, therefore, to have some means of measuring these changes in pressure.

The atmosphere being a gas, its pressure is equal in all directions and equally distributed over any surface with which it is in contact, hence it is only necessary to measure the pressure on a unit surface. In English units this is expressed in lbs. on 1 square inch of surface, in metric units, in grammes per square centimetre. The measurement is made by means of an instrument called a barometer, of which there are two kinds generally used: (a) the mercury barometer; (b) the aneroid barometer.

Mercury Barometer.—The mercury barometer owes its origin to experiments made in 1645 by Torricelli, who found that if a

tube about 36 inches long (Fig. 21), closed at one end, was filled with mercury, and the open end then inverted in a vessel of the liquid, the mercury in the tube would fall for a short distance, and stand at a height of about 30 inches in the tube, leaving an empty space at the top in which there was no air, now called a Torricellian vacuum. He also gave the correct explanation, namely, that the mercury is maintained in the tube by the pressure of the air on the surface of the mercury in the cistern.

The mercury barometer in its simplest form consists of a straight tube about 33 to 36 inches long, and about $\frac{1}{2}$ inch to $\frac{5}{8}$ inch in diameter, closed at one end, and carefully filled with pure mercury, so that all air is ex-FIG. 21. pelled from the tube, which is then inverted in a cistern

of pure mercury and placed in a vertical position, the height of the column from the level of the mercury in the cistern to the level of the mercury in the tube being measured by a special instrument; but this form of barometer is not portable, and is too delicate for ordinary use. In barometers for ordinary use certain modifications are introduced which render them more portable, and the scale is attached to the
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barometer tube, which makes the process of "reading the barometer" easier.

The barometer generally used in colliery work consists of a glass tube about 33 inches long, the upper part of which for about 6 or 8 inches has a diameter of

about 1 inch, whilst the remainder of the tube is of smaller diameter (Fig. The open end of the tube is 22). inverted under mercury contained in a wash-leather bag, which is fitted to a frame through which the tube is inserted. The wash-leather bag rests on a plate which can be raised or lowered by means of a set-screw which passes through the bottom of the case of the barometer. By means of this screw the level of the mercury in the washleather bag can be altered. When the barometer is fixed in its place the screw is lowered to its utmost, so that the column of mercury in the tube is entirely supported by the atmospheric

pressure, but if it be necessary to move the barometer the screw is raised until the mercury fills the tube, when the instrument can be carried about without any fear of air entering the tube.

Another arrangement is to turn the open end up so that it forms a tube shaped like the letter J, when the open end terminates in a large bulb which is open to the atmosphere. The bend prevents the admission of air into the tube, whilst the bulb serves as a receptacle or cistern for the surplus mercury.

These tubes, carefully filled with mercury, are fitted into a wooden case with a glass plate at the top, through which can be seen about 6 or 7 inches of the upper part of the barometer.

The height of the barometer is the height that the column of mercury in the tube stands above the level of the mercury in the cistern, but as the extreme variation in the height of the barometer is only about 3 inches, the scale by which the height is measured is only fixed to the upper part of the tube. This is a scale of inches divided into tenths of an inch, and marked from 27 to 32 inches above the level of the mercury in the cistern.



FIG. 22.

The level of the mercury in the cistern must be constantly varying, for when the barometer rises the mercury passes from the cistern into the tube, and, when the barometer falls, from the tube into the cistern; but because the diameter of the cistern greatly exceeds that of the tube, the level of the mercury in the cistern is not greatly affected by the small quantity of mercury that may pass in or out of it. However, in carefully constructed instruments of the types described, allowance is made in fixing the scale for the alterations in level.

It is necessary to read the barometer to the nearest hundredth of an inch. It is quite easy to read the height to the nearest tenth of an inch with the naked eye, but for the purpose of reading the hundredths of an inch a movable scale, called a vernier, is fixed to the barometer scale, over which it is made to slide by means of a rack and pinion.

The vernier may be made to read from the top downwards or from the bottom upwards; in the first form the vernier is $\frac{11}{10}$ of an inch long, in the second form it is $\frac{9}{10}$ of an inch long. Both forms are divided into ten parts, so that in the first form the length of each division is $\frac{11}{100}$ of an inch, or $\frac{1}{100}$ of an inch greater than $\frac{1}{10}$ of an inch, and in the second form each vernier division is $\frac{9}{100}$ of an inch, and therefore is $\frac{1}{100}$ of an inch smaller than $\frac{1}{10}$ of an inch. Hence in each form of vernier the difference between one scale division and one vernier division is $\frac{1}{100}$ of an inch $(\frac{11}{100} - \frac{1}{10} = \frac{1}{100})$, or $(\frac{1}{10} - \frac{9}{100} = \frac{1}{100})$; between two scale divisions and two vernier divisions the difference is $\frac{2}{100}$ of an inch $(\frac{22}{100} - \frac{2}{10} = \frac{2}{100}$ or $\frac{2}{10} - \frac{18}{100} = \frac{2}{100}$; between three vernier divisions and three scale divisions it is $\frac{3}{100}$ of an inch $(\frac{33}{10} - \frac{3}{10} = \frac{3}{100}$ or $\frac{3}{10} - \frac{27}{10} = \frac{3}{100}$, and so on. In the first form of vernier, which is $\frac{11}{10}$ of an inch long, the 0 is at the top, and the divisions are marked in order downwards from 0 to 10; whilst in the second form, which is $\frac{9}{10}$ of an inch long, the 0 is at the bottom, and the divisions are marked in order upwards from 0 to 10.

To use the vernier when the height of the mercury in the barometer stands between two divisions on the fixed scale, the 0 of the vernier is brought to coincide with the top of the mercury column and is then examined for that division which coincides with a division on the fixed scale, and whatever is the number of that vernier division, that number represents the hundredth of an inch required.

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To read the barometer, therefore, read to the nearest tenth of an inch on the fixed scale, then use the vernier as described above to find the figure that has to be placed in the second decimal place.

For example, in Fig. 23, AB represents the vernier with its graduations marked downwards from 0 to 10. The height, read to the nearest tenth of an inch on the fixed scale, is 29.4, and it is the height, cd, that is read by means of the vernier. The 0 being brought to the level, d, on looking down the vernier scale it is seen that its third division coincides exactly with a scale division, therefore the height, cd, is $\frac{3}{100}$ of an inch, and 3 is the figure to be placed in the second decimal place, making the height 29.43 inches. Let us count the divisions up and see that it is so.



FIG. 23.

Starting from the two divisions that coincide, or the third vernier division, and reading upwards, the difference between

| 1 | vernier | division | and 1 | scale | division | $=\frac{1}{100}$ | |
|---|---------|----------|----------|-------|----------|--------------------|--|
| 2 | >> | " | 2 | ,, | " | $=\frac{2}{100}$. | |
| 3 | " | " | 3 | \$ 2 | ,, | $=\frac{3}{100}$. | |

The last difference is that between 29.4 and the 0 of the vernier scale, or the height, cd, which we had to measure.

The Aneroid Barometer (Fig. 24).—This form of barometer is a mechanical contrivance by which alterations in the shape of a thin metallic box, caused by variations in the atmospheric pressure, are transmitted by a series of levers to an index finger which traverses a dial or clock face. It consists of a metallic box, B (Fig. 25), with a corrugated surface, the sides of which are very elastic. It is perfectly air-tight, and inside is a partial vacuum. In the centre of the box is a stout pillar which is in contact with a strong spring, S. This spring is connected with a bent lever, AFD, which is rigidly fixed to an axle, C, that is movable about a horizontal axis; to the same axle is fixed another lever, E, at the end of which is a light chain which winds round a vertical spindle, W, on which is mounted the index

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finger. The chain is kept taut by means of a hairspring, H. Any alteration in the atmospheric pressure causes a movement of



FIG. 24.



FIG. 25.

the surface of the box; this movement is communicated through the pillar to the spring, and the axle is caused to revolve on its axis. The motion of the axle is then transmitted to the spindle carrying the index finger, which traverses a scale on the dial.

The scale of an aneroid barometer is made by comparison with the mercury barometer by marking the position the index finger takes up when the mercury barometer stands at 28, 29, 30, 31, 32 inches, &c., and dividing the distances between these divisions into 10 or 100 equal parts, as the size of the scale permits.

It is made in a portable form, about the size of a watch, and in larger sizes for fixing permanently in one place. It may also be used for measuring altitudes for surveying purposes, and scales of heights are added to many instruments.

It is, however, affected by the temperature, and when subjected to sudden and excessive alterations in pressure is liable to give inaccurate readings. On account of this its accuracy should, from time to time, be tested by comparison with the mercury barometer, when, if any difference be detected, it can be rectified by means of a small adjusting screw which will be found at the back of every instrument, whereby the index finger can be brought to that mark on the dial which corresponds with the height of the mercury in the barometer.

The height of the mercury barometer depends on the density of the air. The density of the air is subject to variations caused by meteorological changes which produce a daily variation in the height of the barometer even when the instrument is stationary. The density of the air also varies according to our position on the earth's surface, and the barometer on the pit bank will give a lower reading than at the pit bottom, because the density of the air increases as we descend, although both readings register the same meteorological state of the atmosphere. Again, if we carry a barometer up a mountain the mercury will steadily fall as we ascend, because the higher we climb the less dense the air becomes. It is necessary then to fix upon a standard level at which to compare the barometric height, and the standard usually taken is sea-level. At this level a pressure corresponding to a height of 30 inches of mercury at 32° F. is taken as a pressure of one atmosphere.

The pressure in lbs. per square inch corresponding to any given height of the barometer is obtained by multiplying the height in inches by the weight in lbs. of one cubic inch of mercury. If H = the height of the barometer in inches and

W = the weight in lbs. of one cubic inch of |mercury, P = the pressure of the atmosphere in lbs. per square inch,

then P = HW.

Taking W to equal '4908 lbs., the pressure corresponding to one atmosphere as defined above is :---

 $P = 30 \times .4908$ = 14.724 lbs. per square inch.

The variation in the height of the barometer according to its position above or below the sea-level is generally taken to be a rise or fall of one inch for every 900 feet above or below that datum. This is a very rough estimate, and may serve for rough practical approximations. It is only near the truth in the first 900 feet above or below sea-level.

It must be remembered that there is a gradual increase in the density of the air as we descend, and similarly a gradual



decrease in the density as we ascend, consequently the average density of the air in the second 900 feet descended will be greater than that of the air in the first 900 feet; therefore the barometer will rise more than one inch on being lowered from 900 to 1800 feet; or, to put it another way, if the barometer rises one inch on being lowered 900 feet from sea-level, it will rise more than two inches when lowered 1800 feet from sea-level.

In the same way, owing to the gradual decrease in the density of the air as we ascend, if the barometer falls one inch on rising 900 feet above sea-level, it will fall less than two inches if it is taken 1800 feet above sea-level.

The Water-Gauge.—The water-gauge is an instrument for measuring *differences* of gaseous pressure. In its simplest form it consists of a U-tube, which is partly filled with water (Fig. 26). It is fixed on a board, to which is attached a scale between the two legs of the U. The scale has a fixed zero, which marks the level of the water in the tube when the pressure is the same in both legs. The scale is divided into half inches, marked 1, 2, 3, &c., above and below the 0, and subdivided into tenths of inches. When the gaseous pressure is the same in both legs the level of the water in them is the same, but if the gaseous pressure in the two legs differs the liquid moves towards the side of the smaller pressure and comes to rest when the two pressures are equal. The difference of level between the water in the two legs is read off on the scale, and from it the difference in gaseous pressure is calculated.

One of the most improved forms of water-gauge is designed by Davis & Sons, of Derby (Fig. 27). It consists of two glass tubes, A and B, which fit into two sockets that are in communication with one another. The tube B fits into a cover that leads to the tube D, which is used to insert into a hole in a door between the intake and return airways. The tube A is closed with a nut, through which is a small hole. A and B are fixed on to a wooden frame, and behind them is a movable scale which can be raised and lowered by means of a thumb-screw, E. The scale is graduated in inches and tenths of inches, the zero being at the bottom. Between the sockets into which A and B fit is a small valve, C, which can be turned, and cuts off the communication

between A and B. At the top of the frame is a small spirit-level to indicate when the instrument is vertical. To use the instrument, the valve C being open, the tube D is inserted in the hole in a ventilation door (in this case leading from the return to the intake), and the instrument held in a vertical position. When the water ceases to rise in A, the valve is closed and the instrument removed. The scale is then adjusted so that the zero coincides with the level of the water in B, and the height of the water in A above the level in B read off on the scale.



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When the liquid in the instrument is at rest the total pressure in each leg is the same. In B (Fig. 28) the total pressure is equal



to the pressure of the gas and of the column of liquid, *ab*. In A it is equal to the gaseous pressure plus the pressure of the column *cd*. The pressure of the column of water, *ab*, is balanced by a column of equal height in A, namely, the column, *ed*. Therefore the gaseous pressure in B equals the gaseous pressure in A + the pressure due to the column of water, *ce*, or, the difference between the gaseous pressure in B and that in A equals the pressure due to the column of water, *ce*.

The actual pressure represented by the column, ce, is generally calculated in *lbs. per square foot*. If a box, each edge of which is 1 foot long, be filled with water, it holds 1 cubic foot of water, which weighs 62.5 lbs., and this is the pressure due to the water on the bottom of the box, viz. on 1 square foot of surface. Suppose, now, 11 inches of the sides of the box be cut away, there will remain a slab of water 1 inch high and 1 square foot in area, which weighs $\frac{1}{12}$ of 62.5 lbs. = 5.2 lbs. Therefore the pressure on 1 square foot represented by a column of water 1 inch high is 5.2 lbs.

To find the difference of the pressure per square foot due to the water-gauge---

let W.G. = the difference in height of the water in the two legs in inches.

P = difference of gaseous pressure in lbs. per sq. foot. P = 5.2 × W.G. lbs. per sq. foot.

CHAPTER IV

WATER AND HYDROGEN

WATER as a liquid is widely distributed in nature in the seas, lakes, rivers, springs, &c., that abound on the earth's surface, whilst in the form of vapour it is found in the atmosphere, and large masses of solid water, or ice, are found in the Arctic and Antarctic regions.

Though so widely distributed throughout the earth's crust, natural waters are never pure, owing to the facility with which they dissolve a number of solid and gaseous bodies. Pure water can be evaporated, and will leave no residue in the vessel in which it is boiled, but any natural water on evaporation leaves behind some residue, which represents the solid impurities dissolved in it. This is the case even with rain water, which is the purest of all natural waters.

The usual impurities in water are (1) gaseous; (2) solid.

Gaseous Impurities.—The gases usually found in natural waters are nitrogen, oxygen, argon, carbon dioxide, and ammonia. All these gases are dissolved out of the air, whilst certain quantities of carbon dioxide and ammonia are also dissolved from the soil and strata with which the waters come in contact. Other gases are occasionally found in natural waters, such as sulphuretted hydrogen—as, for instance, in the well-known Harrogate waters. Sulphur dioxide is found in the rain which falls in the neighbourhood of towns where combustion of coal occurs, and small traces of marsh gas may be found in some of the waters which occur in coal mines.

Solid Impurities.—The solid impurities in water may be either in *suspension* or in *solution*. The bodies in suspension consist of insoluble substances that are carried down by water as it flows over the earth's surface, whilst the bodies in solution consist of substances that are dissolved by the water as it passes through the solid earth's crust. The character and quantity of

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the solid impurities dissolved in natural waters depend entirely on the composition of the strata with which the waters have come in contact. Waters which meet with only such insoluble rocks as granite and sandstone dissolve but small quantities of these impurities, which are chiefly silicates, whereas waters which pass through the more soluble limestone and chalk become highly charged with these bodies, and if they meet with the still more soluble magnesium sulphate (Epsom salts) or sodium chloride (salt), dissolve still larger quantities of these bodies.

Pit Waters.—The waters which are found in the coal measures are all more or less impure, and some of their impurities are very characteristic.

Gaseous Impurities in Pit Waters.—The chief gases found in pit waters are carbon dioxide and nitrogen, with occasionally small quantities of sulphuretted hydrogen and marsh gas.

The following analysis of gases obtained from water at the Wardley Colliery in Durham was made by Bedson; ¹ 100 c.c. of the water contained 7.81 c.c. gas at N.T.P., and the composition of the gas was as follows :—

| Carbon dioxide | | 81.14 |
|----------------|--|-------------|
| Marsh gas . | | $5 \cdot 2$ |
| Nitrogen . | | 13.92 |

Solid Impurities in Pit Waters.—The solid impurities vary, but the following are found in nearly all pit waters :—

Calcium carbonate (chalk or limestone), Magnesium carbonate, Calcium sulphate (gypsum), Magnesium sulphate (Epsom salts),

probably also calcium chloride and magnesium chloride.

Waters draining into a coal pit occasionally contain large quantities of sodium chloride (common salt), in some cases being so highly charged with this substance that where the waters drop from the roof large stalactites of sodium chloride are formed. Carbonate of iron and sulphate of iron are also found in some waters; these waters on exposure to the air form a yellow or brown deposit of carbonate or oxide of iron, which gives rise to the name of *ochre waters* in many mining districts. The carbonate of iron has doubtless been dissolved from the beds of ironstone that are frequently associated with the coal measures,

¹ Bedson, Jour. Soc. Chem. Ind., vol. vi. p. 715.

whilst the sulphate of iron has probably resulted from the oxidation of iron pyrites, which is found in large quantities in all coal seams. All waters containing sulphate of iron produced from the latter source will also contain free sulphuric acid. Occasionally aluminium sulphate is found in pit waters; it has been produced by the decomposition of the fire and other clays associated with the coal.

Exceptional impurities are found in some pit waters. Bedson¹ found barium and lithium chlorides in waters from the Brockwell seam at the Redheugh Colliery, and lithium chloride in water from the Wardley Colliery.

Many pit waters, owing to the impurities they contain, attack iron rails and pipes, especially those containing sulphuric acid. When they are highly charged with calcium and magnesium carbonates deposits of these substances are liable to form in the pump mains, in some cases completely blocking them.

Hard Water.—Water is said to be "hard" when it does not readily form a lather with soap, and "soft" when it does. Hardness in water is caused by the solid impurities dissolved in it.

The substances that generally cause the hardness in water are :---

Calcium and magnesium carbonates. Calcium and magnesium sulphates. Calcium and magnesium chlorides.

But almost all the impurities present in pit waters will give rise to hardness in the sense of not readily producing a lather with soap. To soften a hard water the impurities causing the hardness must be removed. The hardness of water is of two kinds: (1) temporary; (2) permanent.

Temporary hardness in water can be removed by boiling for a longer or shorter time, whereas permanent hardness in water is not affected by boiling.

Temporary hardness is caused by the presence of calcium and magnesium carbonates, whilst permanent hardness is generally caused by the sulphates and chlorides of calcium and magnesium.

The difference is due to the fact that the carbonates of calcium and magnesium are much more soluble in water containing

¹ Bedson, Jour. Soc. Chem. Ind., vol. vi. p. 713.

carbon dioxide in solution than in water which does not contain this gas. This can be seen if carbon dioxide be passed into lime water; at first a white precipitate of calcium carbonate is formed— $Ca(HO)_2 + CO_2 = CaCO_3 + H_2O_2$. If carbon dioxide is passed into the water after all the lime has been precipitated as calcium carbonate, a certain quantity of the gas is dissolved by the water and the water charged with carbon dioxide eventually dissolves the whole of the precipitated calcium carbonate. boiling a water charged with carbon dioxide and calcium carbonate the carbon dioxide will escape with the steam, and the water thus deprived of the carbon dioxide can no longer hold the calcium carbonate in solution, and this substance is deposited as a crust or powder, leaving the boiled water softer than before it was boiled. But the presence of carbon dioxide in a water is not necessary in order that it shall dissolve calcium or magnesium sulphate or chloride; consequently the removal of carbon dioxide by boiling does not cause these salts to separate, and the hardness caused by them is not affected by boiling.

The use of impure waters for the raising of steam is often very injurious to the boilers. Dissolved oxygen and carbon dioxide exercise a corrosive action on iron, whilst magnesium chloride is one of the commonest causes of boiler corrosion. Sulphuretted hydrogen is also injurious to iron boiler plates, and condensed water contaminated with oils and fats used for lubrication is a source of corrosion.

Hard waters, containing the sulphates and carbonates of calcium and magnesium, cause the formation on the boiler plates of incrustations, called boiler crusts. These incrustations are sometimes so firmly deposited on the boiler plates that they can only be removed with a hammer and chisel, and, being bad conductors of heat, seriously impede the passage of heat from the furnace to the water. When the use of such waters is unavoidable, means are generally taken to prevent the formation of a crust by adding substances known as anti-incrustators to the water in the boiler. These substances may be classified as—

- (1) Saline substances, such as soda crystals, caustic soda, barium chloride, sodium phosphate, &c.
- (2) Fatty bodies, such as tallow.
- (3) Paraffin, and paraffin products.
- (4) Organic bodies, such as peat, potatoes, glycerol, charcoal, &c.

In special cases doubtless some of these bodies may be used with advantage, but generally they are to be condemned as not only useless but as positively injurious to the boiler plates. It is far better to remove the substances which are the cause of boiler crusts before the water enters the boiler. This is generally done by treating the water with the exact quantity of a mixture of lime and sodium carbonate necessary to precipitate the carbonates, sulphates, and chlorides of calcium and magnesium, as, for instance, in the well-known Porter-Clark, Archbutt and Deeley, and Gaillet and Hurt processes.

Physical Properties of Water .- At the ordinary temperature water, when pure, is a clear, transparent, almost colourless, tasteless, and odourless liquid. Under ordinary circumstances it becomes solid on cooling to 0° C. or 32° F. Bodies, on cooling, generally undergo a contraction in volume, but if we take a large bulb at the end of a narrow tube and fill it with water at the ordinary temperature, say at 15° C., and carefully observe what occurs as it is gradually cooled to 0° C., we shall find that at first the volume of the water contracts, but that at a certain temperature its volume becomes stationary for a moment and then expands until its temperature becomes 0° C. On the other hand, if we fill the bulb with ice-cold water, and gradually heat it, we shall first notice a contraction in the volume, and, when a certain temperature is reached, the volume of water will begin to expand and continue expanding till the boiling-point is reached. The temperature at which this change from contraction to expansion on cooling takes place is 4° C. or 39° F. At this temperature the density of water is greater than at any other, and it is known as the temperature of maximum density of water. Taking the density of water at 4° C. as 1, the density at the freezingpoint is .999878, at 8° C. .999882, and at 15° C. .999154.

At 0° C. water is converted into ice, and at the moment of freezing a still further expansion takes place. This increase in volume amounts to about $\frac{1}{11}$ of the volume which the water occupies at 0° C., for one volume of water at 0° C. becomes 1.09082 volumes of ice at 0° C. The sudden expansion of water on freezing is the cause of the bursting of water-pipes during a frost. The water, being confined in the pipe, finds no room for expansion on freezing, and the pressure produced by the sudden increase in volume causes the pipe to fracture, whilst a plug of ice fills up the hole and prevents the escape of water

till the ice melts. This action of water on freezing can readily be shown by filling a small cast-iron shell with water, closing the opening with a screw plug, and surrounding the shell with



FIG. 29.

a freezing mixture (Fig. 29). When the water freezes the shell will burst, and, on examining the fractured shell, ice will be seen adhering to the sides of the interior. This action of water on freezing plays an important part in the disintegration or weathering of some

rocks. Water penetrates into the cracks and crevices in the rock. During the cold winter temperatures the water freezes, and by its expansion splits the rocks into fragments.

Ice, under ordinary circumstances, melts at a temperature of 0° C. or 32° F., but the melting-point of ice is slightly lowered by pressure. In consequence of this, if two pieces of ice be pressed together, a certain quantity of the ice on the surfaces under pressure will melt. On releasing the pressure the melted ice at once freezes and the two pieces become firmly frozen together. The freezing-point of water is also lowered by the presence of salts in solution, and strong solutions of salt (brine) or of calcium chloride can be cooled considerably below 0° C. without freezing. A solution containing 32 parts of salt and 100 of water by weight freezes at -23° C.

| Pressure in Atmos- pheres. | Boiling-Point. Degs. C. | Pressure in Atmos- pheres. | Boiling-Point. Degs. C. |
|--|---|--------------------------------------|--|
| $ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \end{array} $ | $100 \\ 120.6 \\ 133.91 \\ 144 \\ 152.22 \\ 159.22 \\ 165.34$ | 8 9 10 11 12 13 14 | $170.81 \\ 175.77 \\ 180.31 \\ 184.50 \\ 188.41 \\ 192.08 \\ 195.53$ |

On heating, water can be made to boil, when it is converted into an invisible vapour called steam. On issuing into the cool atmosphere the steam at once condenses into a white cloud which is composed of minute drops of water. The temperature at which water boils is determined by the pressure of the surrounding atmosphere. At a pressure of 760 millimetres or 29.99 inches of mercury, water boils at 100° C. or 212° F. This is generally known as the boiling-point of water, but it must be remembered that the temperature at which water boils falls with a fall in the pressure and rises with a rise in the pressure. The table on page 70, given by Zeuner, shows the rise in the boilingpoint of water with increase of pressure.

Latent Heat of Water and Steam .- If we take a block of ice and melt it by heating in a vessel, we shall find that a thermometer placed in the vessel will remain at 0° C. until the whole of the ice is melted, although heat is continually entering the ice: or if 1 lb. of water at 79° C. be mixed with 1 lb. of ice at 0° C. the ice will melt and 2 lbs. of water at 0° C. will be obtained, whereas if 1 lb. of water at 79° C. be mixed with 1 lb. of water at 0° C., 2 lbs. of water at 39.5° C. will be obtained. It is evident, then, that the heat given out when 1 lb. of water at 79° C. cools down to 0° C. completely disappears or becomes unrecognisable by a thermometer when the water at that temperature is mixed with ice at 0° C. This heat has been absorbed in doing the work of converting 1 lb. of ice at 0° C. into 1 lb. of water at 0° C. This heat is called the latent heat of fusion of ice, or the latent heat of water. It is defined as the quantity of heat required to convert 1 lb. of ice at 0° C. into 1 lb. of water at 0° C., and is equal to the quantity of heat which will raise the temperature of 1 lb. of water from 0° to 79° C. The quantity of heat required to raise the temperature of 1 lb. of water 1° C. is called a thermal unit; therefore the quantity of heat required to raise the temperature of 1 lb. of water 79° C. is 79 thermal units, hence the latent heat of fusion of water is 79 thermal units. This latent heat is given out again when the water freezes.

Latent Heat of Steam.—If we heat some water in a flask and insert a thermometer, we shall notice that the thermometer continues to rise until the liquid boils. When the water boils the thermometer becomes stationary and remains stationary until all the water is boiled away; and, if before all the water is boiled away we remove the bulb of the thermometer from the water into the steam, the thermometer will remain unchanged. Boiling water and steam from it have the same temperature. Here, again, heat is continually entering the boiling water, but it is not

registered by the thermometer whether the bulb be immersed in the water or in the steam; the heat has become latent. The heat, which is rendered latent when 1 lb. of water at 100° C. is converted into steam at 100° C., is 537 thermal units.

The absorption of heat when ice melts or water boils is not a property possessed by water alone. All solids absorb heat on melting, and all liquids absorb heat on boiling, and not only on boiling, but whenever they pass from liquid to vapour. It has been pointed out that evaporation is continually going on from any surface of water exposed to the air, and heat is continually absorbed so long as evaporation goes on. The absorption of heat by liquids on evaporation can be shown if we take a small quantity of ether—which is a very volatile liquid—in



a beaker, A (Fig. 30), and, after moistening the outside of the beaker with water, stand it on a small block of wood, B; on making the ether evaporate quickly by blowing air through it the beaker will become frozen to the block, so that on lifting the beaker the block comes with it. On evaporation the ether absorbs heat from the bodies which

surround it, and, when the evaporation takes place quickly, the heat is absorbed so quickly that the temperature of the surrounding bodies is lowered below the freezing-point of water, and the water in contact with the beaker and wood freezes.

Advantage is taken of this property to produce low temperatures. In the freezing process of sinking through wet or loose ground liquid ammonia is used; the liquid is made to evaporate, and the vapours to expand in contact with pipes containing brine. Large quantities of heat are absorbed by the evaporation and expansion, so that the temperature of the brine is lowered considerably below the freezing-point of water. The cold brine is then pumped into pipes embedded in the wet ground, and the water in it is frozen.

Freezing Mixtures.—The solution of certain solids in water is accompanied by a reduction in temperature caused by the rendering of a certain amount of heat latent by the liquefaction of the solid. Very considerable reduction of temperature occurs if certain salts be mixed with ice or snow. When common salt and snow or powdered ice are mixed, the two substances liquefy and absorb large quantities of heat, producing very low temperatures. The greatest possible reduction of temperature is produced when 23 parts by weight of salt are mixed with 100 parts of snow. If equal weights of crystallised calcium chloride and snow are mixed, the temperature falls from 0° C. to -45° C. Mixtures of this kind are called freezing mixtures.

Vapour Pressure of Water.—It is not necessary that the temperature of water be raised to its boiling-point for it to give off steam or vapour. It does so constantly at all temperatures. It is well known that if a vessel of water be exposed to the air the water will evaporate, and in time completely disappear. The vapour which is thus given off exerts a pressure which is called the vapour pressure of the liquid. The higher the temperature the greater the rate of evaporation, and the greater the pressure exerted by the vapour.

There is a limit to the pressure that is exerted by the vapour of any liquid at any given temperature, and when the evaporation takes place in air this limit is reached when the atmosphere is saturated with the vapour (see p. 35). In the case of water, the maximum pressure of its vapour, at one time called the tension of aqueous vapour, has been carefully determined for different temperatures by many observers, and in the following table are given the results of Ramsay and Young for the vapour pressure of water between the temperatures of 0° and 230° C. :--

| Temperature. Degrees C. | Inches of Mercury. | Millimetres of Mercury. | Temperature. Degrees C. | Inches of Mercury. | Millimetres of Mercury. |
|----------------------------|-----------------------|----------------------------|----------------------------|-----------------------|----------------------------|
| 0 | 0.18 | 4.6 | 120 | 58.42 | 1484 |
| 10 | 0.36 | 9.165 | 130 | 79.49 | 2019 |
| 20 | 0.68 | 17.39 | 140 | 106.1 | 2694 |
| 30 | 1.24 | 31.55 | 150 | 140.5 | 3568 |
| 40 | 2.16 | 54.91 | 160 | 183.2 | 4652 |
| 50 | 3.62 | 91.98 | 170 | 233.7 | 5937 |
| 60 | 5.86 | 148.8 | 180 | 294.8 | 7487 |
| 70 | 9.18 | 233.1 | 190 | 370.1 | 9403 |
| 80 | 13.96 | 354.6 | 200 | 457.8 | 11625 |
| 90 | 20.70 | 525.4 | 210 | 560.6 | 14240 |
| 100 | 29.92 | 760.0 | 220 | 683·6 | 17365 |
| 110 | 42.32 | 1075.0 | 230 | 824.2 | 20936 |
| | | | | | |

If aqueous vapour is introduced into an atmosphere already saturated with it the vapour pressure does not increase, but the excess of vapour is condensed to liquid. On the other hand, if water is brought into a closed atmosphere which is not saturated, evaporation takes place until the air becomes saturated, when the maximum vapour pressure is reached. This pressure remains constant so long as the temperature of the air does not alter; but if its temperature falls, condensation of the aqueous vapour takes place until the vapour pressure becomes equal to the maximum pressure at the lower temperature. Tf air not saturated with moisture be cooled no condensation will take place until that temperature is reached at which the air would become saturated by the quantity of vapour present; any slight reduction below this temperature will cause the vapour to condense.

It is a matter of common observation that if ice be placed in a glass of water, in a short time moisture deposits on the outside of the glass. In this case the layer of air immediately in contact with the cold glass is cooled, and a temperature is ultimately reached at which the vapour present is just sufficient to saturate the air, any slight diminution of temperature then causes moisture in the form of dew to deposit on the glass. When the temperature rises the dew disappears. If careful observations are made of the temperatures at which dew is deposited on the brightly polished surface of a silver vessel and afterwards disappears the two temperatures will be found to differ slightly. The mean of these two temperature at which the air would be saturated by the quantity of vapour present in the atmosphere.

Chemical Properties of Water.—Water is a compound of hydrogen and oxygen, which was first proved by Cavendish, who obtained it by exploding a mixture of the two gases. This fact can readily be shown by passing a current of electricity through water made slightly acid with sulphuric acid, when it is decomposed into oxygen and hydrogen. The experiment is easily carried out in an apparatus known as Hofmann's voltameter (Fig. 31). It consists of three tubes, A, B, C. A and B are closed with taps, whilst C is longer than A and B, and terminates in a bulb, D. Two small platinum electrodes, E and F, are fused into A and B, and can be connected with the battery, K, by means of wires, G and I. The gases can then be collected separately, the hydrogen being evolved at the electrode con-

nected with the - ve pole of the battery, whilst the oxygen is evolved at the electrode connected with the + ve pole. As the gases accumulate in the tubes A and B, the liquid is depressed and received into the bulb, D.

Water is decomposed by a large number of metals with liberation of hydrogen. Some metals, such as potassium and sodium, will decompose water at the ordinary temperature.

A small piece of potassium thrown on to water in a trough will float on the surface and burst into flame.

The flame is burning hydrogen, which is liberated from the water and ignited owing to the high temperature produced by the reaction, $K_2 + 2H_2O = 2KHO + H_2$. In a similar manner sodium will decompose water with liberation of hydrogen, Na₂ + 2H₂O = 2NaHO + H₂, but the hydrogen does not ignite, as the temperature produced by the reaction is not so high as when potassium is used.

Other metals which do not readily decompose water at the ordinary temperature will do so at a red heat. For instance, if steam be passed over red-hot iron it is decomposed, magnetic oxide of iron is produced, and hydrogen liberated, $3Fe + 4H_2O = Fe_3O_4 + 4H_2$.

This may be carried out by heating to redness in a furnace iron nails contained in an iron tube, and passing steam from a boiler through the red-hot tube, as shown in Fig. 32. The hydrogen may then be collected in a jar by displacement of water.

It is evident that water is composed of at least two elements, namely, hydrogen and oxygen, and it has been proved by the most searching investigations that only these two elements enter into the composition of water.



FIG. 31.

Hydrogen. Symbol H. At. Wt. 1.

The properties of oxygen have already been described, and before proceeding further it is necessary to study the preparation and properties of hydrogen itself, as it not only enters into



FIG. 32.

the composition of water, but also into the composition of a large number of bodies met with in coal mines; for instance, marsh gas or light carburetted hydrogen, and olefiant gas or heavy carburetted hydrogen, are both composed of hydrogen and carbon, whilst sulphuretted hydrogen is a compound of hydrogen and sulphur. Coal itself, according to the variety, contains from about 2 to 8 per cent. of hydrogen, and many of the bodies obtained by the distillation of coal in the coke ovens contain hydrogen combined with other elements.

Preparation.—Hydrogen can be prepared from water by the methods already mentioned on page 75, and large quantities of the gas are prepared by passing steam over red-hot iron and compressed into cylinders. The usual method for preparing the gas in the laboratory consists in acting on certain metals with certain acids.

The acids most commonly used are sulphuric acid (H_2SO_4) and hydrochloric acid (HCl), whilst zinc and iron are the metals most frequently used, though many other metals will serve the purpose equally well. The acid forms a salt with the metal, and the hydrogen of the acid is set free. Thus when sulphuric acid acts on zinc it forms zinc sulphate and hydrogen, whilst hydrochloric acid in acting on iron gives ferrous chloride (iron dichloride) and hydrogen. The equations which represent these interactions are as follows :—

WATER AND HYDROGEN

$Zn + H_2SO_4 = ZnSO_4 + H_2$ Fe + 2HCl = FeCl₂ + H₂

The manner of preparing hydrogen by this method is as follows: A small quantity of zinc is placed in the flask, A,

covered with water, and dilute acid is poured down the funnel, E. As soon as the acid comes in contact with the metal a brisk effervescence is caused by the rapid evolution of hydrogen. The gas is led through an evolution tube, B, underneath the water in a trough, C, and collected by the displacement of the water in the bottle, D (Fig. 33). Before the gas is collected in the bottle it must be tested



FIG. 33.

for freedom from air by applying a light to a small quantity collected in a test tube. If a slight explosion occurs the gas is mixed with air, and the test must be repeated until no explosion takes place on ignition. When this is the case, the gas may be collected in the bottle.

Physical Properties.—Pure hydrogen is a colourless, odourless, tasteless gas, which can, by intense cold and high pressure, be condensed to a liquid. It is extremely light, 1 litre of hydrogen at 0° C. and 760 mm. pressure weighs 0.0896 grams., and 1 c. ft. at 32° F. and 30 inches pressure weighs 0.0056 lbs., or 0.0896 oz. Its specific gravity is 0.06926, that is, a given volume of air is 14.4 times heavier than the same volume of hydrogen at the same temperature and pressure.

Its lightness may be illustrated in many ways :---

(1) A small collodion balloon filled with the gas and set free will rapidly rise in the air. Before the introduction of coal gas hydrogen was used for filling balloons.

(2) If a jar, A, containing hydrogen be brought mouth upwards under the mouth of an inverted jar, B, containing air (Fig. 34), the hydrogen gas will stream upwards out of A into B, which can be shown by applying a light to B, when a slight explosion will take place.

(3) If an inverted glass vessel, A, be counter-balanced on a balance, B, and a jar of hydrogen, C, be brought with its mouth under the vessel, A, the hydrogen in C will stream upwards into



A, expelling an equal volume of air (Fig. 35). Because the volume of hydrogen that enters A is lighter than the volume of air which has been expelled, the equilibrium of the balance, B, is disturbed, and the arm from which A is suspended rises.

Chemical Properties.-Hydrogen is a combustible gas; it will ignite in air or oxygen if brought in contact with a flame,



Very large amounts of heat are set free when hydrogen burns, and the temperature of the flame produced is very high; on this account hydrogen is a valuable constituent in coal, contributing to the calorific power or heating value of the fuel.

FIG. 36.

When pure hydrogen escapes into air and is ignited

it burns quite quietly, but if the gas be mixed with air or oxygen before ignition, on bringing a light to the mixture an explosion will occur, the violence of which depends on the proportion in which the gases are mixed; the most violent

explosion occurs when two volumes of hydrogen are mixed with one volume of oxygen, or 4.76 volumes of air.

Hydrogen combines directly with other elements besides oxygen. If electric sparks are passed between carbon poles in an atmosphere of hydrogen acetylene is formed, $2C + H_2 = C_2H_2$.

Similarly, if a burning jet of hydrogen be plunged into vapour from boiling sulphur the jet continues to burn owing to the combination of hydrogen with the sulphur to form sulphuretted hydrogen, $2H_2 + S_2 = 2H_2S$.

Composition of Water.—The composition of water has been determined with great accuracy both with regard to the volumes as well as the relative weights of the two gases that combine together.

Composition of Water by Volume.—By this is understood— (1) The relation between the volumes of hydrogen and oxygen that combine together; (2) the relation that the volume of water in the form of vapour produced bears to the volumes of the combining gases.

The relation between the volumes of hydrogen and oxygen that combine together to form water can be roughly estimated by passing a current of electricity through water and collecting the gases in separate tubes as described on page 75. In this experiment it will be seen that the volume of hydrogen is slightly more than twice the volume of oxygen. Cavendish made very careful experiments by exploding mixtures of oxygen and hydrogen, and he proved that the greatest weight of water was formed when the two gases, mixed in the proportions of two volumes of hydrogen to one of oxygen, were exploded.

The importance of knowing the composition of water with great accuracy has led to the repetition of Cavendish's experiments by numerous observers with the most delicate apparatus that modern ingenuity can devise, and the accuracy of his results has been entirely confirmed.

In these experiments the water formed by the combination of the gases is allowed to condense to a liquid, and the volume occupied by the liquid is almost inappreciable, being only about $\frac{1}{2000}$ part of the volume of mixed gases; but if means are taken to prevent the condensation of the water formed it will be found that the volume of water vapour is exactly two-thirds of the volume of the mixed gases, or is exactly equal to the volume of hydrogen that unites with the oxygen. This is

expressed by saying that two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam, all the gases being measured at the same temperature and pressure.

Composition of Water by Weight.—Having ascertained that two volumes of hydrogen combine with one volume of oxygen, it is possible to calculate the proportion by weight in which the gases combine together. One volume of oxygen is sixteen times heavier than one volume of hydrogen, therefore one volume of oxygen is eight times as heavy as two volumes of hydrogen, consequently the

weight of hydrogen : weight of oxygen = 1:8,

if we determine to call the weight of the two volumes of hydrogen 2, then the proportion becomes

weight of hydrogen : weight of oxygen = 2:16.

It is desirable, however, to confirm this by experiment, which has been done by weighing the water produced when a known weight of oxygen combines with hydrogen. Then, from the weight of oxygen used and the weight of water formed, the weight of hydrogen that has entered into combination can be calculated.

An example taken from an actual experiment may make this clear: 59.789 grammes of oxygen produced 67.282 grammes of pure water. The weight of hydrogen that combined with the oxygen is therefore 67.282 - 59.789 = 7.493 grammes. Hence 67.282 grammes of water are produced by the combination of 59.789 grammes oxygen and 7.493 grammes hydrogen. From these numbers it may be calculated that 88.73 grammes of oxygen combine with 11.27 grammes of hydrogen to form 100 grammes of water. This is one example of a very large number of similar determinations, and when the average of a large number of results is taken it is found that the percentage composition of water by weight may be represented by—

> Oxygen, 88.89 Hydrogen, 11.11

The relation between these numbers is—

Weight of hydrogen : weight of oxygen = 1:8 or 2:16, which confirms the result obtained by calculation from the composition by volume.

Let us now see exactly what is the meaning of our results. Firstly, we have 2 volumes of hydrogen combining with 1 volume of oxygen to form 2 volumes of gaseous water. Secondly, we have 2 parts by weight of hydrogen combining with 16 parts by weight of oxygen to form 18 parts by weight of water. Therefore, although the volume of gaseous water is $\frac{2}{3}$ of the volume of the mixed gases, the weight of the water formed is exactly equal to the weight of the mixed gases; so that although there is a contraction in volume there is no loss in weight.

The interpretation of these results may be expressed as follows :----

"Two volumes of hydrogen weighing 2 combine with 1 volume of oxygen weighing 16 to form 2 volumes of gaseous water weighing 18, the volumes of all the gases being measured at the same temperature and pressure."

Temperature and the Thermometer.—Water is used in the construction of a thermometer, the instrument used to measure temperature. Before describing the thermometer and its construction, the student should understand what is meant by temperature.

Temperature measures how hot a body is without giving any indication of the quantity of heat the body contains. Every substance requires a definite amount of heat to raise its temperature one degree, and generally the amount of heat required is different for different substances, so that two different substances at the same temperature will contain different quantities of heat.

To illustrate this, take 1 lb. of water at 100° C. and mix it with 1 lb. of water at 15° C. and the temperature of the mixture will be 57.5° C. Take also 1 lb. of mercury at 100° C. and mix it with 1 lb. of water at 15° C. and the temperature will be 17.5° C. The 1 lb. of water at 100° C. and the 1 lb. of mercury at 100° C. are at the same temperature, but the former raised the temperature of 1 lb. of water at 15° C. 42.5 degrees, whilst the latter only raised it 2.5 degrees. The water at 100° C. must contain more heat than the mercury at the same temperature. It takes about 30 times as much heat to raise the temperature of water one degree as to raise the temperature of mercury one degree.

Increase of temperature usually causes bodies to expand, whilst decrease of temperature usually causes them to contract.

Temperature is measured by means of an instrument called a

thermometer, which registers the temperature of a body by measuring the contraction or expansion of a small quantity of a liquid. The liquid most commonly used is mercury or quicksilver, because its rate of expansion is nearly uniform.

To make a mercurial thermometer a glass tube having a very fine and uniform bore is used; a bulb is blown at one end, whilst the other is left open for the introduction of the mercury. The bulb and tube are completely filled with mercury and heated to the highest temperature the instrument is required to measure. The open end is hermetically sealed whilst the tube is kept full of mercury. On cooling, the mercury contracts and at the ordinary temperature fills the bulb and a portion of the tube. To compare the temperatures of different bodies a scale must be attached to the instrument, for which purpose the position of the mercury in the tube for two known temperatures must be determined; these are the temperature of melting ice or the *freezing-point* of the thermometer, and the temperature of steam



from water boiling under a pressure of 760 millimetres, or the boiling-point of the thermometer (Fig. 37). The former is obtained by plunging the bulb and stem into powdered melting ice and marking the point at which the mercury in the tube becomes stationary. The latter is found by immersing the bulb and stem in the steam from boiling water and marking the position of the mercury when it ceases to rise in the tube. Care must be taken to note the height of the barometer when determining the boiling-point, because

the temperature of steam from boiling water alters with the pressure, and the boiling-point on the thermometer measures the temperature of steam under a pressure of 760 millimetres. If the pressure is greater or less than this the true boiling-point will be below or above the point at which the mercury stands in the tube and a correction must be made accordingly. Having obtained the true freezing and boiling points, the scale is fixed by dividing the distance between them into a certain number of equal parts. In some instruments the scale is etched on the tube of the thermometer, in others the thermometer is mounted on a wooden frame on which the scale is marked.

There are three scales in use : the Centigrade, the Fahrenheit, and the Réaumur scales.

(1) The Centigrade Scale.—In this scale the distance between the freezing and boiling points is divided into 100 equal parts, each of which is a degree Centigrade. The freezing-point is marked zero, or 0° C., and forms the starting-point of the scale, so that the boiling-point is 100° C. This scale is always used for scientific purposes, but only occasionally in England for technical purposes.

(2) The Fahrenheit Scale is the scale usually adopted for technical use in England; in it the distance between the freezing and boiling points is divided into 180 parts, each of which is a degree Fahrenheit. The freezing-point is marked 32° F., so that the boiling-point is 212° F. = 180 + 32. The zero, or 0° F., is obtained by marking 32 of the degrees below the freezing-point.

(3) The Réaumur Scale is only used in Russia and Scandinavia. The freezing-point is the zero, or 0° R., and the distance between the freezing and boiling points is divided into 80 equal parts, so that the boiling-point is 80° R. As the scale is not used in Britain, it will not be referred to in the following discussion of the thermometric scales.

In each scale divisions equal in size to the degrees are marked below the zero and above the boiling-point. All temperatures below zero on any scale are characterised by the minus sign, thus: -1° C., -2° C., &c., mean 1, 2, &c., degrees below 0° C.; and -1° F., -2° F., &c., mean 1, 2, &c., degrees below 0° F.

Conversion of Temperatures on one Scale to Corresponding Temperatures on another Scale.—The same temperature is represented by different numbers on the Centigrade and Fahrenheit scales, and to find the number of degrees on one scale corresponding to a given temperature on the other we must always start from the freezing-point. Between this temperature and the boiling-point there are 100° C. and 180° F., so that the relation between any number of degrees on the Centigrade and

Fahrenheit scales is as 100: 180 = 5: 9, or $1^{\circ}C. = \frac{9}{5}^{\circ}F$. and $1^{\circ}F. = \frac{5}{9}^{\circ}C$.

To convert degrees on the Centigrade scale into degrees on the Fahrenheit scale, multiply the Centigrade degrees by $\frac{9}{5}$. This gives the temperature on the Fahrenheit scale, starting from the freezing-point, or 32° F.; but as 0° F. is 32 degrees below the freezing-point, 32 must be added to the result to obtain the corresponding temperature measured from 0° F.; so the rule to convert Centigrade degrees into Fahrenheit degrees is to multiply by $\frac{9}{5}$ and add 32.

Example: Convert 100° C. and
$$-10^{\circ}$$
 C. into degrees F. $(100 \times \frac{9}{5}) + 32 = 180 + 32 = 212^{\circ}$ F.

Explanation: $100 \times \frac{9}{5} = 180 = \text{number of degrees F. above } 32^{\circ}\text{F.}$ $180 + 32 = 212^{\circ}\text{F.}$, , , F. , 0°F. $(-10 \times \frac{9}{5}) + 32 = -18 + 32 = 14^{\circ}\text{F.}$

Explanation :---

 $-10 \times \frac{9}{6} = -18 =$ number of degrees F. below 32° F. $-18 + 32 = 14^{\circ}$ F. ,, ,, F. above 0° F.

To convert degrees on the Fahrenheit scale into degrees on the Centigrade scale we must start from the freezing-point. By subtracting 32 from the number representing the temperature on the Fahrenheit scale we get the number of degrees reckoned from this temperature, and the number thus obtained multiplied by $\frac{5}{9}$ will give the corresponding temperature on the Centigrade scale. The rule is :—subtract 32 and multiply by $\frac{5}{9}$.

Example: Convert 32° F. and -13° F. into degrees C. $(32-32) \times \frac{5}{9} = 0 \times \frac{5}{9} = 0^{\circ}$ C.

Explanation: 32-32=0= number of degrees F. reckoned from the freezing-point.

 $0 \times \frac{5}{9} = 0^{\circ}$ C. = degrees C. corresponding with 32° F.

 $(-13+32) \times \frac{5}{9} = -45 \times \frac{5}{9} = -25^{\circ} \text{ F}.$

Explanation: -13-32 = -45 = number of degrees F. reckoned below the freezing-point.

 $-45 \times \frac{5}{9} = -25^{\circ}$ C. = number of degrees C. corresponding with -13° F.

CHAPTER V

ATOMS AND MOLECULES

In Chapter I. the two fundamental laws of chemical combination have been explained. The laws are: (1) The law of definite proportions; chemical combination takes place between definite masses of the elements. (2) The law of multiple proportions; when two elements, A and B, combine together in more than one proportion by weight, the relative weights of B that combine with a fixed weight of A bear a simple relation to one another. It was also stated that these laws were simply general statements of facts that had been proved by experiment to be true in every case that had been examined; and, moreover, that they had proved to be true in so many instances that it was reasonable to assume that they were true for all cases.

Having discovered the laws which are founded on the results of experiments it is desirable to imagine a condition of things which will account for the existence of the laws. In the first place a hypothesis is suggested, and if on close examination of the hypothesis all the known facts are found to be in accordance with it the hypothesis becomes a theory.

Theories are of great value in scientific research, as they often suggest, to those who are fully acquainted with the facts with which they accord, new conditions which ought to result if the theories are true. But when a theory ceases to offer an explanation of all the facts connected with the phenomena it is required to explain, the theory must be modified, or rejected for a new one, for the facts cannot be altered.

The student, therefore, must be very careful to distinguish between facts that are established by experiment from which the laws are deduced, and theory which is a matter of speculation and serves as an explanation for the existence of the facts.

The Atomic Theory

The facts relating to chemical combination and the laws based on them were discovered by John Dalton about 100 years ago, and to him we owe the conception of the Atomic Theory.

In this theory the assumption is made that any simple form of matter, or element, is not infinitely divisible, by which is meant that if we proceed to divide and subdivide a piece of any element, such as carbon, we can first reduce it to an exceedingly fine powder, then we can take any one particle from the powder and divide that into smaller particles, and it is possible to conceive that any one of these smaller particles can be still further subdivided, and that this process of subdivision may continue until the particle ceases to be visible. It is also possible to conceive that by chemical agency the invisible particles may undergo still further subdivisions, and the atomic theory supposes that this subdivision cannot go on indefinitely, but that eventually a point is reached beyond which further subdivision of the particle of an element is impossible. The small invisible and indivisible particles are called "atoms."

These atoms are particles of matter, and therefore possess weight, and the atomic theory assumes that all the atoms of any particular element are alike and have the same weight, but that the weights of the atoms of different elements differ. It further assumes that when one element combines with another it is the individual atoms of these elements that unite.

If elements are made up of atoms and chemical interaction takes place between these atoms, the atomic theory offers an explanation of the law of definite proportion. Suppose a compound A B is formed by the union of a definite number of atoms of the element A with a definite number of atoms of the element B. Seeing that all the atoms of A are equal in weight, and that all the atoms of B are equal in weight, it follows that the weight of A that combines with B to form the compound A B must be the same for every particle of A B that is formed.

The same theory also explains the law of multiple proportions. For suppose the two elements of A and B unite together to form two different compounds, and each of those compounds is formed by the union of the same number of atoms of A with different numbers of atoms of B. Each compound will be formed by the union of the same weight of A with different weights of B. The weight of B in each compound will equal the number of atoms of B in each compound multiplied by the weight of an atom of B, so that the weight of B in one compound is to the weight of B in the other compound as the number of atoms of B in the first is to the number of atoms of B in the second. The number of atoms in each compound must be a whole number, as, according to the atomic theory, the atom cannot be divided, therefore half-atoms cannot exist; hence the ratio of the number of atoms of B in the two compounds must be represented by simple and whole numbers.

The atomic theory, therefore, offers an explanation of these two laws of chemical combination.

Atomic Weights. — In the first chapter it has been explained that the relative weights of elements entering into combination can be expressed by very simple numbers which were then called the combining weights, and that these combining weights were represented by symbols. Thus H stands for 1 part by weight of hydrogen, O for 16 parts by weight of oxygen, and C for 12 parts by weight of carbon. It is not possible to determine the absolute weight of the atoms of different elements in grammes or grains, but it is possible to find out how much heavier the atom of one element is than that of another. All that is necessary is to fix on some element as a standard, and compare the weights of the atoms of all the elements with the weight of the atom of the standard element.

The simplest standard to take is the hydrogen atom, because hydrogen is the lightest body known. The relative weight of the hydrogen atom is therefore taken as 1, and the weights of the atoms of the other elements are compared with it. This gives a series of numbers for the other elements which tell us how much heavier their atoms are than the hydrogen atom, and these numbers are called the atomic weights of the elements. The atomic weight of an element is a number which represents how much heavier its atom is than the atom of hydrogen.

When this is done we get a series of numbers identical with those chosen for the combining weights. Thus the atomic weight of oxygen is 16, and the symbol O stands for the atom of oxygen which is 16 times as heavy as the atom of hydrogen, similarly the atomic weight of carbon is 12, and the symbol C stands for the atom of carbon, which is 12 times as heavy as the atom of hydrogen, and so on for all the elements.

Molecules and Molecular Weights .- It has been explained that a compound is formed by the union of different elements with one another. Carbon dioxide is composed of carbon and oxygen united in the proportion by weight of 12 of carbon to 32 of oxygen, or 1 atom of carbon to 2 atoms of oxygen, which gives it the formula CO₂; this particle of carbon dioxide is the smallest particle which can exist. Again, the particle of water composed of 1 atom of oxygen chemically united to 2 atoms of hydrogen, represented by the formula H₂O, is the smallest particle of water that can exist. The smallest particles of compounds are made up of groups of atoms, and are called molecules. The relative weights of these molecules are equal to the sum of the weights of the atoms of which they are composed. Thus the relative weight of the molecule of carbon dioxide is equal to the weight of 1 atom of carbon plus the weight of 2 atoms of oxygen, or $12 + (16 \times 2) = 44$. Similarly the weight of the molecule of water is 18 = 2 + 16, which is the weight of 2 atoms of hydrogen added to the weight of 1 atom of oxygen. These numbers represent how much heavier a molecule of a compound is than an atom of hydrogen, and are called molecular weights.

Further investigations show that there are molecules of elements as well as of compounds; that the molecules of the elements consist in some instances of groups of two or more atoms of the elements, and in others consist of one atom only.

The molecules of hydrogen, oxygen, and nitrogen each consist of 2 atoms, the molecule of the element phosphorus consists of 4 atoms, whilst the molecule of mercury consists of 1 atom. The molecular weights of the elements are obtained by multiplying the atomic weights by the number of atoms in the molecule, and they represent how much heavier the *molecule* of the element is than the *atom* of hydrogen. The following table will illustrate this :--

| | Atom. | Atomic Weight. | Molecule. | Molecular Weight. |
|---|------------------------|--------------------------------|---|-------------------------------|
| Hydrogen . Oxygen . Nitrogen . Phosphorus . Mercury . | H O N P Hg | 1 16 14 31 200 | $\begin{matrix} \mathrm{H_2} \\ \mathrm{O_2} \\ \mathrm{N_2} \\ \mathrm{P_4} \\ \mathrm{Hg} \end{matrix}$ | $2 \\ 32 \\ 28 \\ 124 \\ 200$ |

Avogadro's Hypothesis.—If equal volumes of gases at the same temperature and pressure be weighed the relation between the weights obtained is represented by the numbers representing their molecular weights.

The following are the weights of 1 litre of different elementary and compound gases at 0° C. and 760 mm. pressure:—

| 1 | litre | Hydrogen. | | weighs | ·0896 | grammes |
|---|-------|----------------|---|--------|---------|---------|
| | ,, | Oxygen . | | ,, | 1.43952 | ,, |
| | ,, | Nitrogen . | | " | 1.2511 | 22 |
| | " | Carbon dioxide | | 22 | 1.9712 | ,, |
| | " | Water vapour | | ,, | 0.8064 | " |
| | ,, | Marsh gas | • | ,, | 0.7168 | " |

Dividing each of these numbers by .0896, the weight of 1 litre of hydrogen, the following relative numbers are obtained, which show how much heavier each gas is than hydrogen :—

| Hydrogen . | | | 1 |
|----------------|-----|--|----|
| Oxygen . | | | 16 |
| Nitrogen . | | | 14 |
| Carbon dioxide | | | 22 |
| Water vapour | | | 9 |
| Marsh gas . | . • | | 8 |

The same relation can also be expressed by multiplying each of the above numbers by 2, which gives—

| Hydrogen . | | 2 |
|----------------|--|-----------|
| Oxygen . | | 32 |
| Nitrogen . | | 28 |
| Carbon dioxide | | 44 |
| Water vapour | | 18 |
| Marsh gas . | | 16 |

These numbers, which express the relation between the weights of equal volumes of the gases, are their molecular weights. From these considerations Avogadro deduced his hypothesis, namely, that equal volumes of different gases at the same temperature and pressure contain the same number of molecules. This hypothesis is of equal importance with Dalton's atomic theory. It

has been investigated by chemists and physicists, and in every instance the correctness of the conception has been confirmed.

Vapour Density and Specific Gravity of Gases.—The vapour density of a gas or vapour is a number which expresses how much heavier a given volume of any gas or vapour is than the same volume of hydrogen at the same temperature and pressure. By reference to the table given above it will be seen that these numbers are one half of the molecular weights of the gases. Assuming the correctness of Avogadro's hypothesis, this gives us the means of determining the molecular weight of any gas or vapour, for the relation between the weight of a given volume of a gas or vapour and the weight of an equal volume of hydrogen can be determined experimentally, and if the number obtained be multiplied by 2, it gives the molecular weight of the gas or vapour in question.

The weights of equal volumes of gases are also compared with the weight of an equal volume of air, and numbers are thus obtained which express how much heavier given volumes of the different gases are than the same volume of air at the same temperature and pressure; these numbers are called the *specific* gravity of gases. The specific gravities of the gases mentioned above are :—

| Hydrogen . | | | | ·06926 |
|---------------|------|--|---|--------|
| Oxygen . | | | • | 1.1056 |
| Nitrogen . | | | | 0.9713 |
| Water vapou | r. | | | 0.623 |
| Carbon dioxid | le . | | | 1.5293 |
| Marsh gas . | | | | 0.557 |

There is much confusion as to the true meaning of vapour density and specific gravity. This arises from a very loose use of the word "density." This word is often erroneously used to mean the specific gravity of a gas and sometimes the vapour density. The true meaning of the term "density" is the weight of a unit volume of any substance, and if the litre be taken as the unit volume, it is the weight in grammes of 1 litre of every substance. The vapour density and specific gravity are not weights, but simple numbers which refer to the relation which exists between the weight of a given volume of any gas

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and the weight of the same volume of hydrogen and air respectively at the same temperature and pressure. The following table will show the difference between these terms :—

| | Density or Weight in Grammes of 1 litre of gas at 0° C. and 760 mm. pressure. | Vapour Density, <u>M.W.</u> 2 | Mole- cular Weight, V.D.×2 | Specific Gravity, <u>V.D.</u> 14·4 |
|-----------------------|---|--|-------------------------------------|---|
| Hydrogen | ·0896 | 1 | 2 | 0.06926 |
| Marsh gas | .7168 | 8 | 16 | 0.557 |
| Water vapour | ·8064 | 9 | 18 | 0.623 |
| Nitrogen | 1.2511 | 14 | 28 | 0.9713 |
| Carbon monoxide . | 1.2544 | 14 🛒 | 28 | 0.972 |
| Air ¹ | 1.2932 | 14.4 | | 1 |
| Oxygen | 1.43952 | 16 | 32 | 1.1056 |
| Sulphuretted hydrogen | 1.5232 | 17 | 34 | 1.1781 |
| Argon | 1.7818 | 19.95 | 39.9 | 1.3843 |
| Carbon dioxide | 1.9712 | 22 | 44 | 1.5291 |
| Sulphur dioxide | ••• | 32 | 64 | 2.2471 |

The vapour density of any gas represents how much heavier a given volume of the gas is than an equal volume of hydrogen at the same temperature and pressure, and the specific gravity of a gas represents the same relation between equal volumes of the gas and air at the same temperature and pressure. Air is 14.4 times heavier than hydrogen, hence if V.D. is the vapour density of any gas and S its specific gravity—

$$\frac{V.D.}{14\cdot 4} = S \text{ and } 14.4S = V.D.$$

Combination of Gases by Volume.—Experimental proof of Avogadro's hypothesis is found in the relation that exists between the volumes of gases that combine together and the volumes of gases produced by their union. When hydrogen

¹ NOTE.—Air is a mixture and not a simple substance, therefore it has no molecular weight.

and oxygen combine to form water, the relation between the weights of hydrogen and oxygen combining and of the water formed are as 2:16:18. Being gases, the volumes of these weights can be measured. This has been done with great accuracy, and the results prove that 2 volumes of the hydrogen combine with 1 volume of oxygen, whilst the water formed in the state of vapour occupies 2 volumes. This may be graphically represented thus :—



It has also been proved that when the gases nitrogen and hydrogen combine to form ammonia, the volumes of nitrogen and hydrogen which combine and that of ammonia formed are in the relation of 1:3:2:-



In all the cases that have been examined in which gases enter into chemical changes similar simple relations exist between the volumes of the gases taking part in the change and the volumes produced by the change, and this applies not only to the combination of elementary gases and the gaseous compound formed, but to chemical changes of any kind that take place between gases.

When marsh gas burns in oxygen and forms carbon dioxide and water, 2 volumes of marsh gas and 4 volumes of oxygen
produce 2 volumes of carbon dioxide and 4 volumes of water vapour :----



In the same way 2 volumes of carbon monoxide and 1 volume of oxygen burn and form 2 volumes of carbon dioxide :---



From these facts the law of combination of gases by volume is deduced, namely, that there is a simple relation between the volumes of gases that take part in any chemical change and the volumes of gases produced by the change.

This law must follow if Avogadro's hypothesis be true, because if chemical interaction takes place between the molecules of gases, and equal volumes of gases at the same temperature and pressure contain an equal number of molecules, it follows that the relation between the volumes of interacting gases and the volumes of gases produced by the interaction must be a simple one.

In Chapter I. it was explained that the symbols of the elements represented their combining weights, and the formulæ of compounds the sum of the relative weights of elements which unite to form the compound. It has now been shown (1) that the symbols of the elements represent their atomic weights, because these weights are the numbers chosen for the combining weights; and (2) that the formulæ of gaseous compounds represent their molecular weights. It has also been explained that a chemical equation represents the relation between the weights of the interacting bodies and that of the weights of bodies formed by the change. It is now possible to give an additional meaning to these terms in the case of gaseous bodies. Seeing that equal volumes of gases at the same temperature and pressure contain an equal number of molecules, a molecule of every gas must occupy the same volume at the same temperature and pressure, hence the molecular formulæ of gases represent equal volumes of those gases at the same temperature and pressure.

For example, H_2 , O_2 , N_2 , CH_4 , CO_2 , CO, which represent a molecule of hydrogen, oxygen, nitrogen, marsh gas, carbon dioxide, and carbon monoxide respectively, also represent equal volumes of these gases at the same temperature and pressure. It follows, therefore, that equations which represent interactions between gases denote not only the relative weights of the interacting gases and of those produced by the change but also their relative volumes.

It is usual to take as the unit volume that occupied by the atom of hydrogen, and, seeing that the molecule of hydrogen consists of 2 atoms, its volume is represented as 2 unit volumes or simply 2. Similarly the volume occupied by any gaseous molecule is represented as 2, that is, twice the volume occupied by the atom of hydrogen. To make this clear, take some examples. The equation $H_2 + O = H_2O$ means 2 parts by weight of hydrogen and 16 parts by weight of oxygen unite and form 18 parts by weight of water, and also that 2 volumes of hydrogen and 1 volume of oxygen form 2 volumes of water vapour, all measured at the same temperature and pressure.

The combustion of marsh gas is represented by $CH_4 + 2O_2 = CO_2 + 2H_2O$, which, in addition to representing the relative weights of the bodies concerned, also represents that 2 volumes of marsh gas (1 molecule) and 4 volumes of oxygen (2 molecules) when burnt give 2 volumes of carbon dioxide (1 molecule) and 4 volumes of water vapour (2 molecules).

For purposes of calculation it is very useful to know the volume occupied by 2 grammes of hydrogen or 2 lbs. of hydrogen at a definite temperature and pressure, because whatever

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volume those weights of hydrogen occupy the same volumes will be occupied by the molecular weight of every other gas taken in grammes or lbs. at the same temperature and pressure.

0.0896 grammes of hydrogen occupy 1 litre at 0°C. and 760 mm.

pressure, therefore 2 grammes of hydrogen occupy $\frac{2}{0.0896} = 22.32$

litres at 0° C. and 760 mm. pressure, so that the molecular weight in grammes of any gas occupies $22\cdot32$ litres at 0° C. and 760 mm. pressure. In the same manner it can be calculated that 2 lbs. of hydrogen at 32° F. and 30 inches pressure occupy $356\cdot88$ cubic feet, and therefore the molecular weight in lbs. of any gas occupies the same volume at the same temperature and pressure.

Summary.—From the laws of combination by weight the atomic theory was propounded by John Dalton. According to that theory all elements consist of indivisible particles with definite weights, and when chemical change takes place it does so between these particles. The weights of these particles or atoms, referred to the weight of the hydrogen atom, are the atomic weights of the elements. The union of elements to form compounds results in the formation of molecules, which are the smallest and indivisible particles of the compounds ; also molecules of the elements exist, which in some cases consist of one atom, but in others of two or more atoms.

From the experiments of Avogadro it is proved that the relation between the weight of a given volume of hydrogen and the weights of the same volumes of the elementary gases is, in most instances, the same as the numbers which express their atomic weights, and from this is deduced his hypothesis that equal volumes of all gases at the same temperature and pressure contain an equal number of molecules.

Acting on this hypothesis it is possible to determine the molecular weight of any gas by comparing the weight of a given volume of it with that of the same volume of hydrogen at the same temperature and pressure. The numbers thus obtained give the vapour density of the gas, and the molecular weight is equal to twice the vapour density.

In addition to the laws of chemical combination by weight mentioned in Chapter I., another law of equal importance has

now been established, namely, the law of combination of gases by volume. "The volumes of gases which enter into a chemical change bear a simple relation to one another and to the volumes of gases produced by the change, all volumes being measured at the same temperature and pressure."

CHAPTER VI

Sulphur. Symbol S. Atomic Weight, 32.

THE element sulphur is a lemon yellow solid formerly known as brimstone. It is found native in the volcanic districts of Italy and in the island of Sicily, where it occurs partly in transparent yellow crystals and partly in opaque crystalline masses; small quantities are also found in Mexico and New Zealand. Compounds of sulphur occur in nature in very large quantities, two classes of which are found: (1) sulphides, in which the sulphur is combined with a metal only, such as iron pyrites, FeS_2 ; (2) sulphates, which are composed of sulphur combined with a metal and oxygen, such as gypsum, $CaSO_4 + 2H_2O$. Small quantities of sulphur are associated with coal always in a state of combination. It exists partly as iron pyrites, partly as gypsum, and partly combined with the coal itself, which portion is often known as the organic sulphur.

Iron pyrites (iron disulphide), FeS_2 , is found in the coal measures, sometimes in the form of small balls or nodules having a pale yellow or grey colour, sometimes in bright golden yellow bands irregularly distributed throughout the coal seam and the bind, and sometimes distributed throughout the mass of coal in small particles. The brilliant colour of the yellow variety has given rise to the name of "brasses" amongst miners.

Iron pyrites in the mass is exceedingly hard, and gives out sparks when struck with a pick. It undergoes oxidation in moist air, forming ferrous sulphate (sulphate of iron), $FeSO_4$, and sulphuric acid, H_2SO_4 ,

$$2 \text{FeS}_2 + 7 \text{O}_2 + 2 \text{H}_2 \text{O} = 2 \text{FeSO}_4 + 2 \text{H}_2 \text{SO}_4$$

but it remains unchanged at ordinary temperatures in dry air or in water free from air. The oxidation of iron pyrites is accelerated by high temperature, especially when it is in a finely

G

divided state, consequently in mines where the temperature is high and the atmosphere moist a considerable amount of oxidation takes place; in these pits the waters become charged with sulphuric acid, whilst white feathery crystals of ferrous sulphate are found on the walls of the roadways. The oxidation of iron pyrites is accompanied by a considerable increase in volume, which causes the coal to break up into small slack. When heated in air it decomposes, sulphur distils and takes fire; if heated in contact with wood, coal, or similar organic bodies containing hydrogen, sulphuretted hydrogen is produced.

Gypsum (hydrated calcium sulphate), $CaSO_4 + 2H_2O$, is a white opaque substance which is sometimes found in the coal measures in distinct bands in conjunction with bands of iron pyrites, but more generally in very thin plates, which are seen when the coal is divided along its line of cleavage. Occasionally large transparent crystals of calcium sulphate, known as *selenite*, are found in the coal measures. When gypsum is heated it loses its water of crystallisation, and is converted into anhydrous calcium sulphate, CaSO₄, and if it is heated at a temperature of 80° C. to 90° C., a cream-coloured powder, called plaster of Paris, is produced, which is used for making plaster casts, owing to its property of forming a hard compact mass when treated with water.

Organic Sulphur.—This is the name given to the sulphur in the coal which is not present either as iron pyrites or gypsum. This sulphur is supposed to be combined with the various elements which enter into the composition of coal, and it is, therefore, looked upon as a constituent of the coal itself, which cannot be separated by any mechanical means. The proportion of the total sulphur which exists as organic sulphur varies very considerably in different coals from $2\frac{1}{2}$ per cent. up to 75 per cent.

Another sulphur compound which is met with in coal mines is sulphuretted hydrogen, which is found in some mine waters, and occasionally in a mine's atmosphere.

Preparation.—Sulphur is usually prepared from the native substance found in Sicily and Italy by heating the ore in piles, when the sulphur melts and is allowed to run into vessels, where it is collected. The crude material thus obtained is subjected to a process of distillation in which the crude sulphur is boiled in an iron retort, from which the vapours are conducted into a large brickwork chamber. At first, whilst the chamber is cold, the

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vapours at once condense into a light yellow crystalline powder, which form the *flowers of sulphur* of commerce. After a time the chamber becomes heated above the melting-point of sulphur, and the vapour then condenses to a liquid, which is drawn off from time to time into wooden moulds and cast into sticks, which are known as *roll sulphur* or *brimstone*. Sulphur is also obtained by the distillation of iron pyrites, and in small quantities as a by-product in the manufacture of coal-gas.

Properties.—Sulphur exists in several allotropic modifications, some of which are crystalline, whilst others are amorphous (non-crystalline). The chief of these modifications are (1) rhombic or alpha sulphur, (2) prismatic or beta sulphur, (3) plastic or gamma sulphur. The alpha and beta modifications are crystalline; the gamma modification is amorphous.

Alpha Sulphur.-Sulphur is obtained in rhombic crystals

when a solution of sulphur in carbon disulphide is allowed to evaporate slowly (Fig. 38). Native sulphur is always found crystallised in this form. The specific gravity of this form of sulphur is 2.05. It is insoluble in water, slightly soluble in alcohol and ether, and readily soluble in carbon disulphide, benzene, and turpentine.

Beta Sulphur.—This modification is obtained by melting sulphur and allowing it to cool at the ordinary temperature until a crust is formed on the

surface. On breaking the crust and pouring out the still liquid portion of sulphur the sides of the vessel are found to be covered

> with a mass of long, transparent, needle-shaped crystals (Fig. 39), having a specific gravity of 1.96 and melting at 120° C. Beta sulphur is soluble in carbon disulphide, and from the solution crystals of alpha sulphur are deposited on evaporation.

> Gamma Sulphur.—When sulphur is melted it forms a pale yellow mobile liquid, the colour of which gradually changes to a dark red as the temperature rises to 250° C., and the liquid

becomes more and more viscous until finally it becomes so thick that it can only be poured with difficulty; its colour at the same time becomes darker. On raising the temperature still higher the liquid becomes less viscous, although its dark colour





remains; if the liquid be now rapidly cooled by pouring it into cold water a semi-transparent elastic mass is obtained, which

can be drawn out into long threads, and is known as plastic or gamma sulphur (Fig. 40). This modification has a specific gravity of 1.91 to 1.96.

The beta and gamma varieties are unstable; in course of time they gradually change into the alpha variety, becoming opaque, whilst the elastic gamma sulphur becomes hard and brittle.

Sulphur readily melts at about 115° C., and boils at a temperature of 440° C., giving off a deep red vapour.

Sulphur readily combines directly with a large number of elements. It takes fire, and burns

in air or oxygen with a pale blue flame, forming sulphur dioxide, $S + O_2 = SO_2$. When hydrogen is passed through boiling sulphur the two elements combined together form sulphuretted hydrogen, $H_2 + S = H_2S$. Carbon and sulphur when heated together combine and form carbon disulphide, $C + S_2 = CS_2$. Most metals form metallic sulphides when heated with sulphur; for example, when iron and sulphur are heated together, ferrous sulphide (sulphide of iron) is formed, Fe + S = FeS.

Sulphuretted Hydrogen (Hydrogen Monosulphide). Symbol H_oS. M.W. 34.

Two compounds of sulphur and hydrogen are known, the more important of which and the only one of interest to the mining student is sulphuretted hydrogen. This substance is found in nature in volcanic gases and in certain mineral waters,

such as those of Harrogate. It is produced by the putrefactive decomposition of various animal and vegetable substances which contain sulphur, and the disagreeable odour of rotten eggs is partly due to the formation of this gas.

Preparation. — Sulphuretted hydrogen is formed when hydrogen gas is passed through boiling sulphur, or when sulphur vapour is burnt in hydrogen. It is usually prepared by treating certain metallic sulphides with





dilute acids. Ferrous sulphide (sulphide of iron) is generally used for this purpose; it gives rise to the formation of



FIG. 40.

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sulphuretted hydrogen if treated with difute sulphuric or hydrochloric acid (Fig. 41).

$\operatorname{FeS} + \operatorname{H_2SO_4} = \operatorname{H_2S} + \operatorname{FeSO_4}$: $\operatorname{FeS} + 2\operatorname{HCl} = \operatorname{H_2S} + \operatorname{FeCl_2}$.

The gas obtained by this method always contains small quantities of free hydrogen, because ferrous sulphide is artificially prepared by melting iron and sulphur together, and always contains particles of metallic iron. To obtain the pure gas antimony sulphide is treated with warm hydrochloric acid,

 $Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3$.

Physical Properties.—Sulphuretted hydrogen is a colourless gas, possessing a sweetish taste and a disagreeable fortid odour, resembling that of rotten eggs. It is heavier than air, and its specific gravity equals 1.1781. Sulphuretted hydrogen is very soluble in water, one volume of water absorbing about three volumes of the gas at the ordinary temperature; the gas imparts its own peculiar odour to the solution. Under a pressure of about 17 atmospheres sulphuretted hydrogen gas is condensed to a colourless liquid, which freezes at -80° C. to an ice-like solid.

Chemical Properties .- The gas takes fire at a very low temperature in air or oxygen, burning with a pale blue flame, forming sulphur dioxide and water, $2H_0S + 3O_2 = 2SO_2 + 2H_2O$. During the combustion a portion of the gas is decomposed into hydrogen and sulphur, the former burning to water, whilst the latter is deposited as a yellow incrustation on the sides of the vessel containing the gas. A mixture of 2 volumes of sulphuretted hydrogen and 3 volumes of oxygen explodes violently when ignited by an electric spark. On exposure to the air a solution of the gas in water becomes milky owing to the oxidation of the gas, the hydrogen combining with the oxygen of the air to form water, whilst sulphur separates out. It is a powerful poison, producing headache, smarting of the eyes, and eventually insensibility and asphyxia. According to Lehmann, from 0.05 to 0.07 per cent. will produce serious symptoms, if not death, in man after exposure for about an hour or more. Smaller quantities will prove fatal to dogs and cats. According to Dr. Haldane, accidents from sulphuretted hydrogen occur with great suddenness, and death often occurs after men, unconscious from the action of sulphuretted hydrogen, have been rescued and brought into fresh air. The gas is apparently much

more poisonous than is generally supposed, and great caution is necessary in approaching an atmosphere in which its presence is suspected. For further particulars of the poisonous action of sulphuretted hydrogen, the student should consult Le Neve Foster and Haldane's book on "The Investigation of Mine Air."

Sulphuretted hydrogen readily interacts with metals to form sulphides, many of which are produced when the metals are brought in contact with the gas. For instance, a silver coin at once turns black in the presence of sulphuretted hydrogen, and copper is similarly affected. The sulphides of metals are usually obtained either by passing sulphuretted hydrogen gas through a solution of a metallic salt or by adding a solution of the gas in water. Many sulphides are insoluble in water, and some in hydrochloric acid. Amongst the metallic sulphides insoluble in hydrochloric acid are those of copper, lead, and silver, and when solutions of the salts of these metals are treated with sulphuretted hydrogen, precipitates of the sulphides of these metals are formed according to the following equations:—

(1) $CuSO_4 + H_2S = CuS + H_2SO_4$

(2)
$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$$

(3)
$$2 \text{AgNO}_3 + \text{H}_2 \text{S} = \text{Ag}_2 \text{S} + 2 \text{HNO}_3$$

The sulphides of those metals which are soluble in acids but insoluble in water can be precipitated by adding ammonia to solutions of their salts before adding the sulphuretted hydrogen. For example, if sulphuretted hydrogen be added to ferrous sulphate solution no precipitate is obtained, but if ammonia be first added to the solution, on adding the sulphuretted hydrogen a black precipitate of ferrous sulphide is produced—

 $\operatorname{FeSO}_4 + \operatorname{H}_2 S + 2NH_4 HO = \operatorname{FeS} + (NH_4)_2 SO_4 + 2H_2O.$

The formation of insoluble metallic sulphides affords a ready and sure method for the detection of the gas in the atmosphere of a mine. This is best carried out by soaking a piece of white blotting paper in a solution of lead acetate and hanging it, whilst moist, in a suspected atmosphere. If sulphuretted hydrogen be present the paper will turn brown or black according to the quantity. An almost sure sign of the presence of sulphuretted hydrogen is the tarnishing of silver watch cases and chains, also of the brass work of lamps carried by miners; this is due to the formation of silver and copper sulphides. If the presence of sulphuretted hydrogen be suspected in water, add a few drops of a solution of lead acetate or of silver nitrate; a black precipitate will be produced if there is any of the gas present in the water.

The odour of the gas is often a useful indication of its presence, but this cannot always be relied on as a certain test, for Dr. Haldane, in his book on "The Investigation of Mine Air," already referred to, states: "I have myself met with gas coming from coal which had spontaneously heated, which at once blackened lead paper, but in which I was unable at the time to recognise the specific smell of sulphuretted hydrogen."¹

The existence of sulphuretted hydrogen in a coal mine may be due to various causes : (1) It is often found in stagnant waters, such as those which collect in the sump or behind dams and stoppings. In these instances it is probably formed by the decay of animal excreta, and by the reducing action of bacteria and decaying animal and vegetable matter on sulphates in the water. It is possible, however, that in some instances the sulphuretted hydrogen may be carried into the mine in the waters which flow into it, which have, in their course through the earth's crust, come in contact with a natural source of the gas, and dissolved it.

(2) The gas is always found when coal is heating previous to an outbreak of an underground fire, either in the gob or coal. In this case its formation is due to the decomposition of the coal, for when coal is distilled sulphuretted hydrogen is always found amongst the products of distillation. It is also formed when pyrites is heated in contact with coal or wood or other organic substances containing hydrogen.

(3) Another source of the gas is the use of gunpowder for blasting, as it occurs in small quantities in gunpowder smoke. When the cheaper forms of blasting powder are used the odour of sulphuretted hydrogen is easily recognisable in the atmosphere after blasting operations have been carried on.

(4) Some authorities state that this gas is formed through the action of pit waters containing acid on sulphides. This will doubtless be the case if such waters come in contact with easily decomposable sulphides, but no sulphuretted hydrogen will be produced by the action of these waters on iron pyrites, which

¹ "Investigation of Mine Air," p. 150.

does not yield sulphuretted hydrogen even when treated with the strongest acids.

Oxides of Sulphur.

Sulphur combines with oxygen in two proportions, forming the two oxides, sulphur dioxide and sulphur trioxide.

Sulphur Dioxide. Symbol SO₂. M.W. 64.

When sulphur burns in air a gas having a highly characteristic and suffocating odour is produced; this gas is known as sulphur dioxide. It is found amongst the gases which are produced when coal burns, and therefore it is found in the atmosphere of a mine during an underground fire. Large quantities of this gas are produced in a burning spoil heap in which sulphur is distilled from the pyrites in the interior of the heap, and finds its way to the surface, where it takes fire and burns, producing sulphur dioxide.

Preparation.—This gas is formed not only by the combustion of sulphur in air or oxygen, but also when certain metals, such as copper, mercury, silver, &c., are treated with boiling concentrated sulphuric acid, and for laboratory purposes it is prepared by heating copper with strong sulphuric acid, when the gas is formed according to the following interaction :—

$\mathrm{Cu} + 2\mathrm{H}_2\mathrm{SO}_4 = \mathrm{CuSO}_4 + 2\mathrm{H}_2\mathrm{O} + \mathrm{SO}_2.$

Physical Properties.—Sulphur dioxide is a colourless gas, possessing the well-known suffocating odour of burning sulphur. It is heavier than air, its specific gravity is 2.2639. The gas is easily liquefied by pressure or by cooling to a temperature of about -10° C. It is very soluble in water, 1 volume of water dissolving about 79.75 volumes of the gas at 0° C. and about 39 volumes at 20° C.

Chemical Properties.—Sulphur dioxide does not burn, and it does not support the combustion of a candle or other bodies containing carbon that are combustible in air. It cannot be breathed; it produces a particularly irritating effect on the membranes of the throat and lungs, even when small quantities are present in the air. It readily undergoes oxidation, forming sulphuric acid; this takes place in contact with air and moisture, $SO_2 + H_2O + O = H_2SO_4$, and consequently sulphuric

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acid is found in the atmosphere wherever the combustion of coal and coal-gas is carried on. It is a powerful reducing agent and antiseptic. The solution of the gas has a strong acid reaction, turning blue litmus paper red, whereas the dry gas does not. The solution in water is said to contain sulphurous acid, H_2SO_3 , $H_2O + SO_2 = H_2SO_3$. This acid has not been isolated, but it forms a large number of salts known as *sulphites*, which may be obtained by passing sulphur dioxide into water in which metallic hydroxides or carbonates are dissolved or suspended—

 $2NaHO + SO_2 = Na_2SO_3 + H_2O$. $CaCO_3 + SO_2 = CaSO_3 + CO_2$.

There are two classes of sulphites: (1) Acid or hydrogen sulphites; (2) normal sulphites.

| | | Acid Sulphites. | Normal Sulphites. |
|-----------|---|-----------------|-------------------|
| Sodium | | NaHSO3 | Na_2SO_3 |
| Potassium | ÷ | KHSO3 | $K_2 SO_3$ |

All sulphites are decomposed by dilute acids with evolution of sulphur dioxide : $Na_2SO_8 + 2HCl = 2NaCl + H_2O + SO_2$.

Sulphur Trioxide. Symbol SO₃. M.W. 80.

Sulphur trioxide is a white crystalline solid formed when a mixture of sulphur dioxide and oxygen is passed over heated spongy platinum, $SO_2 + O = SO_3$.

When ferrous sulphate is distilled fuming sulphuric acid is obtained, which consists of a solution of pyrosulphuric acid, $H_{2}S_{2}O_{7}$, in sulphuric acid. On gently heating the fuming acid in a retort, sulphur trioxide distils over and condenses in the form of long transparent needles.

The chief interest attaching to this oxide is that it combines with water and forms sulphuric acid, $SO_8 + H_2O = H_2SO_4$.

Sulphuric Acid. Symbol H₂SO₄. M.W. 98.

Sulphuric acid has been known from very early times, and owing to the fact that it was originally obtained by distilling green vitriol or ferrous sulphate, it was called *oil of vitriol*, a name by which it is often known at the present day. It is manufactured in very large quantities by oxidising sulphur dioxide in presence of steam through the agency of nitrogen

trioxide and peroxide, $SO_2 + H_2O + N_2O_3 = H_2SO_4 + 2NO$, or $SO_2 + H_2O + NO_2 = H_2SO_4 + NO$. The operation is carried out in a large leaden chamber into which a mixture of these gases is conducted, when the interaction takes place and sulphuric acid, diluted with water, collects on the floor of the chamber. The dilute acid is syphoned off and subjected to a process of concentration by heat in glass or platinum vessels, when a heavy oily liquid, consisting of more or less impure sulphuric acid, is obtained, which may be further purified by distillation.

Sulphuric acid is a heavy oily liquid which, when pure, has a specific gravity of 1.834 at 24° C. The commercial liquid, however, is never quite free from water, the purest acid containing about 2 per cent. which cannot be removed by distillation. The specific gravity of sulphuric acid varies with the quantity of water it contains, and tables have been compiled showing the percentage of anhydrous sulphuric acid contained in the acid according to its specific gravity.

Sulphuric acid has a great affinity for water, and a considerable evolution of heat takes place when the two liquids are mixed. Owing to this property concentrated sulphuric acid is largely used for the purpose of drying gases and other substances. It decomposes many organic substances, such as oxalic acid, which is converted into carbon dioxide, carbon monoxide, and water; and alcohol, which is transformed into olefiant gas and water. Wood, sugar, and similar vegetable substances are charred by sulphuric acid. It rapidly attacks flesh and other animal matters. When dropped on the skin it produces a sore which heals with difficulty.

Cold concentrated sulphuric acid does not attack many metals, but the hot acid dissolves such metals as copper, mercury, tin, lead, silver, &c.; with the evolution of sulphur dioxide thus:—

$$\begin{array}{l} \mathrm{Cu}+2\mathrm{H}_{2}\mathrm{SO}_{4}=\mathrm{Cu}\mathrm{SO}_{4}+\mathrm{SO}_{2}+2\mathrm{H}_{2}\mathrm{O}\\ \mathrm{Ag}_{2}+2\mathrm{H}_{2}\mathrm{SO}_{4}=\mathrm{Ag}_{2}\mathrm{SO}_{4}+\mathrm{SO}_{2}+2\mathrm{H}_{2}\mathrm{O} \end{array}$$

Gold and platinum are unattacked even by boiling sulphuric acid. Certain easily oxidisable metals, such as zinc, iron, aluminium, magnesium, &c., are dissolved by the dilute acid, with evolution of hydrogen :---

> $Zn + H_2SO_4 = ZnSO_4 + H_2$ Fe + H₂SO₄ = FeSO₄ + H₂

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The acid readily unites with bases, forming the salts of sulphuric acid called sulphates; for instance, when ammonia is passed into sulphuric acid ammonium sulphate is obtained, $2NH_8 + H_2SO_4 = (NH_4)_2SO_4$.

This is carried out on a large scale in the manufacture of ammonium sulphate from the ammonia liquor obtained in the manufacture of coke with recovery of by-products.

Sulphates.—Sulphuric acid forms two classes of salts: (1) acid salts; (2) normal salts.

Acid Salts.

| Sodium hydrogen sulphate | | NaHSO4 |
|-----------------------------|--|--------|
| Potassium hydrogen sulphate | | KHSO4 |

Normal Salts.

| Sodium sulphate. | | Na_2SO_4 |
|--------------------|--|-------------------|
| Potassium sulphate | | $K_2 SO_4$ |
| Ammonium sulphate | | $(NH_4)_2SO_4$ |
| Barium sulphate . | | BaSO ₄ |
| Calcium sulphate | | $CaSO_4$ |
| Copper sulphate . | | $CuSO_4$ |
| Ferrous sulphate | | FeSO4 |
| _ | | - |

Most sulphates are soluble in water and crystallise well. They are usually prepared by dissolving the metal, or the oxide or carbonate of the metal, in dilute sulphuric acid. The sulphates of calcium, barium, strontium, and lead are insoluble in water; barium sulphate is the most insoluble sulphate known, and this fact is made use of for the detection and estimation of sulphuric acid.

Many sulphates occur in nature and some are well-known important minerals, such as: gypsum, $CaSO_4 + 2H_2O$; heavy spar, $BaSO_4$; Epsom salts, $MgSO_4 + 7H_2O$; Thenardite, Na_2SO_4 .

Sulphuric acid is largely used in the preparation of other acids, and also for the decomposition of substances where the application of high temperature is necessary. Free sulphuric acid is found in the waters of certain volcanic districts, and, as has already been stated, in the waters of coal mines where oxidation of iron pyrites is going on.

CHAPTER VII

Carbon. Symbol C. Atomic weight, 12.

THE element carbon is the most important of all those that enter into the composition of coal. It is one of the most widely distributed elements in nature, being found in the animal, vegetable, and mineral kingdoms. It is a constituent of flesh, bones. and all products of the animal body; in the vegetable kingdom it occurs as a constituent of all plants and vegetable products. In the mineral kingdom it occurs as carbon itself in the form of the diamond and graphite, whilst in combination with other elements, gaseous, liquid, and solid compounds of carbon are found. Amongst the gaseous compounds of carbon found in nature are: (1) carbon dioxide; (2) marsh gas; (3) olefiant gas. Carbon dioxide exists in the atmosphere, in all natural waters, and in certain districts escapes in large quantities from the earth's crust. Marsh gas, or light carburetted hydrogen, escapes in bubbles from the bottom of stagnant pools, and issues in large quantities from the exposed faces of the coal, whilst it is evolved together with other hydro-carbons from petroleum and paraffin-oil wells. Olefiant gas, or heavy carburetted hydrogen. is said to have been found amongst the gases escaping from the coal face.

The liquid compounds of carbon that are found in nature are known as paraffin and petroleum oils, which consist of mixtures of various compounds of carbon and hydrogen.

Solid compounds, containing carbon combined with oxygen and a metal, are found as minerals in the earth's crust; these bodies are known as carbonates, and amongst the carbonates so found are calcium carbonate, barium carbonate, magnesium carbonate, zinc carbonate, ferrous carbonate (carbonate of iron). Of all the various carbonates that exist in nature those of iron, magnesium, and calcium are the most abundant. Carbonate of iron, or ferrous carbonate, constitutes the iron-stone ore of Staffordshire and the blackband ore of Scotland.

Magnesium carbonate forms the mineral magnesite, and a double carbonate of magnesium and calcium is known as dolomite and magnesium limestone.

Calcium carbonate is very widely distributed throughout the earth in a variety of forms; chalk, limestone, and marble are different varieties of this substance, and very large deposits of these bodies are found in different parts of the globe. Calcspar and arragonite are other forms of calcium carbonate, small deposits of which exist. Calcium carbonate occurs in the animal as well as in the mineral kingdom. The shells of all birds' eggs, and of certain shellfish known as mollusca, contain calcium carbonate.

Carbon is found in coal, which, according to the variety, contains from 69 to 95 per cent. of this element, also in bitumen, of which various liquid and solid forms are known. Amber and other fossil resins also contain carbon.

The element carbon is known in a variety of forms. Two of these, the diamond and the graphite, occur in the earth's crust, and are known as natural forms of carbon; the others are obtained by special manufacturing processes, and are called artificial forms.

Natural Forms of Carbon.

The Diamond.—This form of natural carbon is found in India, Brazil, Borneo, South Africa, and other localities. It occurs chiefly in alluvial deposits in the neighbourhood of a micaceous rock called itacolumite. It is usually found in transparent, colourless crystals, though not infrequently yellow, red, green, or brown diamonds occur; a black, opaque, porous form of diamond is also found, which is called carbonado.

The diamond is the purest form of carbon known; when colourless it leaves, after combustion, only a small amount of mineral ash. It is one of the hardest substances known, and is capable of scratching and cutting the hardest of rocks. It is largely used for cutting glass, for polishing gems, and in rock drills, whilst the transparent forms are prized as gems on account of their great brilliancy, which is due to the very high

refractive index which the diamond possesses. The specific gravity of the diamond is 3.6. The diamond is combustible, and when strongly heated in oxygen gas takes fire and burns brilliantly, leaving only a small quantity of ash which amounts to from 0.05 to 0.06 per cent. Heated in the air in the intense heat of the electric arc it swells up and is converted into a black opaque mass of coke, but does not burn.

Several attempts have been made to prepare the diamond artificially. Many of these have been successful in producing minute microscopic crystals possessing the hardness so characteristic of the diamond and having the appearance of a black powder. When viewed under a microscope, the crystals appear transparent.

Graphite.—The second form of natural carbon differs entirely in its appearance and physical properties from the diamond. It is a soft, grey, opaque substance found associated with granite, gneiss, and other igneous rocks. It was formerly found at Borrowdale, in Cumberland, but these mines are now exhausted. It is obtained in large quantities from the United States and California, and is also found in Germany, Bohemia, Southern Siberia, and Cevlon. It usually occurs in compact or granular masses, but is occasionally found in small six-sided tables. It has a steel-grey colour and a soapy touch, and is so soft that it leaves a black mark when rubbed on paper; on account of this it has earned the name of black lead and is largely used in the manufacture of black lead pencils. It is also used for the manufacture of plumbago crucibles and for coating iron surfaces to prevent them from rusting, as in black-leading grates; it serves as a lubricant for coating the surfaces of those parts of machinery which rapidly revolve over one another. It is a good conductor of electricity and is largely used in electrotyping. Its specific gravity is about 2.2. An artificial form of graphite is obtained in the manufacture of grey pig iron. If this form of cast iron be dissolved in hydrochloric acid a black, insoluble residue remains, which contains hard, six-sided plates of graphitic carbon.

Graphite burns, with the formation of carbon dioxide, with difficulty when heated in the air, but more readily when heated in oxygen; a small quantity of mineral ash is left behind. When finely powdered graphite is heated with sulphuric acid and potassium chlorate it is converted into a crystalline

substance known as graphitic acid, having the composition $C_{11}H_4O_5$, which decomposes on heating to redness, with the formation of finely divided graphite. Graphite is insoluble in all ordinary solvents.

Artificial Forms of Carbon.

In addition to the natural forms of carbon, various modifications of this element are obtained by the decomposition of organic substances rich in carbon. When such bodies are heated out of contact with the air, they undergo decomposition with the formation of certain volatile substances which escape, and a black non-volatile residue of carbon. Many of these artificial forms of carbon exist, of which the following are the most important: (1) wood charcoal, (2) animal charcoal, (3) coke, (4) gas carbon, (5) lamp black.

These forms of artificial carbon possess no crystalline structure, and may therefore be classified as the amorphous forms of carbon.

Wood Charcoal, or, as it is often called, charcoal, is prepared by heating wood out of contact with the air. It has been manufactured from very early times, and the old process of charcoalburning, which is carried on even at the present day, consists in allowing heaps of wood covered with earth or sods to slowly burn with a limited supply of air. The heap, also known as a meiler, is constructed by erecting at the centre a quandel, which consists of a stake, or two or three stakes, of wood driven into the ground, round which billets of wood are arranged either horizontally or vertically, extending to a radius of from 5 to 30 feet, and built up so as to form a conical heap. A channel is left at the bottom for the admission of air, and the whole is covered over with a layer of earth, sods, or moist charcoal dust. The heap is lighted at the bottom of the quandel by introducing live coals into the air channel. The lower layers of wood ignite, and by carefully regulating the air the combustion proceeds slowly towards the top of the heap; large amounts of volatile matter escape, and eventually a red-hot mass of wood charcoal This is extinguished by embedding it in sand or by remains. drenching it with water. The time required for charring varies according to the size of the meiler, and may take anything from six days to five or six weeks. During the process constant

attention is necessary, as the volatile products are liable to burst through the covering of the meiler, and when this takes place it is necessary to patch up the covering with fresh material. In some districts the wood is packed in rectangular piles, which are surrounded by walls made by driving stakes into the ground and building up against them planks of wood.

When wood is decomposed by heat certain valuable products, such as wood spirit, pyroligneous acid, and tar, are produced. With the object of recovering these and of increasing the yield of charcoal the wood is distilled in iron retorts, from which the volatile products are conducted through condensing apparatus, where these volatile substances are condensed to liquids and collected, whilst the residue of charcoal remains in the retort.

The yield of charcoal in the meiler amounts to apparently from 21 to 28 per cent., and according to H. M. Pierce an increase of 30 per cent. in the yield is obtained by charring the wood in kilns entirely heated by gaseous fuel generated in separate furnaces.

A form of charcoal known as red charcoal (*charbon roux*) is an imperfectly carbonised form of charcoal, which is produced in France and Belgium. Its chief use is for the manufacture of gunpowder.

Wood charcoal is a black porous solid which usually presents the vascular structure of the wood from which it has been obtained. It floats on the surface of water owing to its porous structure, but if the air in the pores becomes replaced by water it sinks. It rapidly absorbs many times its own volume of gases and vapours; not only are the gases absorbed by the charcoal, but many of them are oxidised by the oxygen contained within its pores. In this way charcoal acts as a deodorising agent, and is useful in destroying the obnoxious gases that escape from decomposing animal matter, such as sewer and similar gases. The volumes of various gases absorbed by one volume of charcoal have been determined by various experimenters, and depend on the kind of charcoal and the The best form of absorbent charcoal appears to temperature. be that obtained from the shell of the cocoanut, one volume of which will absorb the following volumes of the various undermentioned gases measured at 0° C. and 760 millimetres pressure :---

| | Volumes. | I | Jolumes |
|------------------|----------|------------------------|----------------|
| Ammonia . | 171.7 | Phosphuretted hydrogen | 69.1 |
| Cyanogen . | 107.5 | Carbon dioxide | 67.7 |
| Nitrogen dioxide | 86.3 | Carbon monoxide . | 21.2 |
| Methyl chloride | 76.4 | Oxygen | 17.9 |
| Methyl ether . | 76.2 | Nitrogen | 15.2 |
| Ethylene . | 74.7. | Hydrogen | 4.4 |
| Nitric oxide . | 70.5 | | |

Wood charcoal will also remove colouring matters, and, to a certain extent, metallic salts from their solutions in water. Wood charcoal is by no means pure carbon; it contains oxygen, hydrogen, and a small quantity of nitrogen, in addition to its mineral constituents, or ash of the wood. The average quantity of ash in wood charcoal amounts to from 1 up to $3\frac{1}{2}$ per cent. The following table gives the composition of different wood charcoals obtained by Faisst:—

| | Beech Charcoal. | Hard Charcoal made in Iron Cylinders. | Light Charcoal from Wood Gas-works. |
|---|---|--|---|
| Carbon Hydrogen Oxygen and nitrogen . Ash Water | 85.89 2.41 1.45 3.02 7.23 100.00 | $ \begin{array}{r} 85 \cdot 18 \\ 2 \cdot 88 \\ 3 \cdot 44 \\ 2 \cdot 46 \\ 6 \cdot 04 \\ \hline 100 \cdot 00 \\ \hline 100 \cdot 00 \\ \hline $ | 87.43 2.26 0.54 1.56 8.21 100.00 |

Animal charcoal, or bone black, is the form of charcoal obtained as a residue when bones are distilled in iron retorts for the manufacture of bone or Dippel's oil. Bones are composed of about 70 per cent. of mineral matter chiefly calcium phosphate, and about 30 per cent. of organic matter. Bone black consists of a porous mass of calcium phosphate throughout which about 10 per cent. of finely divided carbon is disseminated. Animal charcoal may be obtained from the bone black by treating it with hydrochloric acid, which dissolves the mineral matter and leaves the insoluble carbon as a fine black powder. Animal charcoal is also obtained by evaporating blood with potassium

carbonate, igniting the residue and washing the charred mass with water.

Bone black is usually produced as a hard granular substance, but animal charcoal itself is a fine black powder.

Animal charcoal possesses the property of absorbing gases and removing colouring matters and metallic salts from their solutions in water. In this respect it is much more active than wood charcoal, and large quantities are used in sugar refineries for removing the colour from the dark-brown syrup from which the white crystalline sugar is obtained. After a time the charcoal loses its property as a deodorising and decolourising agent, but this can be to a certain extent restored by washing, and heating in closed vessels.

Coke.—This is a form of impure carbon obtained by the distillation of coal; it might very properly be called **coal charcoal**. When certain coals are heated out of contact with the air, or with a limited supply of air, decomposition takes place, whereby a large quantity of volatile substances are produced and driven off, leaving behind a compact grey residue known as coke. This residue consists chiefly of carbon and the mineral constituents of the coal, together with traces of hydrogen, oxygen, and nitrogen. An idea of the composition of coke may be obtained from the following results of analyses made by the late Sir I. Lowthian Bell :—

| | I. Beehive Coke. | II. Beehive Coke. | III. By-Product Coke. |
|---|--|--|--|
| Carbon Hydrogen Oxygen & Nitrogen Sulphur Ash Moisture | $\begin{array}{c} 89.85 \\ 2.00 \\ 1.06 \\ 6.60 \\ 0.49 \end{array}$ | $\begin{array}{c} 87{\cdot}60\\ 0{\cdot}25\\ 1{\cdot}20\\ 1{\cdot}05\\ 8{\cdot}52\\ 1{\cdot}38\end{array}$ | $\begin{array}{c} 86 \cdot 36 \\ 0 \cdot 51 \\ 1 \cdot 77 \\ 1 \cdot 07 \\ 7 \cdot 94 \\ 2 \cdot 35 \end{array}$ |

Coke is a grey porous substance; it may be soft and friable, when it is chiefly used as a fuel, or hard and strong, in which form it is most valuable for metallurgical purposes. It burns

in the air without flame or smoke and with the production of high temperature. In metallurgical operations it is used partly as a fuel and partly as a reducing agent. The manufacture and properties of coke are fully described in Chapter X.

Gas Carbon.—This form of artificial carbon derives its name from the fact that it separates out on the roof of gas retorts during the distillation of coal for the manufacture of illuminating gas. It is also found as a coating on the floor and sides of the retort coke oven. Among coke burners it is often known as graphite. It is an exceedingly hard iron-grey substance, having a specific gravity of 2.4. It is a good conductor of heat and electricity, and is used in the manufacture of electric batteries and resistances, and carbons for electric arc lamps.

Lamp black is the smoke obtained when substances like tar, resin, turpentine, &c., burn in air. In its manufacture these and similar substances are burnt in a limited supply of air, and the thick black smoke produced is conducted through large chambers hung with coarse cloths on which the lamp black is deposited. It is a fine, light, black powder which usually contains a certain amount of greasy and tarry impurities. These can be removed by heating in chlorine or in covered crucibles. It is one of the purest forms of artificial carbon, and its chief uses are for the manufacture of pigments, varnishes, and printers' ink.

Carbon in all its forms is insoluble in all solvents. It combines directly with certain other elements. When heated in excess of air or oxygen it burns, forming carbon dioxide, $C + O_2 = CO_2$. If electric sparks are passed between carbon poles in an atmosphere of hydrogen, acetylene is formed, $2C + H_2 = C_2H_2$. Carbon disulphide is obtained by heating carbon and sulphur together, $C + S_2 = CS_2$. It combines with nitrogen to form cyanogen (C_2N_2) when the dry gas is passed over charcoal mixed with an alkali and heated to redness.

The heat of combustion of carbon appears to vary slightly with its form. The following results have been obtained by Favre and Silbermann when 1 gramme of carbon is burnt to carbon dioxide :—

| Diamond | | | • | 7779 | calories |
|----------|---|---|---|------|----------|
| Graphite | | | | 7796 | >> |
| Charcoal | • | • | • | 8080 | 33 |

Compounds of Carbon and Hydrogen.

Carbon forms a very large number of compounds with hydrogen, known as hydrocarbons. In this respect it differs from the other elements, which at the most form two or perhaps three hydrogen compounds. Amongst the hydrocarbons are included gases such as marsh gas, olefiant gas, and acetylene; liquids such as benzene, toluene, petroleum, and paraffin oils, and solids such as anthracene, naphthalene, and paraffin wax. The study of these bodies and the vast number of compounds derived from them belongs to that branch of chemistry known as organic chemistry. It is only necessary here to describe three hydrocarbons, namely:—

| Methane or marsh gas | | | CH_4 |
|-------------------------|--|--|-----------------|
| Ethene or olefiant gas | | | C_2H_4 |
| Ethine or acetylene gas | | | C_2H_2 |

Each one of these bodies is the first of three large and distinct series of hydrocarbons. The members of each series interact similarly with reagents under similar conditions, yielding similar derivatives. Each successive member of a series differs in composition from that of the one preceding it by the group CH_2 . Starting with marsh gas we have :—

| Methane | • | | CH_4 |
|---------|---|--|----------------------|
| Ethane | | | $C_2 \dot{H}_6$ |
| Propane | | | $\tilde{C_{3}H_{8}}$ |
| Butane | | | C_4H_{10} |
| etc. | | | 1 10 |

In a similar manner we get the following series, of which ethylene and acetylene are respectively the first members :—

| Ethene or ethylene | $C_{2}H_{4}$ | Ethine or acetylene . | C_2H_2 |
|----------------------|--------------|-------------------------|----------|
| Propene or propylene | C_3H_6 | Propine or allylene . | C_3H_4 |
| Butene or butylene | $C_{4}H_{8}$ | Butine or crotonylene | C_4H_6 |
| Pentene or amylene | C_5H_{10} | Pentine or valerylene . | C_5H_8 |
| etc. | | etc. | |

Any series of hydrocarbons or their derivatives, the successive members of which differ from one another in their composition

by the group CH_2 , is called a homologous series. Each of the above series forms a homologous series. The first is known as the paraffin series of hydrocarbons, the second the olefine series, and the third the acetylene series. On carefully examining the formulæ of the members of any one series it will be noticed that the relation between the number of hydrogen and carbon atoms in their molecules is the same for all members of the series. Thus in the paraffin series the molecule contains two more hydrogen atoms than twice the number of carbon atoms ; in the olefine series the number of hydrogen atoms is exactly twice the number of carbon atoms, and in the acetylene series it is two less than twice the number of carbon atoms.

This makes it possible to represent each series by a general or generic formula; and representing the number of carbon atoms in the molecule by n we have the general formula for the—

| Paraffin series | | | C_nH_{2n+2} |
|------------------|--|---|---------------|
| Olefine series | | • | C_nH_{2n} |
| Acetylene series | | | C_nH_{2n-2} |

Every homologous series can be represented by a generic formula, and amongst others to which reference will be made in studying coal distillation are the benzene series, C_nH_{2n-6} ; naphthalene series, C_nH_{2n-12} ; anthracene series, C_nH_{2n-18}

The hydrocarbons are divided into two divisions: (1) the fatty or alkyl series; (2) the aromatic series. The fatty or alkyl series includes the paraffin, olefine, and acetylene hydrocarbons and their derivatives. From these hydrocarbons derivatives are obtained which are found in fats and most vegetable and animal oils. The aromatic series, so called because the hydrocarbons, or their derivatives belonging to it, are found in essential oils, aromatic gums, balsams, and resins, includes the benzene, naphthalene, and anthracene series of hydrocarbon.

The fatty series of hydrocarbons and their derivatives possess certain distinctive properties, and interact with reagents in a manner characteristic of the series; and the aromatic series of hydrocarbons and their derivatives possess such properties and interact with reagents in such a manner as distinguish them from those of the alkyl series.

Methane or Marsh Gas. Symbol CH₄. M.W. 16.

This gas is known as marsh gas, and to the coal miner as light carburetted hydrogen, fire-damp, or simply gas. It is abundantly found in nature. As its name marsh gas implies, it abounds in marshy districts, and exists amongst the gases which escape from the bottom of stagnant pools. In both these cases it results from the decomposition of vegetable matter. Enormous volumes of this gas escape from petroleum springs in Russia and paraffin wells in America. It is also found in some metalliferous mines, where it may find its way into the mine's atmosphere from the bituminous shales which lie above or below the metallic veins. For instance, in many Derbyshire lead mines this gas has been found, and is derived from the Yoredale shales, which are undoubtedly bituminous; whilst in the salt mines at Stassfürt, in Prussia, and Wieliczka, in Poland, this gas arises from the bitumen which is to some extent associated with the salt.

But it is in the coal measures that this gas is chiefly met with. It continually escapes, mixed with varying quantities of carbon dioxide and nitrogen, from the exposed faces of the coal. Sometimes the gas escapes in a continuous stream with a hissing noise, thus producing what are known as blowers or singers. Occasionally the escape of gas in this way continues for years, in such quantities that it can be conducted to the surface in pipes. Not infrequently sudden outbursts of gas occur either through the floor or roof, doubtless caused by the existence, in cavities, of gas under sufficiently high pressure to break through the walls of the cavity which have become weakened through the removal of the coal. When these outbursts occur very large quantities of gas escape, fouling the air in whole districts of the mine. A water-blast accompanied by gas occurred at the Percy Main Colliery in 1840, when it was calculated that the volume of gas discharged amounted to about 13,000,000 cubic feet. In 1879 there was an outburst of gas at L'Agrappe Colliery in Belgium, and it was calculated that 80,000 cubic feet of gas per minute must have been discharged during the three hours that the outburst continued.

The gases occluded in coal are often under considerable pressure, which varies widely in the same seam. Measurements

| Colliery. | Depth from Surface. | Depth of Borehole. | Maximum Pressure per sq. in. |
|---|---|---|--|
| ¹ Bensham Seam, Boldon Colliery. ¹ Harris's Navigation Colliery } ¹ Merthyr Vale ¹ Celynen ² Strafford Main ² New Oaks, Barnsley | 711 yds. 723 yds. 1058 yds. 1480 yds. 1500 yds. | 30 ft. 26 ft. 9 in. 41 ft. 2 in. 49 ft. 9 in. 42 ft. 47 ft. 10 in. 20 ft. 3 in. 74 ft. 6 in. 74 ft. 6 in. | 461 lbs. 150 lbs. 116 lbs. 220 lbs. 129 lbs. 430 lbs. 318 lbs. 30 lbs. to 135 lbs. |

of this pressure have been made, and the following table gives a few of the more important results :---

The gases which escape naturally from the coal and surrounding strata have frequently been analysed as well as those which are extracted from the coal by placing it under a vacuum. In the following table are given some analyses. The last six examples were obtained by J. W. Thomas from blowers and boreholes in the South Wales coalfield :---

| J J J J J J J J J J J J J J J J J J J | | | | | | | |
|---------------------------------------|---------------|-----------|-------------------------|-------|--|--|--|
| Colliery. | Marsh Gas. | Nitrogen. | Carbon Di- oxide. | Air. | | | |
| Gateshead (Fivequarter Seam) . | 94·2 | | | 5·8 | | | |
| Garswood Hall | 84.16 | 2.24 | •86 | 12.64 | | | |
| | 88.86 | 2.27 | .86 | 8.01 | | | |
| 99 99 • • • • | 93.01 | 3.01 | .27 | 3.95 | | | |
| Hepburn (Banham Seam) | 86.20 | 11.90 | 1.60 | | | | |
| South Wales Colliery (Blower) . | 97.65 | 1.85 | 0.20 | | | | |
| ,, ,, (,,) . | 95.05 | 0.69 | 4·2 6 | | | | |
| ,, ,, (,,) . | 95.47 | 3.91 | 0.62 | | | | |
| ,, ,, (Borehole in the coal) | 97.31 | 2.31 | 0.38 | | | | |
| ,, ,, (,, ,,) | 96.54 | 3.02 | 0.44 | | | | |
| ,, ,, (,, ,,) | 95.42 | 3.98 | 0.60 | | | | |
| | | | | | | | |

Composition of Fire-Damp.

¹ Royal Commission on Accidents in Mines, 1886.

² Narrative of sudden outbursts of gas in collieries working the Barnsley thick coal and the Silkstone coal in the neighbourhood of Barnsley.—*Trans. of the Midland Institute of Mining, Civil, and Mechanical Engineers.*

Preparation.—Marsh gas is generally prepared by heating in an iron tube at a high temperature a mixture of fused sodium



FIG. 42.

acetate, $NaC_2H_3O_2$, and caustic soda; $NaC_2H_3O_2 + NaHO = CH_4 + Na_2CO_8$. Owing to the fusibility of the above mixture, soda lime may be used instead of caustic soda, when the gas is more easily collected. The gas is collected over water. The apparatus for the preparation of marsh gas by this method is shown in Fig. 42.

It is also prepared by the action of water or hydrochloric acid on aluminium carbide, $Al_4C_3 + 6H_2O = 2Al_2O_3 + 3CH_4$ (Fig. 43).



FIG. 43.

The above reaction is accompanied by the evolution of ammonia, which is probably produced by the action of the

water on some nitride. If hydrochloric acid is used, the ammonia is converted into ammonium chloride, and does not escape with the marsh gas. A small quantity of acetylene is also produced, probably owing to the presence of calcium carbide as an impurity in the aluminium carbide.

The gas is also obtained by passing the vapour of carbon disulphide, mixed with sulphuretted hydrogen, over red-hot copper—

$$CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4.$$

Perfectly pure marsh gas is obtained by decomposing zinc methyl, $Zn(CH_3)_{22}$, with water—

$$Zn(CH_3)_2 + 2 H_2O = Zn(HO)_2 + 2 CH_4.$$

Physical Properties.—Pure marsh gas is a colourless, tasteless, odourless gas. A distinct and characteristic odour is said to accompany fire-damp, and experienced miners are said to be able to detect the presence of fire-damp by the odour. The cause of this odour cannot, however, be due to marsh gas, but to a trace of some other substance present in the gas. Marsh gas is lighter than air; its specific gravity is 0.559. It is very sparingly soluble in water. It can be liquefied by the combined action of extreme cold and pressure.

Chemical Properties.—Marsh gas does not readily interact with reagents, such as nitric acid, sulphuric acid, or chlorine in the dark. Chlorine, however, attacks it in sunlight, sometimes with explosive violence. It burns in excess of air or oxygen with a pale blue non-luminous flame, forming carbon dioxide and water—

$$CH_4 + 2O_2 = CO_2 + 2H_2O_3$$

but if the supply of air or oxygen is limited, carbon monoxide is formed according to the following equation :---

$$2CH_4 + 3O_2 = 2CO + 4H_2O.$$

One volume of marsh gas requires 2 volumes of oxygen, or 9.52 volumes of air containing 21 per cent. of oxygen, when carbon dioxide is formed, but for the formation of carbon monoxide only one and a half volumes of oxygen, or 7.14 volumes of air, are required. The temperature of ignition of marsh gas

is from 556° to 700° C. in oxygen and from 650° to 750° C. in air. It has a higher temperature of ignition than any other gas, except cyanogen, and its ignition is not instantaneous, but requires a certain small interval of time to elapse after the application of the flame.

When marsh gas and air are mixed together in certain proportions explosion occurs on ignition. According to experiments made for the Royal Commission on Accidents in Mines, an atmosphere containing 5 to 5.5 per cent. of marsh gas (1 of CH_4 to 19–17 of air) is explosive, whilst Coquillon found that 1 of marsh gas to 16 of air, 5.9 per cent. of gas, is explosive, which has been confirmed by Wullner and Lohmann in experiments made for the Prussian Fire-damp Commission (1881 to 1887).

The violence of the explosion increases with the proportion of marsh gas until, with 1 of gas to 8.3 of air (10.3 per cent. CH₄), according to Mallard and Le Chatelier, the greatest explosive violence is obtained. Further increase in the quantity of gas causes the violence of the explosion to diminish, and when more than 1 of marsh gas to 5.25 of air, or 16 per cent. of gas, is present the mixture is inflammable but not explosive. Smaller quantities than 5 per cent. of marsh gas in the air are inflammable, and according to the Royal Commission on Accidents in Mines of 1886, 4 per cent. of marsh gas under certain conditions is dangerous. It appears probable that the scale on which experiments on the explosive properties of marsh gas are made affect the results, for whereas in a tube 1.75 inches in diameter a mixture containing 5.5 per cent. of marsh gas is not explosive, in tubes of larger diameter atmospheres containing smaller quantities of gas are able to propagate combustion.

The presence of coal dust in the atmosphere increases the sensitiveness of marsh gas to explosion. Galloway found that even 0.892 per cent. of gas was rendered explosive in presence of coal dust, whilst Abel found that 2 to 2.75 per cent. of marsh gas in a coal-dust laden atmosphere travelling at 600 feet per minute would readily explode, whilst some dusts were so sensitive that 1.5 per cent. of marsh gas was rendered explosive in currents of low velocity.

The ignition of mixtures of fire-damp and air can be effected by red-hot wires, and all mixtures containing 5.9 per cent. of the gas and upwards can be ignited, that containing 6.6 per cent. being most easily fired. The ignition takes place more

readily as the surface area of the heated wire and the velocity of the air current increase. The material also appears to influence the ease with which the gas is ignited, platinum wires firing the gas more readily than iron wires, whilst, on the other hand, wire gauze acts more easily than single wires.

Marsh gas when largely diluted with air can be breathed with impunity. It simply acts as a diluent of the oxygen, and has no definite physiological action on the human system. According to Dr. Haldane, air containing 45 per cent. of marsh gas when breathed causes slightly deeper inspirations, whilst the presence of 70 per cent. of the gas endangers life. Much caution, however, is required in entering an atmosphere highly charged with fire-damp, as, for instance, in ascending an incline to restore the ventilation, because the percentage of gas is apt to increase very rapidly, and a man may thus unconsciously enter an atmosphere in which there is not sufficient oxygen to support life, and if unconsciousness overtake him he will suffocate.

The presence of marsh gas in a mine is usually determined by its action on the flame of a safety lamp. The presence of 2 to $2\frac{1}{2}$ per cent. of marsh gas in the air causes the ordinary flame of a safety lamp to slightly elongate, whilst with larger percentages the flame "spires," as it is technically called—that is, it stretches up into the gauze of the lamp in the form of a long, thin, smoky thread of flame. The detection of marsh gas by this means will be fully described in a later chapter.

Ethene or Ethylene. Symbol C₂H₄. M.W. 28.

This gas is also known as ethylene, olefiant gas, and heavy carburetted hydrogen, and forms the first member of the olefine series of hydrocarbons. Very few instances of the occurrence of this gas in "pit gas" are recorded. Bischoff found 6.05 per cent. in the gas from the Wellesweiler Colliery and 1.90 in gas from the Gerhardt Colliery, whilst in the gas which escaped from a borehole sunk for an artesian well in the princedom of Schaumberg, in Germany, he found 16 per cent. If coal be heated in vacuo certain quantities of gas can be collected, amongst which ethene occurs.

This gas is obtained when sulphuric acid or other dehydrating agents interact with alcohol, C_2H_6O , from which the elements of water are withdrawn and the gas evolved—

$$C_2H_6O = C_2H_4 + H_2O.$$

Physical Properties.—Ethene is a colourless gas with a slight ethereal odour. It is very slightly soluble in water, but more soluble in alcohol. Its specific gravity is 0.9784. At a temperature of -100° C., and under strong pressure, it is condensed to a colourless liquid, which boils at -75° C. under a pressure of 4 atmospheres.

Chemical Properties.—Ethene burns in air or oxygen with a luminous flame. One volume of the gas requires 3 volumes of oxygen, or 14.28 volumes of air for complete combustion, when 2 volumes of carbon dioxide and 2 volumes of gaseous water are formed—

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

If the supply of oxygen is limited carbon monoxide is formed, which is produced according to the following equation—

$$C_{2}H_{4} + 2O_{2} = 2CO + 2H_{2}O.$$

One volume of the gas mixed with 3 volumes of oxygen, or 14.28 volumes of air, equal to 6.54 per cent. of the gas, forms a very powerfully explosive mixture. It is fortunate that it only occasionally occurs in pit gas, otherwise the danger arising from the presence of "gas" would be greatly increased.

Ethene, as well as all members of the olefene series of hydrocarbons, is absorbed by strong sulphuric acid, and by bromine, and by this means readily distinguished from the paraffin series of hydrocarbons which are not absorbed by these reagents.

Ethine or Acetylene. Symbol C₂H₂. M.W. 26.

This gas is one of the gases found in coal-gas, and is always formed by the incomplete combustion of other hydrocarbons. It is produced by exposing carbon to a very high temperature in an atmosphere of hydrogen, $2C + H_2 = C_2H_2$. It is prepared in large quantities by the action of water on certain metallic carbides. Calcium carbide is chiefly used for this purpose—

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

Physical Properties.—Acetylene is a colourless gas. It possesses an exceedingly unpleasant and penetrating odour, and is highly poisonous. Its specific gravity is 0.92 and it is soluble

in water, which, at the ordinary temperature, dissolves its own volume of the gas.

Chemical Properties.—Acetylene burns with an intensely bright white flame. It is acted on by fused metallic potassium forming the compounds, C_2HK and C_2K_2 , which are highly explosive black powders. When passed through an ammoniacal solution of cuprous chloride a red compound is formed, called cuprous vinyl oxide ($C_2Cu_2H_2O$). This reaction is used to indicate the presence of the gas. Silver forms a similar compound, $C_2Ag_2H_2O$; both these compounds decompose with explosive violence on heating or by percussion.

Compounds of Carbon and Nitrogen.

Cyanogen. C₂N₂. M.W. 52.

Cyanogen, a gaseous compound of carbon and nitrogen, is found among the gases that are obtained by distilling coal.

Preparation.—It is prepared by heating mercuric cyanide $Hg(CN)_2 = Hg + C_2N_2$. The gas is soluble in water, and therefore must be collected over mercury.

Physical Properties.—Cyanogen is a colourless gas possessing an odour resembling that of peach blossom. It is soluble in water and alcohol; at the ordinary temperature 1 volume of water dissolves $4\frac{1}{2}$ volumes of the gas, and 1 volume of alcohol dissolves 23 volumes. It is readily condensed by cold or pressure to a colourless liquid which is insoluble in water. The liquid boils at -21° C. and freezes at -35° C. The specific gravity of the gas is 1.806.

Chemical Properties.—Cyanogen burns in air or oxygen with a reddish violet flame. If excess of air be present, carbon dioxide and nitrogen are formed, $C_2N_2 + 2O_2 = 2CO_2 + N_2$; but if the oxygen be not in excess carbon monoxide and nitrogen are formed, $C_2N_2 + O_2 = 2CO + N_2$. In the former case 1 volume of cyanogen requires 2 volumes of oxygen, or 9.52 volumes of air, and in the latter case 1 volume of oxygen, or 4.76 volumes of air. When the gas is mixed with oxygen or air in these proportions the mixture explodes on ignition. Exposed to the influence of electric sparks, cyanogen decomposes into carbon and nitrogen, $C_2N_2 = 2C + N_2$. It is a poisonous gas. When passed over heated potassium it unites directly with the metal, forming potassium cyanide, $2K + C_2N_2 = 2KCN$.

Cyanogen gives rise to a very large number of derivatives, of which the following are of importance to the mining student, namely the cyanides, thiocyanates, and compounds of ferrocyanogen.

Cyanides.

The cyanides are a group of metallic salts of hydrocyanic acid.

Hydrocyanic Acid. HCN. M.W. 27.

This acid is commonly known as prussic acid.

Preparation. — Hydrocyanic acid is prepared by passing sulphuretted hydrogen over dry mercuric cyanide heated at 30° C., $Hg(CN)_2 + H_2S = HgS + 2HCN$. By this means the anhydrous acid is obtained.

An aqueous solution of the acid is usually prepared by distilling potassium ferrocyanide with dilute sulphuric acid, $2K_4FeC_6N_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe_3C_6N_6 + 6HCN$.

Physical Properties.—The anhydrous acid is a colourless liquid possessing the characteristic odour of oil of bitter almonds. The liquid freezes at -18° C. and boils at 26.5° C., and forms a colourless vapour having the specific gravity 0.947. Hydrocyanic acid is very soluble in water.

Chemical Properties.—Hydrocyanic acid is inflammable; it burns with a violet flame forming carbon dioxide, water, and nitrogen, $2\text{HCN} + 50 = \text{H}_2\text{O} + 2\text{CO}_2 = \text{N}_2$. Its aqueous solution decomposes on exposure to light, and concentrated acids as well as boiling alkalies convert it into ammonia and formic acid, $\text{HCN} + \text{H}_2\text{O} = \text{NH}_3 + \text{CH}_2\text{O}_2$. Hydrocyanic acid is one of the most powerful of poisons.

It is a weak acid and unites with bases to form a group of salts called cyanides, the most important of which are potassium cyanide KCN, and sodium cyanide NaCN, which are used in the recovery of gold by the cyanide process. They are white solids, which are soluble in water, and are just as poisonous as the acid. Ammonium cyanide $\rm NH_4CN$ occurs in small quantities in the ammoniacal liquor obtained in the recovery of by-products from the coking of coal. When potassium or sodium cyanide is fused with sulphur, potassium, or sodium thiocyanate is formed.

Thiocyanates.

The thiocyanates are derived from thiocyanic acid.

Thiocyanic Acid. HCNS. M.W. 59.

Thiocyanic acid, also known as sulphocyanic acid, is only known in the anhydrous state; in contact with water it decomposes. It yields an important group of salts called thiocyanates, of which potassium thiocyanate KCNS and ammonium thiocyanate (NH_4)CNS are important. The latter is found in certain quantities in the ammonia liquor, and also in the spent oxide from oxide of iron purifiers. See Chapter XI.

Compounds of Ferrocyanogen.

No simple cyanide of iron is known, but when potassium carbonate, iron, and organic nitrogenous bodies, such as horn, hide, &c., are fused together, a compound of cyanogen with iron and potassium, called potassium ferrocyanide, K_4 FeC₆N₆, is formed. This body is the potassium salt of hydro-ferrocyanic acid, H_4 FeC₆N₆.

The group $Fe(C_6N_6)$ is known as the ferrocyanogen group, and from it are derived two groups of metallic salts—(1) the ferrocyanides, salts of hydro-ferrocyanic acid, already mentioned; (2) the ferricyanides, derived from hydro-ferricyanic acid, $H_aFeC_6N_6$.

Ferrocyanides.

Potassium ferrocyanide $K_4 FeC_6 N_6$ is the most important of the ferrocyanides, because it forms the starting-point for the preparation of most of the cyanogen compounds. It is prepared as mentioned above. It forms sulphur-yellow crystals, which are soluble in water. When a solution of ferric chloride is added to a solution of potassium ferrocyanide, a deep blue precipitate is formed of ferric ferrocyanide $Fe_7C_{18}N_{18}$. This substance is known as Prussian blue. It is a deep blue powder, insoluble in water and dilute acids, but readily soluble in oxalic acid and ammonium acetate. Prussian blue is decomposed by alkalies forming soluble alkaline ferrocyanides and ferric hydroxide. Ammonium ferrocyanide $(NH_4)_4 FeC_6N_6$ is found in ammonia liquor.

Ferricyanides.

The ferricyanides are derived from the ferrocyanides by oxidation. For instance, if chlorine be passed into a solution of potassium ferrocyanide, it is converted into potassium ferricyanide, $2K_4FeC_6N_6 + C1_2 = 2K_3FeC_6N_6 + 2KC1$, which forms shining red crystals that are readily soluble in water. When a ferric salt is added to a solution of potassium ferricyanide no precipitate is formed, but if a solution of a ferrous salt, *e.g.* ferrous sulphate, be added, a deep blue precipitate of ferrous ferricyanide, or Turnbull's blue $Fe_5C_{12}N_{12}$ is obtained. Turnbull's blue is a deep blue powder, similar in appearance to Prussian blue. This reaction serves to distinguish between ferrous and ferric salts.

In the following table are given the formulæ of some of the metallic salts of the above acids of cyanogen, which serve to show the relation between the cyanides and thiocyanates, and between the ferrocyanides and the ferricyanides :---

| | Salts of— | | | | |
|---|---|--|--|--|--|
| Metal. | Hydro- cyanic Acid, HCN, or Cyanides. | Thiocyanic Acid, HCNS, or Thio- cyanates. | Hydroferro- cyanic Acid, $H_4FeC_6N_6$, or Ferro- cyanides. | Hydroferri- cyanic Acid, H ₃ FeC ₆ N ₆ , or Ferri- cyanides. | |
| Potassium . Sodium Ammonium . Silver Copper | $\begin{array}{c} \mathrm{KCN} \\ \mathrm{NaCN} \\ \mathrm{(NH_4)CN} \\ \mathrm{Ag(CN)} \\ \mathrm{Cu(CN)_2} \end{array}$ | $\begin{array}{c} \mathrm{KCNS} \\ \mathrm{NaCNS} \\ \mathrm{(NH_4)CNS} \\ \mathrm{AgCNS} \\ \mathrm{Cu_2(CNS)_2} \end{array}$ | $\begin{array}{c} {\rm K_4FeC_6N_6} \\ {\rm Na_4FeC_6N_6} \\ ({\rm NH_4})_4{\rm FeC_6N_6} \\ {\rm Ag_4FeC_6N_6} \\ {\rm Cu_2FeC_6N_6} \end{array}$ | $\begin{array}{c} {\rm K_3FeC_6N_6}\\ {\rm Na_3FeC_6N_6}\\ ({\rm NH_4})_3{\rm FeC_6N_6}\\ {\rm Ag_3FeC_6N_6}\\ {\rm Cu_3(FeC_6N_6)_2} \end{array}$ | |

Carbon Disulphide. CS₂. M.W. 76.

When sulphur vapour is passed over red-hot charcoal the two elements combine and form carbon disulphide, $C + S_2 = CS_2$. It is a very volatile liquid having, when pure, a sweetish smell. The impure liquid possesses a most offensive odour, due to the presence of other sulphur compounds of carbon. Carbon
CARBON

disulphide boils at 46° C., its vapour is exceedingly inflammable, and takes fire at a temperature of 149° C. The liquid has a specific gravity of 1.29232, is insoluble in water, and is very poisonous. It is valuable as a solvent of oils, fats, and indiarubber.

Carbon disulphide is formed during the manufacture of coke by the action of the sulphur in the pyrites and coal on the redhot carbon. In the recovery plant a large proportion of the carbon disulphide is retained as an impurity in the benzol, and some is found in the gases that pass back to the oven flues.

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CHAPTER VIII

FLAME AND THE SAFETY LAMP

IF we observe a coal fire and a coke fire the most noticeable difference between them is that the coal fire burns with a bright flame, whereas the coke fire does not. This is because, when coal is heated, a large quantity of combustible gases is produced, which take fire, producing flames, whilst under similar conditions no gas is produced from coke.

When solids and liquids burn with flame they are first converted into gas. Take the example of a candle flame; when a lighted match is brought to the wick the wax in and around the wick melts, and is converted into gas, which surrounds the wick and enters into chemical combination with the atmospheric



FIG. 44.

oxygen, producing flame. This can be illustrated by an experiment due to Faraday. If a bent tube, A (Fig. 44), has one end placed over a candle flame, B, whilst the other end passes into a flask, C, unconsumed gas and vapours will pass along the tube into the flask.

To produce a flame it is necessary to have two gases in an active state of chemical interaction which will produce sufficient heat to raise the burning gas to a temperature at which it will give

out light, or, in other words, it becomes *incandescent*. Flame then is defined as a gas raised to incandescence by chemical interaction. All flames produced in air are caused by the chemical interaction of combustible gases with the oxygen of the air.

The Structure of Flame.—Most gas flames are hollow. If a sheet of paper be pressed over a candle flame (Fig. 45) till it nearly touches the wick a charred ring is formed with a central unburnt portion.

A match may be inserted in the centre of the flame of a bunsen burner without taking fire (Fig. 46), whilst if a small heap of gunpowder on a plate has some alcohol poured over it the alcohol may be ignited and the gunpowder remains unburnt although surrounded with flame (Fig. 47). As the alcohol is consumed

Fig. 47). As the alcohol is consumed the flame becomes smaller, and eventually touches the gunpowder, which then takes fire. This hollow portion of the flame is known as the zone of noncombustion, and in the candle flame is marked by the conical blue central portion of the flame, A (Fig. 48).

Outside the zone of non-combustion the gases become mixed with a certain amount of air, but not sufficient to produce complete combustion, hence partial or incomplete combustion takes place,

often with the separation of solid particles produced by the decomposition of the burning gases. This portion of the flame is known as the zone of incomplete combustion, B (Fig. 48), and in the candle or luminous gas flame is represented by the yellow or luminous portion of the flame.

Where the flame comes into direct contact with the air complete combustion takes place, and con-

> sequently there is a mantle of flame surrounding the whole of the zone

of incomplete combustion, known as the zone of complete combustion. This is usually marked in the candle by a small conical blue portion, C (Fig. 48), at the base of the flame, where the gases as they are formed mix freely with the air and burn. Continuing from this blue cone is a thin mantle, D (Fig. 48), surrounding the flame. This mantle is so transparent as only to be visible when the luminous portion of the flame is shielded from the eye.

Luminosity of Flame.—Flames are of different degrees of brilliancy. Under ordinary circumstances the flames of hydrogen, marsh gas, alcohol, sulphur, &c., give out very



FIG. 46.



FIG. 47.

FIG. 45.

little light, whilst those of coal-gas, oil, a candle, heavy carburetted hydrogen, benzene, &c., are brightly luminous. The luminosity of flames is probably due to three causes :---

(1) To the presence of solid particles, as in the case of a candle or coal-gas flame. A cold plate placed in a candle or oil flame is at once covered with soot, caused by the deposition of particles of carbon which exist within the flame. These particles of carbon become red hot and emit light. A hydrogen or marsh gas flame may be made luminous by injecting solid particles of carbon, which, becoming white hot, emit light, and in the incandescent burner non-luminous gas flames heat a solid mantle, which becomes luminous.

(2) To the density of the burning gas. A hydrogen flame becomes luminous if the gas is burnt under pressure, although it contains no solid particles, and doubtless in the candle and oil flames very dense gases, which burn with luminous flames, are produced by incomplete combustion.

(3) To the temperature of the burning gas. In the ordinary bunsen burner the gas burns with a non-luminous flame, but if the tube through which the gas is passing be heated to redness the flame becomes luminous, but loses its luminosity if the tube be allowed to cool.

Properties of Flame.—It has been mentioned when describing combustion that to cause a body to burn with flame it must be heated to its temperature of ignition; when once the combustion is started the heat generated is sufficient to maintain that



temperature, and the flame continues so long as the supply of gas is kept up, but if the temperature of the gas falls below the temperature of ignition the flame is extinguished. A candle or gas flame can easily be extinguished by surrounding it with a cold metal. For example, place a helix of cold copper wire

over a candle flame and it will extinguish the flame, whereas if the helix is previously heated to redness it will not extinguish the flame (Fig. 49). Copper is one of the best conductors of heat, and when the cold helix is placed over the candle flame it conducts the heat away from the burning gases so rapidly that their temperature falls below their temperature of ignition, and the flame is extinguished, but when the helix has been made red hot it does not cool the gases sufficiently to lower their temperature below their temperature of ignition.

It was this property of flame that Sir Humphry Davy applied to the invention of his safety lamp. In the course of his experiments he showed that if an explosive mixture of marsh gas and air, containing 8 per cent. of marsh gas, be made to issue from a vessel through a metal tube of small diameter and of sufficient length, then on igniting the gas at the end of the tube the flame will begin to retreat towards the vessel containing the gas, but, owing to the good conducting power of the metal for heat, the flame is extinguished before reaching the other end of the tube, and no explosion occurs.

To illustrate this, a glass tube, A (Fig. 50), is closed at each end with corks through one of which a copper tube, B, passes, whilst

coal-gas can be led in at the other end through the tube, C, and ignited as it escapes at the end of the tube B. If the cork at C be removed when the glass tube A is filled with gas, the flame will continue to burn at B, whilst air will enter at the open end, C. Eventually an explosive mixture will be formed, when the flame will begin to retreat down the tube



B towards the glass tube A. If the tube B be 12 inches long and $\frac{1}{4}$ inch in diameter, inclined at the proper angle, the flame will reach A and explode the gas in A, but if the diameter of B be $\frac{1}{8}$ of an inch the flame is extinguished before it reaches the tube A, and no explosion occurs, though it can be shown by introducing a burning taper into A that it contains an explosive mixture.

Davy further showed that by increasing the number of tubes the cooling effect increases, and that if the diameter of the tubes is sufficiently small the length of the tubes can be considerably reduced. This led him to construct what he called "safety

canals," or "flame sieves." These consisted of a number of metal cylinders, $1\frac{1}{7}$ inches deep, arranged concentrically one

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FIG. 51.

within the other, so that the spaces or canals between the cylinders were from $\frac{1}{25}$ of an inch to $\frac{1}{40}$ of an inch wide (Fig. 51). By continuing his researches with the object of finding to what extent the tubes could be shortened, Davy eventually discovered that brass wire gauze $\frac{1}{200}$ of an inch thick, the apertures of which were $\frac{1}{120}$ of an inch, would act as well as his tubes. Also, that brass gauze, $\frac{1}{50}$ of an inch thick, having 100 apertures to the square inch, was

safe when cold, but would pass the flame when hot, or when subjected to quick lateral movement; whilst the same gauze with 196 apertures per square inch would pass the flame when hot, but not when cold, or when subjected to any motion. With iron-wire gauze of $\frac{1}{40}$ of an inch thick and with 240 apertures per square inch the flame passed when the gauze was strongly heated; but gauze $\frac{1}{50}$ of an inch thick, and having 576 apertures per square inch, appeared safe under all conditions.

To show this action of the gauze, hold a piece of fine wire gauze over the tube of a bunsen burner, and turn on the gas.



FIG. 52.

On bringing a light above the gauze the gas will burn on the upper side of it, but there will be no flame below it (Fig. 52); or if the light be brought to the under surface of the gauze the gas will burn at the burner, but no flame will pass to the upper surface of the gauze, though it may be shown that the gas passes through by bringing a light to the upper surface, when it will ignite.

If, however, the gauze be held in the upper part of a bunsen flame till it reaches a bright red heat and then quickly pressed down on the flame, the flame will pass through the gauze and burn on the upper surface.

An experiment similar to the one already described on p. 133, but with the copper tube replaced by a glass tube, B, about

5 of an inch in diameter, covered at the lower end with a cap of gauze, will illustrate how the gauze will stop the flame of an explosive mixture of coal-gas and air, for when the flame retreats down the small glass tube it is not extinguished, but passes down to the gauze cap, where it continues to burn, but does not pass through and explode the gas in the wide tube (Fig. 53).



FIG. 53.

The gauze acts as a large number of very minute tubes, through which the hot gases pass in thin streams. The burning gases thus come in contact with a comparatively large mass of metal, which, whilst cold, lowers their temperature below their temperature of ignition and extinguishes the flame.

Davy Lamp.—The safety lamp which ultimately resulted from these researches of Davy consists of an oil vessel, A (Fig. 54),



carrying a wick tube and pricker; on this is screwed a frame, B, consisting of four standards. supporting a cylinder of iron-wire gauze, C. having 784 meshes to the square inch. This gauze cylinder is closed at the top with a disc of gauze, and the top of the cylinder, which is liable to become very hot, is covered with a short cap of gauze, D, as an additional precaution. The lamp is provided with a suitable lock to prevent its being opened in the mine. A ring is attached to the top of the lamp, which serves for the purpose of carrying or suspending it. The FIG. 55. gauze cylinder is usually about 6 inches high



and 11 inches in diameter, a larger cylinder being objectionable, as it can enclose a larger volume of explosive gas in a state of combustion, which impairs the safety of the lamp, as the gauze would be liable to be more quickly raised to a red heat. Fig. 54 is an illustration of a very early type of Davy lamp, and Fig. 55 shows the modern type.

The ventilation of the Davy lamp is effected by the air entering at the bottom of the gauze and impinging directly on to

the flame, whilst the products of combustion rise up the middle of the gauze cylinder and escape through the upper part of the gauze (Fig. 56).

FIG. 56.

Stephenson's Lamp.-This lamp was the invention of George Stephenson, whose idea was to so control the ventilation of the lamp that an inflammable gas

should pass the flame at such a rate that it would not ignite at the flame, but becoming mixed with the products of combustion in the upper part of the lamp, would cease to be inflammable. The ultimate form taken by the Stephenson

lamp, known amongst miners as the "Geordie," is shown in Fig. 57. A is the oil vessel, on to which is screwed the frame carrying a wire-gauze cylinder, B, about 6 inches long and 21 inches in diameter. Within the gauze cylinder is a glass chimney, C, which reaches to within about 1 inch of the top of the gauze. The air is admitted through a triple row of perforations in the bottom ring of the frame and enters the lamp



FIG. 57.



FIG. 58.

below the glass and gauze; ascending it passes the flame and enters the upper portion of the lamp, where it mixes with the products of combustion and finally escapes through the gauze above the glass chimney.

Clanny Lamp.—This lamp (Fig. 58) was the invention of Dr. Clanny, and in the form now used it consists of a short glass cylinder, A, which surrounds the flame, above which is a ring, B. carried on four short standards. To this ring is attached a gauze

cylinder, C, and the standards necessary to support it. The

ventilation of this lamp is effected as follows: Air enters at the bottom of the gauze, just above the glass cylinder, and passes downwards close to the glass towards the flame, whilst the products of combustion pass up the centre of the lamp. By this method of ventilation the air on entering becomes mixed with products of combustion, and its composition is completely altered before it meets the flame.

These three lamps are the prototypes of most modern safety lamps. For their safety they all depend on the gauze which was first used by Davy and ultimately adopted in the modified forms of the Stephenson and Clanny lamps. The method of ventilation, however, is different in each, and forms so distinct a feature that it serves as a means of classifying most modern lamps.

Conditions to be Fulfilled by an Efficient Safety Lamp.

Before describing the modern safety lamp it may be as well to state the essential conditions to be fulfilled by an efficient safety lamp as set forth in the Report of the Royal Commission on Accidents in Mines, 1886. These are :---

- (1) The source of light within the lamp should be unable, under any circumstances at all likely to occur in working coal, to cause an ignition of an inflammable mixture of fire-damp and air when this is passing at a high velocity.
- (2) The lamp should yield a sufficiently bright and steady light even when exposed to a strong current of air.
- (3) It should be of simple construction.
- (4) It should admit of easy and thorough inspection when ready for use.
- (5) It should not be liable to extinction when handled with ordinary care.
- (6) It should readily give indication of the presence of abnormal quantities of gas by changes in the flame.
- (7) When in an atmosphere containing a dangerous quantity of fire-damp it should be possible to cut off the supply of air to the lamp.
- (8) The weight of the lamp should not be excessive.

If we apply these conditions to the three original types of lamps we find that they fail to fulfil the first and most impor-

tant. The experiments carried out by the Royal Commission on Accidents in Mines, 1886, the Midland Institute of Mining, Civil, and Mechanical Engineers, and others, have shown that the flame will pass through the gauze of the Davy and Clanny lamps when the current of air exceeds 5 feet per second, and though the Stephenson lamp is safer it may often cause an ex-



FIG. 59. Modern Safety Lamp.

FIG. 60. Davis's A1 Deputy's Lamp.

plosion. In the rapid ventilating currents used to-day, which may attain a speed of 20 to 25 feet, or even up to 35 feet per second, the use of these lamps becomes a source of the greatest danger. The Davy and Stephenson lamps also have a very poor illuminating power owing to the fine texture of the gauze which obstructs the light, consequently they fail to fulfil the second condition.

Great improvements have been effected in the construction of safety lamps, and there are many lamps to-day which afford considerable safety even under conditions of great danger, but it must be remembered that so long as a flame is the source of illumination, absolute safety is hardly possible.

Modern Safety Lamps.—It is beyond the scope of an elementary text-book to describe the various forms of modern lamps in use. A general description only will be given, whilst the student is referred to "Chemical Technology," by Groves and Thorp, vol. ii. "Lighting"; and to the Final Report of the Royal Commission on Accidents in Mines, 1886, for descriptions of the various modern lamps.

A modern safety lamp consists of an oil vessel fitted with either a round or flat wick-holder and pricker. On to the oil vessel screws a frame consisting of an upper and lower ring, joined together with standards about 2 inches long. In this frame is the glass cylinder, held firmly in position by a metal ring, which screws into the bottom ring of the frame, the joints between the glass and the metal being made gastight by asbestos rings. To the upper ring of the frame the gauze cylinder is fixed, and the whole is covered by a metallic shield, or bonnet, with perforations at the top to allow the products of combustion to escape, and when the air enters at the top of the glass, as in the Clanny lamp, there are admission holes at the bottom of the shield. The lamp is fitted with a locking arrangement to ensure that it shall not be opened in the pit. Many lamps have special features; for instance, the Marsaut lamp is fitted with two, and sometimes three, gauzes, whilst in the Muesseler and Thorneburry lamps there are chimneys within the gauze. Two glasses are sometimes used, one being of smaller diameter than the other, so that when they are fitted into the lamp there is an annular space between them which is generally protected at the bottom and sometimes also at the top by a ring of gauze; this is the case with the Thorneburry lamp. The Hepplewhite-Gray lamp is particularly suitable for gas testing. In this lamp the standards are hollow; through them air is admitted to the lamp, and it can be taken in either at the top or bottom of the tubes at will, which makes it possible to take in air quite close to the roof.

Many attempts have been made to devise a lamp which cannot be opened without extinguishing the flame. One type which is largely adopted is known as the Protector lamp. In this lamp the frame carrying the glass is covered at the bottom with a metal plate, A (Fig. 61), having a thick metallic tube, B, in the centre.

The wick tube, C, of the oil vessel is long and of a sufficiently small diameter to allow of it passing up through the tube B.

B C C C

FIG. 61.

The oil vessel and wick tube are usually cast in one piece, a small hole being left for filling. When the lamp is fitted together it can be lighted by electricity; when the lamp is opened by unscrewing the oil vessel, the flame is drawn through the tube B and extinguished. Lamps of this description can only be lighted after they have been fitted together ready for use. They are lighted usually by heating a platinum wire to redness by means of a current of electricity, and in order to effect ignition by this means it is necessary to use benzolene or some easily volatile paraffin as fuel.

In the Ackroyd and Best lamp an electric ignition is used, though the lamp is not of the

Protector type. This lamp is distinguished from other lamps by its magnetic lock, which acts in such a manner that the oil vessel can only be unscrewed when the lock is held down with a powerful magnet. A special feature of the type of lamp known as the Deflector lamp is the arrange-

ment by which the air is deflected on to the flame. In this lamp (Fig. 62) there is a short metal cylinder, A, about 1 inch high, surrounding the lower part of the gauze, but not closely touching it. Above this cylinder is an angle ring, B, fitting closely to the gauze and the bonnet. The air is taken in at the bottom of the bonnet between it and the cylinder; when it meets the angle ring its upward progress is stopped and it is deflected downwards between A and the gauze on to the flame.

The comparative values of safety lamps in explosive atmospheres travelling at high velocities have been the subject of numerous experim

cities have been the subject of numerous experiments. It is quite beyond the scope of a small text-book to enter into a detailed account of the experiments, and it is only necessary to refer to a few of the more important results. All experiments have shown the importance of the bonnet in shielding the gauze from direct contact with the ventilating current and so increasing the safety of the lamp. In no instance has an



FIG. 62.

unbonneted lamp failed to cause an explosion in an explosive atmosphere travelling at the rate of 50 feet per second. In regard to this the Committee of the Midland Institute of Mining, Civil, and Mechanical Engineers, in its Report on Safety Lamps, 1881, states :---

"The conclusion, therefore, that the committee arrive at, taking all the facts proved by these experiments, is the unmistakable value of the bonnet over an exposed gauze, and that all lamps fed from above and provided with this protection are safer than any other; the bonnet, moreover, has a further advantage in keeping gauze free from dust and dirt."

An unbonneted lamp becomes a source of danger during shot firing, for it has been shown by Prof. Galloway that the sound wave produced when a shot is fired striking an unbonneted lamp, within the gauze of which an explosive atmosphere is burning, may force the flame through the gauze and cause an explosion, whereas it has no effect on a bonneted lamp.

The material of which the gauze is made has considerable effect on the safety of the lamp. Iron-wire gauze is much safer than copper or brass wire gauze, as these gauzes are liable to fuse or burn through if they become red hot in an explosive mixture, owing to the greater fusibility of these metals. Absolutely new gauze may pass the flame owing to the slight film of grease or oil with which it is coated not being completely removed, but after this has disappeared the gauze will not pass the flame under the same conditions. This points to the necessity of keeping the gauze free from oil and grease.

A good modern safety lamp placed in an explosive mixture travelling at 50 feet per second should be extinguished and not pass the flame.

Illuminating Power.—The construction of the safety lamp is not compatible with high illuminating power, the restricted ventilation so necessary for its safety being opposed to the most favourable conditions for the combustion of the illuminant. The illuminant and the condition of the wick have an effect on the brightness of the light given out. Mineral oils and benzene give a higher illuminating power than undiluted animal and vegetable oils. The illuminating power of the latter is improved by dilution with from 66 to 75 per cent. of mineral oil.

The wick should be of slightly larger dimensions than the wick tube, loosely plaited and well dried before use. Its

length should be only slightly longer than the depth of the oil vessel.

Illuminants.—These consist of :--

- (1) Animal or vegetable oils.
- (2) Animal or vegetable oils mixed with "mineral colza."
- (3) Mineral oils.
- (4) Benzene.
- (5) Petroleum spirit or "benzolene."

The animal oils chiefly used are seal and whale oil, whilst the vegetable oils are colza and niger seed oil. When undiluted all these oils burn badly causing the wick to char, or, as it is technically described, to "crozzle," which renders constant attention necessary if a good light is to be maintained. When mixed with 75 per cent. of "mineral colza" these oils burn much better. Mineral colza is a mineral oil, but not the ordinary paraffin oil used for burning in lamps. The latter has a flash point between 75° F. and 120° F., whereas the flash point of mineral colza is commonly from 240° F. to 260° F. In some mines, however, its low flash point may be considered an objection to its use.

Mineral oils are generally used in lamps which are ignited by electrical means after being fitted together. Benzene is used in some lamps, such as the Wolf lamp, which is very largely used in Belgium and Germany.

Petroleum spirit, or benzolene, is a low-boiling paraffin or mineral oil used in the Protector form of lamp, which can only be lighted after the lamp has been fitted together; it being very volatile, considerable care is necessary to prevent explosion in the lamp cabin or building where the lamps are cleaned, and no naked lights should be allowed within that building.

Testing for Fire-Damp.—The presence of small percentages of fire-damp or any inflammable gas or vapour in the atmosphere has a distinct effect on the ordinary flame of a safety lamp. In consequence the safety lamp may be used to show when fire-damp is present. The first indication of the presence of gas is shown by a slight flickering or jumping of the flame; this is followed by an elongation and smoking of the flame. The elongation increases as the percentage of fire-damp increases until the flame stretches up into the gauze of the lamp in the form of a long, thin, smoky column of flame. After this the flame will leave the wick and either continue to burn in the





5 per cent.



FIG. 63. 1 per cent. 2 per cent. 3 per cent. 4 per cent. Reduced Flame. upper part of the lamp or become extinguished. The action of the flame is due to the formation of an "aureole," or "cap," of burning fire-damp which surrounds the lamp flame.

This cap is very transparent and non-luminous, and is invisible owing to the brightness of the lamp flame behind it. Its presence, however, has been revealed by photography in experiments made by Messrs. Whalley and Tweedie.¹

To render this cap visible it is necessary to make the lamp flame non-luminous, which is done by pricking down the flame until only a small non-luminous speck of flame remains.

When such a flame is introduced into an atmosphere containing fire-damp the first indications of its presence are a slight elongation of the flame, and as the quantity of fire-damp increases a transparent aureole of flame is seen to surround the base of the lamp flame without showing any clearly defined outline in the upper part. Further increase in the quantity of fire-damp produces a clearly defined cone of flame terminating in a sharp point. The height of this cone increases as the quantity of gas increases until it eventually forms a long thin cone of pale blue flame which stretches up into the gauze of the lamp. When this point is reached any increase in the quantity of fire-damp present causes the flame to leave the wick and burn inside the gauze or to be extinguished.

The effect of different percentages of gas on the reduced flame of a safety lamp is shown in Fig. 63, taken from Messrs. Whalley and Tweedie's paper.

The size of the cap produced by any fixed percentage of fire-damp with any given illuminant depends on the size of the testing flame, and very different indications will be obtained unless some standard flame is used. It has been suggested to make use of a flame of a given height; but this is always a matter of difficulty as it is almost immittitit possible to judge of the exact height of the flame.

Messrs. Whalley and Tweedie have described what they call a "standard flame."² This is regulated by pricking down the wick (Fig. 64) until there

FIG. 64.

appears a clear blue zone of flame which entirely surrounds a small luminous and yellow spot of light. To produce this flame satisfactorily the wick should be carefully trimmed. If

¹ Trans. Inst. M. E., vol. xxxviii. p. 527.

² Loc. cit.

the wick be a flat one the flame should extend right across the wick, and if a round one should completely cover the wick. With some illuminants a crust (crozzle) forms on the wick after a short time, and this materially interferes with the adjustment of the standard flame.

The size and appearance of the standard flame adjusted as just described depend on the illuminant used, and some of the more volatile oils used, such as naphtha, benzene, &c., show a "cap" when the flame is adjusted in an atmosphere free from fire-damp. This cap is due to the evaporation of the volatile oil from the oil vessel and other parts of the lamp, which causes the air in the lamp to be charged with a small quantity of inflammable vapour. This cap is called by Messrs. Whalley and Tweedie a "fuel cap"; it has nothing to do with the flame itself, and always makes its appearance on the outside edge of the testing flame and seldom shows a visible tip. It may often be mistaken for an indication of the presence of fire-damp unless the precaution is taken to carefully adjust the flame in a gasfree atmosphere and examine it for a fuel cap before testing for fire-damp.

In the case of a flat wick the cap produced in an atmosphere containing fire-damp is more distinctly seen if the flame be viewed end on instead of broadside on. The difference is clearly shown by the accompanying figure taken from Messrs. Whalley and Tweedie's paper (Fig. 65).

With a flame properly adjusted it is possible to estimate the percentage of gas from the size of cap produced, provided the lamp and its illuminant have been standardised in atmospheres containing definite percentages of gas.

The Behaviour of the Standard Flame in Different Percentages of Gas.—When using white rose paraffin oil Messrs. Whalley and Tweedie found that the first indications of gas are shown when about 1 per cent. of gas is present. By careful observation a very faint cap without a visible tip can then be seen. When 2 per cent. is present the tip becomes just visible (Fig. 63) and the cap is slightly longer. The length of the cap continues to slowly increase between 2 and 3 per cent., and more rapidly between 3 and 4 per cent., and still more rapidly between 4 and 5 per cent., when it spires into the gauze. These results are shown in the accompanying curve taken from Messrs. Whalley and Tweedie's paper.



Appearance of Flame Caps viewed edgeways and broadside on. FIG. 65.



Petroleum Spirit. Caps shown with different Illuminants in 2 per cent. of Coal Gas. Wolf Naphtha. Thorneburry Oil.

FIG. 67.

Paraffin.

Colza.



FIG. 66.—Approximate Percentage of Fire-Damp.

The Relation between Illuminants and their Caps.—Tests made by Messrs. Whalley and Tweedie show that very different sized caps are given by the same percentage of gas when different illuminants are burnt in the same lamp. The following measurements of caps produced by the standard flame of different illuminants in a 2 per cent. mixture of coal-gas were obtained, and are illustrated in Fig. 67 :—

| | Colza. | Paraffin. | Thorneburry Oil. | Wolf Naphtha. | Petroleum Spirit. | |
|--------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|--|
| Caps . Flames . | Inches. 0·32 0·10 | Inches. 0·40 0·07 | Inches. 0·40 0·08 | Inches. 0·42 0·10 | Inches. 0·50 0·12 | |

Colza oil gave the least satisfactory result, and was difficult to work with because the flame requires constant adjustment to maintain it at the standard height. Paraffin oil showed quite a distinct cap with small percentages of gas, but the lamp became very hot in a stagnant atmosphere, and is liable under these conditions to give a "fuel cap." Naphtha gave excellent results, and when this fuel is used the flame requires less adjustment to maintain it at the standard height.

Effect of Temperature on the Size of Cap produced.--It might be supposed that different indications would be produced

K

by the same lamp as the temperature of testing increases, especially when oils of low boiling-point are used and the lamp itself gets hot.

There is no doubt that the fuel cap is formed by volatile oils, and this cap increases with the temperature of the lamp; therefore it is probable that as the temperature of the lamp increases the same amount of gas would give different indications. The experiments made by Messrs. Whalley and Tweedie, however, have not given any definite results on this point.

Effect of the Presence of Black-Damp.—Experiments made in 2 per cent. of marsh gas to which 1, $1\frac{1}{2}$, 2, and 3 per cent. of carbon dioxide had been added did not show any difference in the size of caps produced. If, however, the carbon dioxide were produced by burning the oxygen out of the air, it is most likely that there would be a considerable difference in the indications because of the reduction in the percentage of oxygen.

Quantity of Gas that can be Detected by an Oil Flame.— According to Dr. Clowes, with the ordinary lamp burning colza

> oil fairly satisfactory indications are obtained with 3 per cent. of gas, but smaller quantities are not indicated at all, or are too variable to be relied on. It would appear, however, from later results obtained by Messrs. Whalley and Tweedie, that careful observations with a properly regulated standard flame will show the presence of 1 per cent. of gas, and 2 per cent. is distinctly shown by a well-formed conical cap.

> As the exact indication given by any percentage of gas depends on the fuel and the lamp it would seem desirable that a fire-trier's lamp should be carefully standardised, so that the user may become familiar with its capabilities for gastesting.

> It is sometimes necessary to detect smaller quantities of gas than 2 per cent., in which case special lamps burning special fuel are used. The fuels generally used are benzolene, alcohol, or hydrogen.

A benzolene lamp for detecting fire-damp has been introduced by Ashworth; alcohol is used in the Pieler, Chesneau, and Stokes lamps, and hydrogen in the Clowes lamp.



FIG. 68.

The Pieler lamp (Fig. 68) consists of an oil vessel, on to which is screwed an elongated wire-gauze chimney; a circular wick is carried on a tube which can be raised or lowered by a rack and pinion worked by a thumb-screw from the outside. The wick tube carries a small conical shield which screens the flame and thus renders the cap more visible. The top of the cone is 1.2inches above the top of the wick tube. The whole lamp is enclosed in a shield or tin can in which is fitted a narrow longitudinal window with a scale marking the height of the caps to be obtained with different percentages of gas. When using the lamp the height of the flame is adjusted till no tip of flame is visible above the conical shield. Considerable inconvenience is experienced by the condensation of moisture on the glass and from the heating of the alcohol reservoir, which may cause the alcohol to boil. With a flame 1.2 inches (30 millimetres) high, the following sizes of caps have been obtained :---

| Percentage of Marsh Gas. | | | | | | | Height of Cap. | | |
|--------------------------|------|--|--|--|---|--|----------------|-------------|--|
| | 0.25 | | | | | | 30 m | illimetres. | |
| | 0.50 | | | | | | 65 | ,, | |
| | 0.75 | | | | | | 75 | " | |
| | 1.00 | | | | • | | 90 | ,, | |

The **Chesneau lamp** is somewhat different to the Pieler lamp. Methyl alcohol, containing 1 gramme copper nitrate and 1 gramme ethylene chloride (Dutch liquid) per litre, is used instead of ordinary alcohol. A green flame is thus obtained which gives rise to a greenish blue cap, which is said to be visible in the light from an ordinary safety lamp. The size of flame used when testing for gas is 1.28 inches (37 millimetres), and the lamp is said to indicate the presence of 0.1 per cent. of gas. The heights of caps obtained when testing with this lamp are as follows :—

| tage of M | arsh | Gas. | | | | Heig | ght of Cap | э. |
|-----------|------|------|---|---|---|-----------|------------|----|
| 0.1 | | | | | | 15 m | illimetre | s. |
| 0.2 | | | | | | 24 | " | |
| 1.0 | | | | | | 34 | >> | |
| 1.2 | • | | | | • | 46 | ,,, | |
| 2.0 | • | | • | • | | 64 | >> | |
| 2.5 | | | • | • | | 90 | " | |
| 3.0 | | | | | | 140 | | |

Percen

Ashworth has designed an alcohol-testing lamp in which the alcohol reservoir is fitted with three wick tubes, which converge towards a common centre, and carry circular wicks about $\frac{3}{16}$ of an inch in diameter. These three wicks are simultaneously raised or lowered by a rack and pinion worked by a thumb-screw from the outside. The lamp is of the Ashworth-Hepplewhite-Gray type, with an elongated glass; the air enters the lamp through a single widened tube. The wick tubes are surrounded by a brass conical shield, mounted on a ring of gauze, through which the air passes to the flame. The flames from the convergent wicks unite into one large broad flame; this is racked down when using the lamp until no cap or aureole of flame is seen above the top of the cone in air free from fire-damp.

The great drawback to these lamps is that they have no illuminating power, and an oil lamp must be carried at the same



FIG. 69.

time. To avoid this inconvenience Mr. Stokes, late H.M. Inspector of Mines, devised a lamp which is both an oil lamp and an alcohol-testing lamp.

The Stokes lamp (Fig. 69) is an ordinary Hepplewhite-Gray lamp, with an elongated glass, fitted with the usual oil vessel and wick-holder for burning oil.

In the bottom of the lamp is a sunken circular cavity which can be closed with a screw-plug. and from the top of which a tube passes up through the oil vessel. This tube is covered with a cap which presses tightly on the top. The alcohol tester consists of a small cylindrical vessel fitted with a narrow wick tube through which two strands

of cotton wick are threaded. This vessel when not in use is covered with a cap and carried separately from the lamp. When required for use the cap is removed from the vessel, and the wick tube passed up through the tube, whilst the alcohol vessel is screwed into the sunken cavity ; the act of screwing the vessel into the cavity raises the cap, and when the vessel is screwed home the tops of the alcohol and oil wick tubes are on the same level.

To use the lamp a test is first made with the reduced oil flame; if no indication of gas is obtained the oil wick is raised, the alcohol vessel inserted, and the tester lighted by slightly inclining the lamp so that the oil flame heats the alcohol wick tube. When the alcohol wick has ignited the oil flame is extinguished and a test made with the alcohol flame. On completion of the test the oil wick is raised and lighted at the alcohol flame; the alcohol tester is then withdrawn. The height of the alcohol flame should be adjusted to about 13 millimetres, or 0.52 inches. With this standard flame the following results have been recorded :---

Percentage of Gas. Height of Cap. 0.5 0.60 inches. 1.00 1.00 1.501.44 . 12 2.00 1.68 22 2.502.00 ••

The cap with 0.5 per cent. is not clearly defined.

To obtain the best results with alcohol-testing lamps absolute alcohol must be used, as its flame is practically non-luminous. Methylated spirits gives a more or less luminous flame, which obscures the cap when only small percentages of gas are present.

Hydrogen, owing to the high temperature and non-luminous character of its flame, is most valuable for testing for small quantities of fire-damp. Several attempts have been made to adapt it to this purpose, and the problem has obtained a practical solution in the invention of the **Clowes hydrogen lamp** (Fig. 70). It is a lamp of the Hepplewhite-Gray type, with an elongated, conical glass, and adapted to burn either oil or hydrogen. The hydrogen, under pressure, is carried in a small steel cylinder to which is attached a nozzle which fits into a socket in the side of the oil vessel. At the upper end of the cylinder is a plug which fits into an attachment in the upper part of the lamp frame. From the socket in the oil vessel a narrow copper tube passes through the oil vessel into the lamp and terminates on a level with the oil wick tube; through this tube the hydrogen passes. On the

lamp glass five lines are marked, the two lower ones serve for regulating the height of the hydrogen flame to the standard



FIG. 70.—Clowes Lamp. From "Chemical Technology," by Groves and Thorp, vol. ii., by permission of Messrs. J. & A. Churchill. height of 10 millimetres (0.4 inches), whilst the three upper ones mark the height of the cap to be obtained with 0.5, 1, and 2 per cent. of gas.

To use the lamp the oil flame is first used to test for gas in the usual way. If no indication of gas is obtained the hydrogen is gently turned on by opening the cylinder valve with a key provided for the purpose. When the gas is ignited at the mouth of the jet the oil flame is extinguished and the hydrogen flame adjusted to the standard height. After the test is completed the oil wick is raised and lighted at the hydrogen flame and the hydrogen turned off by closing the valve.

It is claimed for this lamp that it serves to indicate the presence of carbon dioxide by a change in the colour of the flame. When 2 per cent. of this gas is present the reddish colour of the hydrogen flame turns to pale blue.

Some idea of the relative values of different fuels for testing for fire-damp may be obtained from the table given on page

151, which is taken from "Detection of Inflammable Gas and Vapour," by Clowes and Redwood, p. 116.

Garforth's Gas Collector.—In some cases where it is impossible or inconvenient to use the safety lamps directly for testing for gas the Garforth gas collector (Fig. 71) may be used. It consists of an india-rubber ball with a metal nozzle which can be fitted into a socket formed in the bottom of the oil vessel of a lamp, and from which a tube passes through the oil vessel and terminates just below the top of



the wick tube. To use the collector the air is expelled by squeezing the ball, which is allowed to resume its original

FLAME AND THE SAFETY LAMP

shape when surrounded by the air to be tested. The nozzle is then fixed in the socket and the sample of air expelled by gently squeezing the ball. Only comparatively large proportions of gas can be detected by this method.

Heights of Flame Caps in Millimetres over Test Flames in Air containing Methane.

| Percentage of Methane present in the Air. | Hydrogen Flame. | | | Pieler | Ashworth | Colza-Petroleum Flat Flame. | |
|---|---------------------------------|---|------------------------------|---|-------------------------------|--------------------------------|--|
| | Standard. 10 mm. | 15 mm. in the Gas. | 5 mm. in the Gas. | Alcohol Flame, 30 mm. | Benzolene Flame, 30 mm. | Small Blue, 3 mm. | Flame partly luminous, 6 mm. |
| 0.25 0.50 1.0 2.0 | 17 18 22 31 | 37 42 60 Enters top of lamp. | | 30 ? 55 90 140 Reaches top of lamp. | 7? 10? 14 | 7·5 | 7·5 |
| $\left. \begin{array}{c} 3.0 \\ 4.0 \\ 5.0 \\ 6.0 \end{array} \right\}$ | 52 Enters top of lamp. | ••• | 14.5 22.2 35.0 60.0 | | 20 25 30 35 | 7.5 12.0 29.0 67.0 | 7.5 24.0 41.0 Enters top of lamp. |

Whilst the safety lamp is, without doubt, the most convenient gas-testing instrument for general use, and in experienced hands capable of great accuracy, other forms of apparatus for the detection of fire-damp have been devised in which the use of the lamp is avoided. Among these may be mentioned :---

(1) Ansell's Fire-Damp Indicator (Fig. 72), which depends for its action on the difference in the rate of diffusion of gases of different densities. In its ultimate form this apparatus consists of a small pocket aneroid barometer the chamber of which is closed by a plate of unglazed or biscuit earthenware, whilst the dial is marked to indicate the percentage of fire-damp. The porous plate is protected by a brass cap when the instrument is not in use. If the cap be removed in an atmosphere of less density than that of the air inside the instrument the pressure inside the instrument increases, and the index finger moves and indicates

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the percentage of fire-damp present. It is also claimed that this instrument will indicate the presence of carbon dioxide.



FIG. 72.

The presence of this gas increases the density of the air, and if the density of the air, and if the density of the atmosphere is greater than that of the air within the instrument, when diffusion takes place the pressure inside the instrument is reduced. The objections to the use of the instrument are: (a) the pores of the plate are liable to become choked with coal dust, in which case it ceases to act; (b) it is possible for the ex-

ternal air to contain such quantities of fire-damp and carbon dioxide that the diffusion effects of each gas may neutralise one another even though the fire-damp be present in explosive quantities; (c) the presence of water vapour, whose specific gravity is 0.628, tends to magnify the quantity of fire-damp present.

(2) M'Cutcheon Gas Indicator.—A more recent apparatus, also depending for its action on the diffusion of gases, and known as the M'Cutcheon gas indicator, is of much more complicated construction than Ansell's indicator, and is said to detect less than 0.125 per cent. of marsh gas.

(3) Liveing's Fire-Damp Indicator.—This instrument serves to detect fire-damp by comparing the brightness of two glowing platinum wires, one of which is enclosed in an air-tight vessel, the other exposed to the atmosphere. If air containing fire-damp comes in contact with a red-hot platinum wire slow combustion takes place, which raises the temperature of the wire, causing it to glow more brightly. The greater the amount of fire-damp present the greater the amount of combustion and the brighter the glow.

The instrument (Fig. 73) consists of a box divided into an upper chamber and a lower chamber. The lower chamber, A, contains electrical apparatus for heating the wires. The upper chamber contains two platinum spirals, one of which, C, is enclosed in an air-tight glass tube, whilst the other, B, is surrounded with a wire-gauze cylinder having a glass cap. These two wires are in connection with the electric apparatus and can be simultane-

ously made red hot by turning a handle. In the lid of this chamber is a window, D, beneath which is a scale, E, marked with percentages of firedamp; along this scale a pointer, H, can be moved. The pointer has a chamfered top



FIG. 73.

to which mirrors are fixed, and the sloping surfaces are illuminated by the glowing wires. The milled head works the screw, G, which moves the pointer. There are two openings. F and F, in the cover, by means of which air can be drawn through the apparatus. In using the apparatus the pointer H is adjusted to the zero of the scale, the air to be tested is aspirated through the chamber, and the handle of the electrical apparatus turned. By observing H it is at once seen if the two faces of the pointer are equally illuminated, if not the pointer is moved by means of the screw, G, until there is no difference in the illumination of the two surfaces. The position of the pointer, H, on the scale, E, indicates the percentage of fire-damp present. The instrument is said to determine quantities of gas from 0.25 per cent. upwards, and this has been confirmed by James Grundy, who found it gave very accurate determinations of "gas" from 0.11 to 2.2 per cent. One great drawback to the use of this instrument is its weight, and another the fact that the spiral exposed to the gas undergoes a marked change in its electrical resistance after it has been used for some time, so that in gas-free air the two spirals do not glow equally, which necessitates an adjustment of the zero of the scale in gas-free air.

(4) The Beard-Mackie Indicator (Fig. 74) is an instrument which also depends on the glowing of platinum wires produced by the slow combustion of marsh gas. It consists of a brass frame or standard, A, attached to a plate, B, for support. A hole is pierced in the plate so that it can be passed over the wick tube of

a lamp and firmly fastened by the screw cap of the oil vessel. Across the frame a number of wires are stretched, the lowest being

FIG. 74.

of iron, the others platinum. The iron wire is used to adjust the flame, which should barely touch the iron strand. The hot gas comes in contact with the platinum wires, and undergoes slow combustion causing the strands to glow. Two forms of this indicator are used, one having 6 strands of platinum wire, which is said to indicate $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, and 3 per cent. of "gas," according to the number of strands which glow. A lamp with an elongated glass is required to make the best use of this indicator (Fig. 75), for with a lamp with the ordinary glass cylinder the indicator passes up into the gauze and the upper strands are hidden from view, whilst

reflection from the rings supporting the gauze interferes with the proper observation of the glowing wires.

The other form has only two strands of platinum wire, and is intended only to show the presence of "gas," without indicating the quantity. When the lower or warning strand glows it is an indication to the deputy or miner that gas

is present, whereas if the upper strand glows it shows that there is a dangerous quantity of gas. This form can be fitted to an ordinary safety lamp with the ordinary glass cylinder.

In using this indicator it is essential that the platinum wires should be clean and free from soot. Unless great care be taken in adjusting the flame sooting of the wires occurs, and when covered with soot they are useless for gas testing. It is also of importance that the strands of wire should be exactly over the flame, otherwise they will not act.

From tests made in the mine by Mr. Hepplewhite, it would appear that this indicator does not begin to act until more than 1 per cent. of "gas" Davis's Deputy's is present, which the author can confirm from tests he has made in the laboratory.

In addition to the indicators already described, there are others based on the chemical properties



FIG. 75. Lamp, fitted with Beard-Mackie Indicator.

of marsh gas, which serve to show the quantity present without

making a complete analysis of the air. Of these the Coquillon-Le Chatelier apparatus measures the reduction in pressure due to the contraction that takes place when the marsh gas in the air is completely burnt; whilst others, such as the Le Chatelier tube and the Shaw gas tester, are used to measure the quantity of gas that must be added to that already present in the air to make an explosive mixture. Such methods as these are largely in use on the Continent, but they are not much used

in England. They require a certain amount of manipulative skill and cannot well be used in the pit, but are suitable for daily tests of return air where facilities exist for transferring samples from the mine to the laboratory.

The latest improvement in the safety lamp as a fire-damp indicator is a modification of Chesneau's idea of colouring the cap so as to render it more visible (Fig. 76). It is the invention of Sir Henry Cunynghame and Dr. Cadman, and consists in introducing a small quantity of a sodium salt into the flame of the lamp, which colours the cap yellow.

The device consists of a small piece of asbestos paper which is twice dipped in a saturated solution of sodium carbonate to which a little hydrochloric acid has been added. The strip of asbestos is carried in a clip which can be worked in the lamp like the pricker. The strip is arranged so that its edge is parallel to the edge of the wick and about one-fifth of an inch above the top of the wick. When introduced into the flame it has



FIG. 76. Miner's lamp fitted with the Cunynghame-Cadman device.

the effect of lowering the flame, and by so adjusting the asbestos strip that it covers about two-thirds of the thickness of the flame, any cap that is produced by fire-damp is coloured yellow.

A complete account of the methods of analysis of mine air is to be found in Le Neve Foster and Haldane's "Investigation of Mine Air."

CHAPTER IX

THE OXIDES OF CARBON

Two oxides of carbon are known, carbon monoxide and carbon dioxide. They are both formed by the direct union of carbon with oxygen. The former is produced if the quantity of oxygen is limited, and the latter if it is in excess.

Carbon Monoxide. Symbol CO. M.W. 28.

Carbon monoxide is known to the miner as white-damp. Although Bedson and Meyer have shown that this gas may exist amongst the gases which are occluded in the pores of the coal, there does not appear to be any evidence of it occurring naturally in the atmosphere of a coal mine. It always results from the incomplete combustion of carbon or bodies containing carbon, and is produced whenever carbon dioxide is passed over red-hot carbon, $C + CO_2 = 2CO$.

Preparation.—To prepare it in this manner a porcelain tube, A, filled with charcoal, is heated to redness in the furnace, B, whilst carbon dioxide, generated in the apparatus C, is slowly passed through the tube (Fig. 77). The gas escaping from the tube is passed through caustic soda to purify it from the excess of carbon dioxide, and finally collected over water in the jar, D. Carbon monoxide is formed in the ordinary clear redhot coal or coke fire in the following manner. The incoming air first forms carbon dioxide, which, passing over large masses of red-hot carbon in the grate, is converted into carbon monoxide, and this gas burns with a pale blue flame as it escapes at the top of the fire.

The gas is usually prepared by heating formic acid, CH_2O_2 , or oxalic acid, $C_2H_2O_4$, with strong sulphuric acid.

When formic acid is used pure carbon monoxide is obtained, $CH_2O_2 = CO + H_2O$, but when oxalic acid is used a mixture of equal volumes of carbon monoxide and carbon dioxide is pro-

THE OXIDES OF CARBON

duced, $C_2H_2O_4 = CO + CO_2 + H_2O$. Oxalic acid is generally used for the preparation of the gas unless a gas of special purity is required. The preparation is carried on as follows :—

A mixture of oxalic and strong sulphuric acids is gently heated



FIG. 77.

in the flask, A (Fig. 78). The gases formed are passed through a solution of caustic soda contained in the Woulf's bottle, B, where most of the carbon dioxide is absorbed, and afterwards through the tower, C, containing soda lime, where the last traces



of carbon dioxide are removed. The carbon monoxide free from carbon dioxide is then collected over water in the jar, D.

The gas may also be prepared by heating finely powdered potassium ferrocyanide, $K_4 FeC_6 N_6$, with 8 or 10 times its weight of strong sulphuric acid—

 $\begin{array}{c} \mathrm{K_4FeC_6N_6+6H_2O+6H_2SO_4=6CO+2K_2SO_4+3(NH_4)_2SO_4+}\\ \mathrm{FeSO_4.} \end{array}$

Physical Properties.—It is a colourless, tasteless gas, possessing a faint odour. It condenses to a liquid under high pressure and intense cold. It is lighter than air, its specific gravity being 0.9678, and it is only very slightly soluble in water.

Chemical Properties.—It will not support combustion, but burns in air with a characteristic pale blue flame, forming carbon dioxide. Two volumes of carbon monoxide interact with 1 volume of oxygen to form 2 volumes of carbon dioxide, $2CO + O_2 = 2CO_2$. Mixed with oxygen it explodes on ignition. Dixon has shown that absolutely dry carbon monoxide will not burn in air quite free from moisture. Owing to the readiness with which this gas combines with oxygen it serves as a means of converting metallic oxides into metals at a red heat—

$$Fe_{2}O_{3} + 3CO = Fe_{2} + 3CO_{2}$$
.

Carbon monoxide is not absorbed by alkalies. It combines directly with certain metals, forming compounds known as carbonyls. For instance, when passed over finely divided nickel cooling from 400° C. to 100° C., it unites to form nickel carbonyl, Ni(CO)₄, which is a volatile liquid.

It is an exceedingly poisonous gas, very small traces in the atmosphere produce fatal results. It combines with the hæmoglobin of the blood to the exclusion of oxygen, and so produces a paralysing effect on the muscles, and eventually unconsciousness and death.

Blood charged with carbon monoxide has a bright scarlet colour, and the bodies of victims poisoned by carbon monoxide have a remarkably fresh life-like appearance instead of the usual pallor characteristic of death. This is due to the colour of the blood which fills the veins of the body.

The combination of hæmoglobin with carbon monoxide is about 200 times as strong as with oxygen, so that the proportion of carbon monoxide to oxygen combining with the blood may be very great, even though very small quantities of the former gas be present in the air breathed. The severity of the symptoms of carbon monoxide poisoning depends to a great extent on this proportion. These symptoms are very insidious; very little discomfort is experienced at first, and the senses and powers of judgment and locomotion are often impaired before the person is aware of any danger; with excitement and increased exertion the symptoms are aggravated, and unconsciousness may occur with very little warning.

The volume of blood in a man of average weight is about 3 litres (5.2 pints), and it is capable of absorbing 600 c.c., or 1 pint of either oxygen or carbon monoxide, when it is said to be saturated with either gas; if it contains 300 c.c., or $\frac{1}{2}$ pint of each of these gases, it is said to be 50 per cent. saturated, whereas if it contains 200 c.c. of carbon monoxide and 400 c.c. of oxygen it is said to be 33 per cent. saturated with carbon monoxide, and so on.

With 20 per cent. saturation of the blood the chief symptoms are dizziness and shortness of breath, and these gradually increase as the saturation increases, until at 50 per cent. saturation paralysis of the limbs sets in, accompanied by loss of consciousness on exertion. With higher degrees of saturation unconsciousness and death quickly follow; whilst if death occurs gradually the blood is usually found to be about 80 per cent. saturated.

The degree of saturation will depend upon the quantity of carbon monoxide present, and the length of exposure to the atmosphere. The ordinary rate of breathing when a man is at rest is about 7 litres (12 pints) of air per minute, of which about 5 litres or 8.5 pints reach the blood, so that if the air contains 0.1 per cent. carbon monoxide not more than 5 c.c. per minute of this gas will reach the blood, and assuming that all this is absorbed, in one hour the blood will absorb $60 \times 5 = 300$ c.c., and become 50 per cent. saturated; but during exertion and when walking a man probably breathes twice as fast as when at rest, therefore with 0.1 per cent. present the blood will become 50 per cent. saturated in half an hour; under the same conditions it will become 50 per cent. saturated in a quarter of an hour if 0.2 per cent. is present, or in ten minutes if 0.3 per cent. is present, and in about three minutes if 1 per cent. is present.

It is probable that the whole of the carbon monoxide in the air is not absorbed by the hæmoglobin, as in an experiment made during rest Dr. Haldane found that with 0.2 per cent. of the gas in the air the blood did not become 50 per cent. saturated till after 70 minutes' exposure. The same authority states that "0.17 per cent. is sometimes fatal to animals, though usually about 0.4 per cent. is required to cause death within a moderate time. Anything above 0.15 per cent. must be regarded as distinctly dangerous, whilst probably anything above 0.03 per cent. would in time produce symptoms distinctly felt on exertion" ("The Investigation of Mine Air," Le Neve Foster and Haldane, p. 147).

The detection of carbon monoxide underground is a matter of great difficulty, as the small quantities that produce poisonous results have no effect on the flame of a miner's lamp; its chemical reactions are not adapted for use underground. Its chief reactions are those produced with palladium chloride and blood.

It gives a black deposit of metallic palladium when a piece of white filter paper, moistened with palladium chloride, is exposed to the gas.

Blood Test.—The following simple test has been described by Dr. Haldane: If ordinary oxygenated blood be diluted with about 200 times its volume of water a yellowish red solution is obtained, whereas if blood saturated with carbon monoxide be similarly diluted it gives a distinctly pink solution. To apply this test a small quantity of blood is obtained by pricking one's finger and diluting with 200 times its volume of water. The solution is divided into equal parts in test tubes of equal diameters; on shaking the blood solution in one test tube with air containing carbon monoxide and then comparing its tint with that of the oxygenated blood by holding both test tubes side by side and examining them by transmitted light the difference in tint will be easily seen. As daylight is necessary for this test it cannot be applied underground.

The test has been applied by Dr. Haldane to estimate the quantity of carbon dioxide in the air. A mouse is introduced into the suspected atmosphere for ten or fifteen minutes, then killed. A solution of oxygenated blood is made as described above and divided into equal parts in test tubes of equal diameter; one of these is shaken with ordinary illuminating gas (which contains carbon monoxide) until it is saturated, a drop of blood is taken from the heart of the mouse and carefully diluted until its tint is equal to that of the saturated blood. A comparison of the volumes of the two solutions will give an estimate of the degree of saturation of the blood of the mouse. From this the percentage of carbon monoxide can be ascertained, for the blood of the mouse will be 66 per cent.
saturated with 0.16 per cent. of carbon monoxide, 50 per cent. saturated with 0.08 per cent., 33 per cent. saturated with 0.04 per cent., and 20 per cent. saturated with 0.02 per cent., &c.

In entering an atmosphere in which the presence of carbon monoxide is suspected, Dr. Haldane recommends the miner to carry a mouse in an open cage. As soon as the animal begins to show signs of sluggishness and exhaustion it is time for the miner to retire into purer air, as probably a dangerous quantity of carbon monoxide is present.

Carbon monoxide, or white-damp, is found in a coal mine's atmosphere :---

(1) During an underground fire, when its formation is due to the combustion of carbon in a limited supply of air.

In the following table are given analyses of air in the neighbourhood of underground fires. Nos. 1 and 2 are taken from the Report for 1905 of Mr. W. N. Atkinson, H.M. Inspector of Mines for the Stafford District, No. 9; whilst Nos. 3 and 4 are samples of air from the Snaefell mines in the Isle of Man, where the firing of timber underground caused a serious disaster in 1897.

Composition of Air in the Neighbourhood of Underground Fires.

| | (1) | (2) | (3) | (4) |
|--|--|---|--|--|
| | Coneygre | Hamstead | Snaefell | Snaefell |
| | Colliery, | Colliery, | Mine, | Mine, |
| | S. Staffs. | S. Staffs. | I. of Man | I. of Man. |
| Carbon dioxide . Nitrogen Oxygen Marsh gas Carbon monoxide . Hydrogen | 3·12 81·875 14·49 0·40 0·115 | $\begin{array}{c} 2.69 \\ 80.24 \\ 15.55 \\ 0.75 \\ 0.52 \\ 0.25 \end{array}$ | $\begin{array}{r} 4.22 \\ 78.75 \\ 15.48 \\ \dots \\ 1.07 \\ 0.48 \end{array}$ | 4·26 79·12 ¹¹ 15·52 1·10 |

(2) After the use of explosives for blasting purposes. This is especially the case with gunpowder, guncotton, and probably some of the nitro-glycerin explosives.

¹ Including Hydrogen.

(3) After an explosion of fire-damp or coal dust. If the combustion of fire-damp in an explosion were complete the gaseous products of the combustion would be carbon dioxide and steam, and after the latter had condensed to liquid the remaining atmosphere would consist of carbon dioxide and nitrogen mixed with more or less air. No satisfactory analysis of the atmosphere remaining after an explosion has yet been made, but the medical examination of the blood of victims of a colliery explosion and the effect of the atmosphere on explorers invariably reveal the presence of carbon monoxide. There is no doubt that both carbon monoxide and carbon dioxide are produced in a colliery explosion. The relative proportions in which these gases are found will depend on the composition of the explosive mixture. If the explosion is a purely gas explosion the greater the proportion of fire-damp in the exploding atmosphere the greater the proportion of carbon monoxide formed, but it would appear from the results of Professor Dixon and others on the combustion of gaseous carbon that carbon monoxide will always be formed even when excess of air is present.

When dust takes part in the explosion; either in the presence or absence of fire-damp, it is probable that the proportions of carbon monoxide will be considerably increased, as, in addition to the quantity of that gas which directly results from the explosion, a further quantity will be formed by the action of the red-hot particles of coke on the carbon dioxide. Sulphur dioxide may also be present, especially after a coal-dust explosion, owing to the combustion of sulphur in the coal.

After-Damp.—The atmosphere that remains after a colliery explosion is known as *after-damp*; and it will be gathered from what has been stated above that this gas is composed of carbon dioxide, carbon monoxide, nitrogen, and possibly sulphur dioxide, diluted with air in varying proportions. Such an atmosphere may or may not support combustion, according to the quantity of air present; it will in any case be very poisonous. According to Dr. Haldane there must be at least 1.8 per cent. of carbon monoxide in undiluted after-damp, whilst there is probably on the average 3 per cent. of that gas present. The effect on man of breathing air containing varying quantities of after-damp in which 3 per cent. of carbon monoxide is present is as follows:—

| Percentage After-Damp. | Per cent. CO. | Effect on Man. | Effect on Lamps. |
|---------------------------|------------------|---|-----------------------|
| 2 per cent. | 0 ·06 | After half an hour or more slight giddi- ness on exer- | Nil. |
| 3.5 " | 0.102 | Inability to walk. | Nil. |
| 7 ,, | 0.21 | Loss of con- | Nil. |
| 10 " | 0.3 | Death. | Burn rather dimly. |
| 16 ,, | 0.48 | Death. | Extinguished. |

After-damp containing 3 per cent. of Carbon Monoxide.¹

Carbon Dioxide. Symbol CO₂. M.W. 44.

This gas is known amongst miners as "stythe" or "chokedamp." At one time black-damp was supposed to be carbon dioxide, but Dr. Haldane and Mr. W. N. Atkinson have shown that this gas is a mixture of carbon dioxide and nitrogen. Carbon dioxide is often called "carbonic acid," but it is not an acid, inasmuch as there is no hydrogen in its composition. The name "carbonic acid" has been handed down from the time when the term "acid" was not so clearly defined.

Carbon dioxide is found very widely distributed in nature. The purest air contains about 0.03 per cent., whilst it is found dissolved in all natural waters, some deep springs in the chalk and mountain limestone being highly charged with the gas. In volcanic districts it is discharged in large quantities from fissures in the earth's surface, whilst the atmosphere of many caves and subterranean cavities is often highly charged with this gas. It escapes with fire-damp from the coal face into the atmosphere of a coal mine, and instances are known of outbursts of this gas into the workings of the mine.

In combination with bases it gives rise to a series of salts called "carbonates," many of which are found as minerals in

¹ "Report on Causes of Death in Colliery Explosions," Dr. J. Haldane.

the earth's crust. The most widely distributed of the carbonates is calcium carbonate, $CaCO_3$, which, in the form of chalk, lime-

stone, and marble is found most extensively in Great Britain and all parts of the globe. In smaller quantities, the same substance is found in two distinct crystalline varieties, namely, calcite and arragonite (dogtooth spar). It is also the chief constituent of the shells of mollusca and of birds' eggs. Mountain limestone or dolomite is a carbonate of calcium and magnesium (CaMg)CO₃, whilst amongst others may be mentioned the ironstone ores of Scotland and Staffordshire, which are more or less impure iron carbonate, $FeCO_{q}$.

FIG. 79.

Preparation.—Carbon dioxide is produced by the combustion of carbon, or any body containing carbon, in excess of air or oxygen. If a piece of charcoal is ignited in air and plunged into a jar of oxygen it burns with great brilliancy, forming carbon

dioxide (Fig. 79). It is not prepared in this way, but usually by the interaction of an acid with a carbonate. Calcium carbonate is chiefly used for this purpose (Fig. 80). A few lumps of chalk or marble are placed in the flask, A, and covered with water, and some strong hydrochloric acid is poured down the funnel, B, when a brisk evolution of carbon dioxide takes place. The gas is conducted to the bottom of the jar, C, in which, owing to its great



FIG. 80.

density, it can be collected by the displacement of the air. The jar is full of gas when a taper is readily extinguished at the mouth of the jar—

 $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$.

Other carbonates may be used instead of calcium carbonate, and if specially pure carbon dioxide is required, it is prepared by acting on sodium carbonate with dilute sulphuric acid—

 $Na_{2}CO_{3} + H_{2}SO_{4} = Na_{2}SO_{4} + H_{2}O + CO_{2}.$

Carbon dioxide is also obtained by heating calcium carbonate— $CaCO_{9} = CaO + CO_{9}$.

In the process of lime-burning large quantities of carbon dioxide are produced. In this process chalk or limestone is heated in kilns and undergoes decomposition according to the above equation.

Physical Properties.—Carbon dioxide is a colourless gas. If inhaled it produces a slight irritation of the air passages, and has a somewhat sharp taste. It is soluble in water, which, at the ordinary temperature, dissolves about its own volume of the gas. The gas is about 1½ times as heavy as air, its specific gravity being 1.53. Owing to its great specific gravity the gas can be poured down-



FIG. 81.

wards. If a burning candle be placed in a beaker (Fig. 81) and a jar of carbon dioxide be slowly inverted over the lip of the



FIG. 82.

weight of the equal volume of air expelled. When carbon dioxide enters in large quantities into the air it immediately sinks and forms

a layer of gas close to the floor. This can be illustrated by pouring carbon dioxide into a beaker and then dropping a soap bubble filled with air into it. The bubble will sink in the beaker until it meets with the layer of carbon dioxide at the bottom, on which it will float (Fig. 83). It is owing to its great specific gravity that it accumulates on the floor of the workings, in dip workings, in the sump, and at the bottom of wells and disused shafts.

beaker, the gas will descend and extinguish the candle.

If a beaker be balanced on a balance (Fig. 82), and carbon dioxide poured into it, the beaker will show an increased weight, because the weight of the volume of carbon dioxide that has entered is greater than the weight of the equal



FIG. 83.

Carbon dioxide is readily converted into a liquid under a pressure of thirty-six atmospheres at 0° C., whilst if the liquid be rapidly evaporated so much heat is absorbed that a portion is converted into a snow-like solid.

Chemical Properties.—Carbon dioxide does not burn nor does it support the combustion of bodies that burn in air. A taper plunged into the gas is extinguished, whilst the gas does not take fire. It readily combines with bases to form salts

(carbonates), for which reason, when shaken with lime water, it turns it milky owing to the formation of insoluble calcium carbonate—

$$Ca(HO)_2 + CO_2 = CaCO_3 + H_2O.$$

Its absorption by bases to form carbonates is readily shown by filling a tube, A (Fig. 84), with carbon dioxide and shaking it with a few cubic centimetres of caustic soda solution whilst the thumb is tightly pressed on the open end of the tube. The gas is rapidly absorbed and a considerable vacuum produced in the tube, so that if the open end be brought under water in a trough, B, and the thumb removed the water will rise in the tube—

$2NaHO + CO_2 = NaCO_3 + H_2O.$



Dry carbon dioxide has no action on litmus, but in presence of moisture it colours the litmus

wine-red; on standing, this colour disappears owing to the escape of the gas.

The carbonates thus formed are salts of carbonic acid, which, if it were known, would have the formula, H_2CO_3 . Carbonic acid, however, does not exist, for whenever a carbonate is treated with an acid it is decomposed with effervescence and yields carbon dioxide and water instead of carbonic acid, thus—

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_3$$

This reaction is perfectly general for all carbonates, most of which are insoluble in water, but are readily dissolved by most acids.

Carbon dioxide undiluted with air cannot be breathed, and when present in great excess in the air is a distinctly poisonous gas. Small quantities in the air can, however, be breathed

continually without producing injurious effects. Naturally the air contains about 0.03 per cent. of the gas, and this quantity can be gradually increased without producing any inconvenience to the breathing of man until from 3 to 4 per cent. is present, when the breathing becomes perceptibly deeper. The respirations increase in frequency and depth as the quantity increases, until at 6 per cent. panting occurs accompanied sometimes with frontal headache. At 7 to 8 per cent. the panting becomes greater, and at 10 to 11 per cent. the distress becomes severe. As the quantity increases the senses become more or less numbed, and at 15 per cent. there is partial loss of consciousness, although life may not be endangered; at 25 per cent. death will eventually take place. The effects of carbon dioxide poisoning are not so persistent as those of carbon monoxide. The patient quickly recovers on removal to fresh air, though he may suffer more or less severely from headache.

The action of carbon dioxide in extinguishing a flame has already been described on p. 50.

Black-Damp.

Black-damp is an extinctive gas or mixture of gases which is usually met with in old workings or in ill-ventilated parts of coal mines, whilst occasionally it issues from the goaf owing to a fall in the atmospheric pressure, and in shallow mines it often exudes in somewhat large quantities from the coal face. It can usually be found in small quantities in the return air in almost any mine. It has generally been considered to consist of carbon dioxide only, but Dr. Haldane and Mr. W. N. Atkinson,¹ H.M.I.M., have shown that it is usually composed of mixtures of nitrogen and carbon dioxide, and from their analyses it would appear that the composition of the gas undiluted with air is—

Occasionally a much smaller quantity of carbon dioxide has been found in the gas, but this may be due to the gas coming in contact with water, which has dissolved some of the carbon dioxide.

¹ Trans. Inst. M. E., vol. viii. p. 549.

Usually a small quantity of marsh gas is found in air containing black-damp.

Only a few analyses of return air have been made recording the proportion of black-damp, and it is not possible to state the quantity that may be found in return air with any degree of certainty. Dr. Haldane, however, found from 1.14 to 4.06 per cent. present.

The specific gravity of a gas having the above composition is about 1.05, or only about 5 per cent. heavier than air. The presence of marsh gas tends to reduce its specific gravity, and if mixed with 10 per cent. of marsh gas its specific gravity will be the same as that of air. Its specific gravity is also reduced as the temperature of the gas rises, and if its temperature is between 14° to 15° higher than that of the atmosphere into which it is escaping it will also have the same specific gravity as that atmosphere; therefore, whilst the gas is often found spread along the floor of the roadways in dip workings and in the sump, it may at times be found near the roof and in rise workings, when its specific gravity has been reduced below that of the surrounding atmosphere either by admixture of marsh gas or because the temperature of the black-damp is considerably above that of the air.

The formation of black-damp is supposed by Dr. Haldane and Mr. Atkinson to be due to the oxidation of the coal and coal dust in the goaf and in old and disused workings. This doubtless takes place, and when a sudden fall in the atmospheric pressure occurs the gas, obeying Boyle's Law, issues into the workings. Whether oxidation is capable of producing the whole of the black-damp found in coal mines requires further investigation. Nitrogen and carbon dioxide are contained in the fire-damp that drains from the coal, and it is possible that the black-damp usually found in the return air-way comes from this source, though Dr. Haldane and Mr. Atkinson appear to think that even these gases have, at all events partly, been formed at the expense of the air which has penetrated into the coal.

Pure black-damp will not support the combustion of bodies that burn in air. The action of black-damp in extinguishing a candle flame is practically the same as that of pure carbon dioxide and nitrogen, namely, it dilutes the oxygen of the air. About 15 to 19 per cent. of this gas is necessary in order that an atmosphere may extinguish a candle or oil flame.

Pure black-damp cannot be breathed. Owing to the presence of carbon dioxide in black-damp the gas exerts a distinct physiological effect as soon as the amount of it present in the air gives rise to 3 per cent. of carbon dioxide. This occurs when about 26 to 27 per cent. of black-damp is present, when the depth of breathing becomes sensibly greater and gradually increases as the percentage of black-damp increases, until with 50 to 55 per cent. present violent panting and marked distress occur, accompanied by throbbing and headache over the brow, whilst the face becomes slightly bluish. With a still further increase in the quantity of black-damp the colour of the face gradually assumes a leaden hue, which is particularly marked at the lips and ears. The appearance of this leaden colour is a sign of imminent danger of loss of power over the limbs, and is usually reached when 60 per cent. of black-damp is present. Confusion of mind usually accompanies these symptoms.

It is evident that man can breathe an atmosphere containing a quantity of black-damp far greater than that required to extinguish a lamp flame, but in entering an atmosphere known to contain black-damp it is not safe to proceed after it ceases to support the combustion of a lamp. All atmospheres containing more than 15 per cent. of black-damp will extinguish a lamp flame; hence whilst there must be at least that quantity present it does not follow that the atmosphere may not contain a much larger quantity, even sufficient to be dangerous to life.

CHAPTER X

COAL

UNDER the name of coal are included most extensive deposits of fossil fuel, which occur at varying depths below the surface of the earth. It usually consists of a dark brown or black substance without crystalline structure, and occurs in horizontal or more or less inclined beds or layers known as "seams" or "veins." Its value consists in the large proportion of combustible matter it contains and the intense heat produced when it burns.

Many varieties of coal are known, but so far as its occurrence is concerned it may be divided into those coals which are found in the interstratified beds that lie between the Devonian and Permian formations, and are known as the Carboniferous formation, and those coals which are found in the Triassic and more recent formations. But in whatever geological formation coal may be found it is undoubtedly of vegetable origin. In the coals of more recent formation, known as lignites, distinct traces of vegetable structure may often be seen, which leave no doubt of their origin; but in those coals which occur in the Carboniferous formation all traces of vegetable structure have generally disappeared, though the existence of upright fossil trees passing through the coal seams with their roots embedded in the underlying clays, and the occurrence of the impressions of plants in the adjacent strata afford the strongest analogical evidence of their vegetable origin. Many and varied are the plants from which the coal seams have been formed; not less than from 200 to 300 species have been found in the coal measures alone, most of which appear to have belonged to the non-flowering plants, such as ferns, club mosses, and horsetails, of which classes the well-known coal measure fossils, lepidodendron, calamites, stigmaria, and sigillaria, are examples.

The manner in which coal seams have been formed is partly

a geological and partly a chemical question. The former deals with their origin and deposition, whilst the latter treats of the changes that have resulted in the production of coal from the vegetable matter.

It is beyond the scope of this book to enter largely into the geological history of coal, but an account of the chemistry of coal would not be complete without a short reference to the subject.

It is generally admitted by all geologists that the plants of the carboniferous period were land, not water, plants, and that they grew in great luxuriance, often in forests such as are seen to-day growing on the deltas of large rivers in warm climates. With regard to the deposition of the beds of vegetable matter, two theories have been suggested—(1) the "in situ" theory; (2) the "drift" theory.

The "in situ" theory assumes that plants grew in swamps traversed by rivers, and that the beds of vegetable matter were deposited over the area in which the plants grew. Owing to the subsidence of the surfaces these areas at times became submerged beneath waters. These waters were constantly fed by the rivers and streams carrying down detritus in the form of sand and mud, which deposited on the vegetable bed and so formed a covering of mineral matter. The mineral matter would at first be more or less mixed with vegetable matter, but as the thickness of the deposit increased the mineral matter alone would be deposited. Later, owing probably to volcanic agency, an upheaval occurred, bringing the submerged tract above the water level, when a further growth springing up led to the formation of another vegetable deposit.

By alternate subsidence and elevation of the earth's surface the formation of seams of coal in parallel beds, one above the other, separated by mineral deposits of varying thickness, can be accounted for; and this theory is to a certain extent confirmed by observations made, in a few instances, where the coal has been worked by quarrying instead of by mining. Sir Charles Lyell quotes the case of the Parkfield Colliery, near Wolverhampton, where in 1844 the coal was got by open work, and where in a space of quarter of an acre no less than 73 stumps of trees with their roots attached were found passing through the coal seams, whilst several trunks broken off close to the roots were lying in every direction. These were

flattened to a thickness of 1 or 2 inches and converted into coal, whilst their roots formed a stratum of coal 10 inches thick resting on a bed of clay 2 inches thick, below which was a second forest resting on a 2-foot seam of coal. Five feet below this again was a third forest with large stumps of lepidodendra, calamites, and other trees.¹

At first sight it would appear difficult to account for the extreme purity of the coal formed in this way. The waters which traversed the swamp would doubtless carry with them mud and sand, which might be expected to become largely mixed with the vegetable deposit. The explanation offered is derived from observations of what occurs to-day in the vast forest-covered swamp of the valley and delta of the Mississippi There a dense growth of reeds and other plants surrounds river. the swamps, and the waters in running through it are filtered, and so prevented from carrying mineral matter down to the area in which the vegetable matter is accumulating. Assuming that similar dense filter beds surrounded the carboniferous forests, it is possible to understand that vast thicknesses of vegetable matter would accumulate uncontaminated with mineral impurities.

The "Drift" Theory.—By some geologists it has been supposed that the coal fields have resulted from the deposition of vegetable matter carried down by rivers in times of flood. This by long immersion eventually became waterlogged, and sank at the mouth of the rivers, where it gradually became buried beneath sand and mud. This theory is based on what happens in many of the large rivers in America, which, on the breaking up of the ice and at times of flood, are known to tear up and carry away to the mouth numbers of large trees which, becoming waterlogged, sink.

This theory would account best for the formation of those seams which lie directly on a hard floor without the interposition of an under-clay.

Probably both explanations are true, some coal fields being produced from deposits laid down "in situ," whilst others have been produced from drifted timbers.

Changes which have Resulted in the Conversion of Vegetable Matter into Coal.—The changes that the vegetable matter has undergone in its conversion into coal is largely a chemical

¹ "Elements of Geology," Lyell, p. 380.

question, and the first fact that strikes us in examining the subject from a chemical point of view is that the same elements enter into the composition of woody fibre and coal, which, taken in conjunction with the geological evidence, offers a probable confirmation of its vegetable origin. In the following table is given the composition of wood and some of the more important classes of coal, whilst for comparison analyses of decayed wood and peat are added :---

| | Carbon. | Hydrogen. | Nitrogen. | Oxygen. | Sulphur. | Ash. | Analyst. |
|---|--|--|--|--|--|--|---|
| Oakwood Decayed oak Lignite from Bovey Lignite from Bovey Wigan cannel Silkstone (York- shire) . Newport steam Anthracite (South Wales) | 50·10 53·47 54·03 66·31 80·07 81·98 81·47 90·39 | 6.07 5.19 5.21 5.62 5.52 5.70 4.97 3.28 | 2·30 0·56 2·12 1·83 1·63 0·83 | 43.68 41.37 28.17 22.86 8.08 5.26 5.22 2.98 | 0·56 2·36 1·50 1·52 1·10 0·91 | 0·15 9·73 2·27 2·70 2·36 5·51 1·61 | Miller. Liebig. Vaux. " " Miller. Vaux. |

From these results it is seen :--

- (1) That the proportion of carbon in wood is smaller than in coal, whilst the proportion of hydrogen and oxygen is greater.
- (2) That the more recently formed coals contain a higher proportion of oxygen than the coals of earlier origin.

These facts are perhaps more clearly seen if the quantities of hydrogen and oxygen combined with 100 parts of carbon in wood and the different varieties of coal are compared. In the table on page 174 these numbers are calculated from the results given in the preceding table for hydrogen and oxygen only.

It is impossible to follow step by step the changes which have led to the conversion of woody fibre into coal, but a study of the changes that take place in the formation of peat and the microscopic examination of the more recent varieties of coal show that the chemical decomposition is of a very complex character. In the peat bogs the soft and more easily decomposed parts of

| | Carbon. | Hydrogen. | Oxygen. |
|---------------------|---------|--------------|--|
| Oakwood | 100 | 12.11 8.47 | 87·32 |
| Lignite | 100 | | 34·47 |
| Wigan cannel | 100 | 6·97 | $\begin{array}{c} 10 \cdot 09 \\ 6 \cdot 41 \end{array}$ |
| Yorkshire Silkstone | 100 | 6·08 | |
| Newport steam | 100 | 6.08 | 6·41 |
| Anthracite | 100 | 3.62 | 3·29 |

the plants apparently undergo change through the agency of a limited amount of oxygen absorbed from the air and from the sulphates in the water and soils which surround them; gases, such as marsh gas and carbon dioxide, are evolved, together with others having a more or less disagreeable odour, whilst the vegetable matter becomes soft and brown, and certain substances which dissolve in the waters and colour them brown are formed; eventually the vegetable matter is converted into a soap-like mass, which becomes consolidated by pressure, and varies in colour from brown to black according to the depth below the surface at which the peat is formed. A microscopic examination of sections of peat and coals of different ages shows that during these changes a black amorphous deposit forms within the cells and on the walls of the vessels of the plant structure; the cells become ruptured through the formation of the gases which cannot readily escape, the plant gradually loses its structure, and so the vegetable matter is transformed into a black amorphous mass or a yellow resinous substance.

How far the changes that have resulted in the formation of coal were identical with those taking place in the peat bogs it is impossible to say, but there is no doubt they were more or less similar in character.

Whatever the character of the actual decomposition may have been, it has been experimentally shown by Liebig and others that when woody fibre is buried in the ground in presence of small quantities of moisture, marsh gas, carbon dioxide, and water are produced These bodies are formed at the expense of the hydrogen, oxygen, and carbon in the vegetable matter, leaving a residue in which the quantities of hydrogen and oxygen bear a smaller proportion to the carbon than those in woody Marsh gas and carbon dioxide are always found in the fibre. coal measures; they exist in the pores of the coal and probably in cavities in the adjoining strata. Their presence is at least presumptive evidence that changes similar to those mentioned above have taken place during the formation of coal ; whether the changes have resulted in the passage of vegetable matter into peat and peat into coal it is difficult to say. It may have been so, but it is unlikely that every coal seam has been formed under similar conditions of temperature, pressure, and moisture. Difference of temperature and pressure will doubtless have tended to modify the course of the chemical changes, in some cases accelerating them, in others retarding them, so that whilst the general result has been the same, we find different varieties of coal not only in different coal fields, and in different seams in the same coal field, but even in the same seam.

Varieties of Coal.—Coal is usually divided into three classes, namely :—

Brown coal, or lignite.

Bituminous coal.

Anthracite.

The bituminous coal and anthracite comprise those coals found in the carboniferous formations, whilst the coals which occur in the more recent formations are included under the names of lignite, or brown coal.

In each class of coals there are different varieties, and although there are certain well-known characteristics which mark the difference between the more clearly defined varieties of each class, it is impossible to draw any sharp lines of division between the three classes.

Brown coal, or lignite, is found in most countries. The chief deposits are found in Westphalia, Lower Austria, Russia, North and Central America. In England it has been worked chiefly at Bovey Tracey in Devonshire, where it has been used as fuel in the local potteries. It occurs in the tertiary geological formations in three varieties.

(1) Fibrous brown coal, or lignite, presents more or less distinct traces of a vegetable structure, in some cases so well defined that flattened stems crossing one another in all directions, and the

more delicate structures, such as leaves and fruit, may be seen. It is usually dark in colour, soft when freshly got, but becomes brittle on exposure to the air, fracturing in the direction of the fibres of the wood.

(2) Earthy brown coal. This variety only occasionally shows any distinct indications of a vegetable structure; it is usually structureless, more or less friable, and has an earthy texture. Its colour varies from light to dark brown.

(3) Pitchy brown coal is the densest and hardest variety of brown coal; its colour is dark, often black; some varieties have a bright lustre, whilst others are dull and lustreless. It seldom shows any visible signs of a vegetable structure, and its fracture is conchoidal (shell-like).

The composition of lignite, or brown coal, is chiefly characterised by a comparatively low percentage of carbon, and a high percentage of oxygen, moisture, and ash. The following table gives the results of actual analyses of certain German lignites :---

| | Carbon. | Hydro- gen. | Oxygen. | Nitro- gen. | Sulphur. | Moisture. | Ash. |
|-------------|---------|----------------|---------|----------------|----------|-----------|-------|
| | | | | | | | |
| Lignite- | | | | | | | |
| Bavarian. | 56.68 | 4.20 | 32.91 | trace | 0.70 | 3.31 | 2.20 |
| Weimar . | 56.23 | 5.17 | 26.18 | | 0.67 | 10.77 | 0.98 |
| | 60.44 | 5.30 | 22.01 | trace | 0.86 | 10.74 | 0.65 |
| Brown coal- | | | | | | | |
| Bavarian. | 34.80 | 3 00 | 20.70 | 2.40 | 3.80 | 22.40 | 12.90 |
| | 39.10 | 2.75 | 8.25 | 0.90 | 6.20 | 23.50 | 19.00 |
| | 24.60 | 2.59 | 23.00 | | 4.32 | 17.00 | 28.50 |
| Pitch coal- | | | | | | | |
| Bavarian. | 75.10 | 4.30 | 18.80 | | | 2.70 | 1.10 |
| Prussian. | 70.60 | 3.54 | 20.75 | | 0.70 | 2.80 | 1.61 |
| Hungarian | 44.79 | 3.10 | 7.88 | 0.92 | 1.45 | 26.77 | 15.06 |
| U | | | | | | | |

Moisture in Brown Coal.-The quantity of moisture in freshly got lignite varies within wide limits : as much as 30 to 48 per cent. has been found, though sometimes the quantity present is only 1 or 2 per cent.; usually lignite contains about 10 to 20 per cent. A certain proportion of the moisture evaporates on exposure to the air, whilst the completely dried coal when exposed to the air will absorb as much as 8 per cent. of moisture. Ash of Brown Coal. - The quantity of ash in brown coal varies

greatly, and is frequently largely increased by the infiltration of water containing salts. It is seldom below 5 per cent. or above 10 per cent., though varieties are known containing as much as from 25 to 30 per cent. of ash. The amount of ash in the same deposit and even in the same piece may vary very greatly.

Sulphur in Brown Coal.—Frequently as much as from 4 to 6 per cent. of sulphur may be present, though some varieties contain less than 1 per cent.

Specific Gravity of Brown Coal.—There is considerable variation in the specific gravity of brown coal; it has been found as low as 1.1 in some cases and as high as 1.85 in others. On the average it is about 1.25, in which case a cubic foot of the coal will weigh about 80 lbs.

Brown coal burns freely with much flame and smoke, often producing a very disagreeable smell. It does not possess a very high value as a fuel owing to the high percentage of oxygen and large proportions of ash and moisture it often contains.

It is chiefly used on the Continent either direct from the pits or in the form of briquettes.

Bituminous Coal.

The name bituminous, which is applied to this class of coal, is somewhat misleading, as it implies that the coal contains bitumen, which is a carbonaceous mineral more or less soluble in ether, benzene, naphtha, &c.

Bituminous coal contains on the average only about 2 or 3 per cent. of matter soluble in these solvents, and therefore can hardly be said to contain bitumen. The name, however, has been given to this class of coal because certain varieties behave like bitumen when heated—that is, they swell up and give off large volumes of gases which burn with a brilliant flame.

Many varieties of bituminous coal are known which differ in their appearance and structure. Some are of a deep black colour with a brilliant lustre, whilst others are of a dull black, brown, or even grey colour. Some are soft or "tender," easily breaking when handled, and clearly showing the stratified character of their formations, whilst others are hard and compact, showing a less clearly defined stratified structure. The fracture also differs greatly, varying from a smooth conchoidal surface, closegrained and compact, to an uneven and splintery surface somewhat slaty in colour.

Various methods are adopted for the classification of bituminous coals.

Firstly, they may be divided into coking and non-coking coals, according to their behaviour in the coke oven. The former undergo semi-fusion and yield a coherent mass of coke, whilst the latter do not. This classification, however, does not include a certain variety of bituminous coal which only partially cokes when used alone in the coke oven, and is known in Germany as "Sinter Coal," whilst it may include anthracite and lignite, which are non-coking coals.

Secondly, certain physical properties of the coals are used as a means of classification, and the terms Hards or splint coal, Softs or cherry coal, Brights, Cannel or parrot coal, are frequently employed to distinguish different varieties of the same seam.

Thirdly, coals are classified according to their commercial use, namely, as gas, house, steam, coking, manufacturing coals. This method, though useful for commercial purposes, is somewhat indefinite, as many coals are equally well adapted for various purposes.

Attempts have been made to base a classification on chemical analysis without any definite success, and it may be said that a scientific method of classification has yet to be discovered. Perhaps in the present state of our knowledge it is best to combine the first three methods and divide all bituminous coals into coking and non-coking coals, subdividing the latter into hard or splint coal, soft or cherry coal, cannel or parrot coal.

Coking Coals are usually black and highly lustrous, and possess a close-grained or uneven fracture. When heated in the coke oven they form a pasty mass from which bubbles of gases escape as from dough, and eventually the mass solidifies forming a porous and coherent mass of coke of a totally different shape to that of the original coal. In consequence of this property slack or smudge may be converted into coherent masses of coke.

Coking coals usually burn with a long yellow flame, but are not very suitable for furnace use owing to their coking properties, which cause them to form a sticky mass which requires constant stirring.

Non-coking Coals do not yield a coherent mass of coke when heated in the coke oven. They do not pass through a pasty

condition, hence the particles of slack do not fuse together, whilst the coke produced from large coal retains the shape of the original lumps.

Hard or splint coal has usually a dull black colour, though sometimes it shows a bright resinous lustre. Its fracture varies greatly, being in some varieties irregular and splintery, in others fine-grained and conchoidal. It is kindled with difficulty, but in burning gives out great heat and is valuable for raising steam.

Soft or cherry coal is usually a brilliant lustrous coal of deep black colour. As its name implies it is easily broken, when it usually shows a straight and slaty fracture. It kindles easily and burns rapidly with a bright yellow flame, often coking.

Cannel or parrot coal. The name "cannel," supposed to be a corruption of the word "candle," is derived from its property of burning with a bright luminous flame resembling that of a candle. It is dense and compact, of a dull black colour, and does not soil the fingers. It splinters in the fire and burns clearly and brightly. Its chief value consists in the high illuminating power of the gas produced by its distillation. It is capable of receiving a high polish. Its fracture is smooth, either conchoidal or slaty.

. The properties which should distinguish coals according to their commercial uses are as follows :----

Gas coals are distinguished by yielding a large volume of gas when distilled above a temperature of about 1700° F., usually from 9000 to 11,000 cubic feet per ton. Their value is increased by their yielding at the same time from 1 to 1.5 per cent. of ammonium sulphate and about 4 per cent. of tars which contain hydrocarbons of the benzene series, and phenols.

House coal should burn freely at first with a bright hot flame, without coking, eventually yielding a clear bright red fire which radiates a considerable amount of heat. A small quantity of ash and freedom from sulphur are desirable.

Steam coals should not coke in the furnace. They should not burn too quickly, but with a long hot flame. The ash should be infusible and not given to clinker, whilst freedom from sulphur and pyrites is important owing to the destructive action which these bodies have on the fire-bars.

Composition of Bituminous Coal.—The amounts of the chief

constituents in bituminous coal vary within certain limits, namely :---

Carbon from 80 to 90 per cent. Hydrogen about 5 per cent. Oxygen from 7 to 14 per cent. Sulphur from 0.5 to 1.5 per cent.

The following table contains some typical examples of the composition of bituminous coals :---

| | Carbon. | Hydro- gen. | Nitro- gen. | Sulphur. | Oxygen. | Ash. |
|-------------------|---------|----------------|----------------|----------|---------|------|
| Welsh- | | | | | | |
| Graigola | 84.87 | 3.84 | 0.41 | 0.45 | 7.19 | 3.24 |
| Rock Vein | 82.25 | 5.84 | 1.11 | 1.22 | 3.58 | 6.00 |
| Newcastle- | | | | | | |
| Hartley Main . | 81.85 | 5.29 | 1.69 | 1.13 | 7.53 | 2.51 |
| Yorkshire- | | | | | | |
| Barnsley Seam . | 76.68 | 4.79 | 1.76 | 1.28 | 7.56 | 3.93 |
| Silkstone | 81.98 | 5.70 | 1.83 | 1.52 | 5.26 | 2.36 |
| Derbyshire | | | | | | |
| Blackshale | 76.84 | 5.22 | 1.59 | 2.34 | 5.60 | 4.45 |
| Lancashire— | | | | | | |
| Arley | 83.54 | 5.24 | 0.98 | 1.05 | 5.87 | 3.32 |
| Pemberton, 4 foot | 77.01 | 3.93 | 1.40 | 1.02 | 5.52 | 1.09 |
| Little Delf . | 82.70 | 5.55 | 1.48 | 1.07 | 4.89 | 4.31 |
| | | | | | | |

Ash of Bituminous Coal.—The amount of ash in clean samples of bituminous coal is usually low, but in the commercial article it is often increased by the presence of a certain amount of dirt which it is impossible to pick out completely. The amount varies from 1 to 7 per cent. in clean coal, though it may rise to 10 or 14 per cent. in particularly dirty coal.

The colour of the ash varies from pure white to dark red or brown. The red colour indicates the presence of iron, which is usually derived from pyrites, whilst the shade of red is often an intimation of the quantity of pyrites present.

The ash of bituminous coal consists chiefly of aluminium silicate, with varying quantities of ferric oxide, lime, and sul-

phuric acid. In some cases the composition of the ash resembles that of the fireclay found in conjunction with the seam.

Sulphur in bituminous coal usually amounts to from 0.5 to 1.5 per cent., though occasionally larger quantities are found.

The Specific Gravity of Bituminous Coal.—The specific gravity of bituminous coal varies from 1.2 to 1.3, the weight of a cubic foot being from 75 to 81.5 lbs.

Anthracite.

Anthracite, stone coal or culm, is probably the oldest form of fossil fuel. It is the densest, hardest, and most lustrous of all varieties. It has a deep black colour, does not soil the fingers, and possesses a conchoidal fracture. Its chemical composition differs greatly from other varieties of coal, and is characterised by a very high percentage of carbon (from 90 to 94 per cent.) and small quantities of hydrogen, oxygen, and nitrogen. The quantity of ash is unusually small.

The composition of anthracite is given in the following table :---

| Locality and Seam. | Carbon. | Hydrogen. | Nitrogen. | Oxygen. | Sulphur. | Ash. |
|--------------------|---------|-----------|-----------|---------|----------|------|
| Welsh- | 00.00 | 0.00 | 0.54 | 1.05 | 0.00 | 1.00 |
| Timber Vein | 93.00 | 3.08 | 0.24 | 1.67 | 0.68 | 1.03 |
| Low Level . | 94.18 | 2.99 | 0.20 | 0.76 | 0.29 | 0.93 |
| Kilgetty . | 93.27 | 2.72 | 0.18 | 2.47 | 0.15 | 1.21 |
| Big Vein . | 92.56 | 2.11 | 4. | 68 | 0.12 | 0.43 |
| Brass Vein . | 91.11 | 3.58 | 3. | 42 | 0.59 | 1.51 |
| American- | | | | | | |
| Pennsvlvania | 86.91 | 2.80 | 3. | 89 | 0.43 | 5.97 |
| French- | | | | | | |
| Sablé | 87.22 | 2.49 | 3. | 39 | | 6.90 |
| Isire | 94.00 | 1.49 | 0. | 85 | | 4.00 |
| | | | | | | |

Anthracite splinters when heated, ignites with difficulty, and burns without smoke. The smokeless character of its combustion makes it valuable for use on board the ships of the navy and in the drying of malt and hops. It may also be burnt in specially constructed stoves for domestic purposes. It is a noncoking coal. Its specific gravity varies between 1.3 and 1.75.

The ash of anthracite consists chiefly of silica, alumina, and oxide of iron.

Constituents of Coal.—Amongst the constituents of coal, carbon and hydrogen are the most important; it is by their combustion that the heat is generated on which the value of coal as a fuel depends.

Nitrogen has no value when coal is used as a fuel, but it has considerable value when coal is distilled in the gas retort, or retort coke oven, when a certain proportion is obtained as ammonia among the volatile products recovered, and this is subsequently converted into ammonium sulphate.

The presence of oxygen does not add to the value of coal as a fuel. It is generally assumed that during combustion the oxygen in the coal forms water with the hydrogen; hence the greater the quantity of oxygen in the coal the smaller the quantity of hydrogen that is available for combustion with atmospheric oxygen, which naturally reduces the amount of heat produced by the combustion.

Sulphur is a specially injurious constituent of coal. It is present partly as an impurity, as iron pyrites, FeS_2 , and as gypsum (calcium sulphate), $CaSO_4 + 2H_2O$, and partly as a constituent, when it is known as "organic sulphur."

The presence of large quantities of sulphur is objectionable, whether the coal is used as a fuel or for metallurgical purposes. When used as a fuel part of the sulphur is converted into sulphur dioxide, which pollutes the atmosphere, and a part acts on the fire-bars of the furnace, forming fusible sulphide of iron; this is especially the case if large quantities of iron pyrites are present. Sulphur acts most injuriously on most metals, often producing red shortness and destroying their malleability and ductility; hence it is desirable that coal used for metallurgical purposes should be as free from sulphur as possible.

| No. of Sample | s. | | Coal. | Mean per cent. Sulphur. |
|------------------|----|--|------------|----------------------------|
| 37 | | | Welsh | 1.42 |
| 8 | | | Derbyshire | 1.01 |
| 28 | | | Lancashire | 1.42 |
| 17 | | | Newcastle | 0.94 |
| 8 | | | Scotland | 1.45 |

Ash of Coal.—The ash of coal is the incombustible mineral matter which remains after complete combustion of the fuel has taken place. It exists in the coal partly in the form of an inseparable constituent and partly mixed with the coal in the form of dirt or bind. Sometimes the dirt is so intimately mixed with the coal that it is difficult to separate it, but when this is not the case it can be removed either by hand-picking or washing.

| Coal. | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | K ₂ 0 Na ₂ 0 | SO3 | P_2O_5 |
|--|------------------|--------------------------------|--------------------------------|--------------|--------------|---------------------------------------|-------------|----------|
| Lignite Bituminous— Average of five samples of | 34•53 | 16•86 | 14.23 | 13•33 | 0.86 | 6.06 | 13.04 | 0.84 |
| Welsh coal (Phillips) . Average of five samples of Scotch coal | 42.67 | 43 | 56 | 6.62 | 1.08 | | 4•46 | 0.66 |
| (Phillips) . Newcastle . Anthracite— Average of | 49•63 59·56 | 38 [.] 12·19 | ·21 15·96 | 3·18 9·99 | 1·41 1·13 | 1·13 | 6·26 8·2 | 1·03 |
| American . | 52·08 | 36-45 | 7.98 | 1.79 | 1.28 | ••• | ••• | |

Composition of Ash of Coal.

The presence of ash in the coal diminishes its value as a fuel by reducing the proportions of combustible matter. The fusibility of the ash is also of some importance. A fusible ash is apt to clinker in the furnace, causing considerable trouble in keeping the fire clean, and it is also liable to arrest combustion of the fuel by forming a glaze on the lumps before all the combustible matter has been completely burnt.

An excessive quantity of phosphoric acid in the ash is highly prejudicial when the coal is used for iron smelting, causing the metal to become cold short.

Small quantities of arsenic are present in coal. Sir Edward Thorpe has found about 0.0004 per cent. in coal in a form which is not volatilised during combustion but is retained by the ash. He has also shown that any arsenic that may be present in the iron pyrites is partly volatilised during combustion, but by far the greater quantity is not volatilised (Thorpe, J. Chem. Soc., vol. lxxxiii. p. 969).

Moisture in Coal.—Freshly got coal always contains moisture which can be expelled at a temperature between 100° and 110° C., and the coal thus dried will absorb a certain amount of moisture on exposure to moist air.

The quantity of moisture varies greatly in bituminous coals; in some varieties it only amounts to 1 or 2 per cent., in others as much as 6 to 11 per cent. may be present.

Moisture reduces the calorific value of coal inasmuch as a certain proportion of the heat of combustion is absorbed by its evaporation.

Coke.

Coke is the carbonaceous residue which remains after coal has been subjected to destructive distillation. It chiefly consists of carbon and the mineral ash of the coal, together with smaller quantities of hydrogen, oxygen, nitrogen, and sulphur.

When coal is subjected to distillation either in absence of air or in presence of very limited quantities of air, it undergoes decomposition into carbon and certain gaseous and liquid bodies which are called "Volatile Products." The volatile products are formed at the expense of the hydrogen, oxygen, nitrogen, and sulphur in the coal, which combine with one another and with carbon.

When a coking coal is used the residue forms a porous or cellular but coherent mass, but if a non-coking coal is used the residue is non-coherent. The difference in the result obtained with these two classes of coals is due to the fact that coking coals pass through a pasty condition during the process of distillation, and the pasty mass subsequently carbonises, whereas a non-coking coal does not pass through the pasty condition.

Up to the present time no satisfactory explanation has been given of the cause of the difference in the behaviour of these two kinds of coal. The coking properties of a coal cannot be judged from the yield of "volatile products," for although coking coals usually yield from 17 to 33 per cent. of volatile products, noncoking coals often yield the same amount.

It has been suggested that the "disposable hydrogen," or the proportion of hydrogen in excess of that required to form water

with the oxygen in the coal, may determine the coking properties, but this was disproved by Dr. Percy. Another suggestion is that in coking coals the ratio of hydrogen to carbon is from 1 to 15 to 1 to 17, but coking coals are known in which the ratio is 1 to 10.

Professor W. Carrick Anderson states that coking properties are possessed by coals which contain 5 to 6 per cent. of hydrogen, 10 per cent. of oxygen, and 4 per cent. of disposable hydrogen, whilst their specific gravity is 1.35. The general application of this theory has not been tested.

It is unlikely that any definite conclusion as to the cause of the coking properties of coking coals will be arrived at until more is known about the various constituents of coal. Until then the only method of determining its coking properties is to test the coal in a coke oven.

Coke is chiefly used in metallurgical processes, and of these the most important is the manufacture of iron and steel. The properties which a good metallurgical coke should possess are porosity, hardness, and resistance to the action of carbon dioxide.

The porous structure is necessary to allow the air for combustion to penetrate through the mass of the coke and so promote combustion throughout the whole mass of the fuel instead of only at the surface.

Hardness is essential to enable the coke for use in the blast furnace to resist the pressure of the charge above it without being crushed to powder, otherwise the passage of the gases up the furnace will be obstructed, and when the fuel reaches the zone where it has to meet the air from the tuyère it will burn away too rapidly and the proper temperature will not be produced.

Coke should not readily interact with carbon dioxide to form carbon monoxide, otherwise in the blast furnace this action will take place in the upper zones of the furnace and there will be a deficiency of fuel when it reaches the combustion zone.

The porosity is determined by the rate of coking, and this is largely determined by the quality of the coking coal. Some coking coals which yield a very large percentage of volatile products become exceedingly fluid at high temperatures, and if too rapidly heated the gases escape very quickly, the pasty mass settles down before carbonisation begins, and the resulting coke is deficient in porosity; other coals less rich in their yield of volatile products do not become so fluid, and unless rapidly heated to the highest possible temperature are liable to form too large cavities and pores, the walls of which are weak.

The porosity of coke is measured by the percentage volume occupied by the cells, and it is stated by Fulton¹ that the most favourable results are obtained with coke in which the volume occupied by the cells is about 56 per cent. of the total volume of the coke.

The hardness of the coke depends on the temperature at which the coking takes place. The hardest coke is produced at the highest temperatures and by maintaining the charge at a high temperature after the coking process is completed.

Experience alone can tell what treatment will give the best results with any particular class of coal, though it may be stated generally that fat coals require to be more gradually heated to the highest coking temperature than lean coals.

The resistance to the action of carbon dioxide is mainly determined by the hardness of the coke. Sir I. Lowthian Bell gives the following composition of the gas obtained by passing 800 cubic centimetres of carbon dioxide over red-hot coke during thirty minutes :--

| | | I | Hard Coke | . Soft Coke. |
|--------|----------|---|-----------|--------------|
| Carbon | dioxide | | 94.56 | 69.81 |
| Carbon | monoxide | | 5.44 | 30.19 |

Whilst the temperature which produces the best result is largely determined by the class of coal coked, the temperature at which the pasty condition, so essential for the production of good coke, takes place is considerably above that at which coal begins to decompose, namely, 300° C., and often prolonged heating at 300° C. causes the loss of coking properties in some coals and considerably lessens them in others. The usual coking temperature is about 1100° to 1500° C.

Purity of Coke.—The purity of the coke is of the highest importance. Ash, sulphur, and phosphorus form the chief impurities.

The ash is derived from (1) the dirt mixed with the coal; (2) natural mineral constituents of the coal. The dirt can be

removed by washing the slack previous to coking, and a washer is rapidly becoming an essential part of every coking plant, especially in connection with by-product ovens, where the presence of about 10 per cent. of water in the coking slack is necessary. When washing is resorted to the ash then found in the coke is derived from the mineral constituents of the coal, and the amount present depends on the percentage of ash in the coal and the yield of coke.

A high percentage of ash is usually objectionable; firstly, because when coke is used as fuel the proportion of carbon decreases as the proportion of ash increases, and labour in stoking is greater owing to the increased attention that has to be given to the fires. Secondly, because when coke is used for metallurgical purposes there is a smaller proportion of carbon, and the coke ash has to be removed in the slag together with the impurities in the ore, and the higher the proportion of ash the larger the quantity of flux that must be used in the smelting process.

Sulphur is perhaps the most injurious constituent in coke. When coke is used as fuel excess of sulphur causes destruction of the fire-bars owing to the formation of fusible iron sulphide. In smelting operations the sulphur in coke usually combines with the metal, with the most injurious consequences, especially in the manufacture of iron and steel, when it produces red shortness.

The sulphur in coke is derived from (1) pyrites, (2) gypsum, (3) the organic sulphur. When washing of the slack is resorted to the pyrites and gypsum are more or less completely removed, but the organic sulphur remains as a constituent of the coal. During coking only a portion of the organic sulphur is expelled with the volatile products, whilst a portion always remains in the coke, partly as sulphates and partly as sulphides. The actual proportion of the total sulphur that remains in the coke is largely determined by the character of the coal. Coke for steel smelting and for foundry purposes should not contain more than 1 per cent., and the best qualities contain less; 1 to 1.2 per cent. of sulphur is considered sufficiently high for blastfurnace coke.

Sulphur in coke acts so injuriously on iron and steel that many processes have been devised for reducing the quantity present. Some of these consist in adding lime, salt, dioxide of manganese, and similar bodies, to the slack before coking. These substances, however, tend to increase the quantity of sulphur in the coke, and at the same time to increase the quantity of ash. Other processes consist in treating the coke, whilst red-hot, with steam or air under pressure; the former interacts with the sulphides, forming sulphuretted hydrogen, which escapes, whilst the latter is supposed to burn the sulphur away. Both these processes do remove small quantities of sulphur, but in doing so large quantities of carbon are burnt away, hence they are not economical.

It has been proposed to treat the incandescent coke with acetic acid, which was successful in removing small quantities of sulphur; but the difference was so slight that for practical purposes the process is ineffectual.

 $\hat{P}hosphorus$ is present in the ash of coke as phosphoric acid combined with bases, and cannot be eliminated in the coking process. The quantity is small, amounting to about 0.01 to 0.3 per cent.; it produces "cold shortness" in iron and steel.

Two other impurities in coke are of importance, namely, arsenic, and volatile matter.

Arsenic.—The presence of arsenic in coke is of importance when the coke is used for stoving malt. If volatile forms of arsenic are present they will escape with the products of combustion, and traces of arsenic will be found in the malt. Sir E. Thorpe, who has investigated the subject, finds that the arsenic present in coke does not volatilise during combustion, hence no danger arises of contamination of malt with arsenic volatilised from coke when it is used as fuel in stoving kilns. A slight danger may arise from particles of ash in the form of dust being carried into the kilns and settling on the malt.

Volatile Matter.—Small traces of volatile matter are always found in coke, and usually do not affect its value, but if an appreciable amount is present it gives rise to smoke during combustion, which is very objectionable if the coke is used for drying malt and hops.

Water in Coking Slack.—Wherever washing is resorted to wet slack is used for coking. A certain proportion of water is beneficial, and sometimes even necessary. Firstly, it causes the particles of slack to pack more closely together and so reduces the air spaces in the mass, consequently the loss of carbon by burning is less. Secondly, in retort ovens, where the

volatile products are recovered, it reduces the amount of coal dust that is carried over into the gas mains. Excess of water, however, is most injurious because of the large amount of heat absorbed in its evaporation, which tends to reduce the temperature of the coking mass in the early stages and to prolong the time taken to reach the proper coking temperature. The steam produced also acts injuriously on the fabric of the ovens.

Specific Gravity of Coke.—The specific gravity of coke may be either "real," that is, the specific gravity of the coke particles, or "apparent," the specific gravity of the porous mass. The quality of the coal used in coking influences the specific gravity of the coke, and the "real" specific gravity generally varies between 1.6 and 1.8, whilst the "apparent" specific gravity varies from 0.6 to 1.

Good metallurgical coke generally gives a sonorous metallic ring when struck.

Coke attracts moisture from the air, and too much exposure to the weather renders it soft and liable to crumble.

Good coke for metallurgical purposes is a hard grey substance with a highly developed cellular structure. It should be uniform in quality, free from dirt, and capable of being roughly handled without breaking up into breeze.

The Coking Process.

The manufacture of coke is carried out to-day either in the Beehive oven or the retort oven, and in both cases the process may be conducted with or without the recovery of by-products from the volatile substances produced by the distillation.

The Beehive Coking Process.—This process is usually conducted without the recovery of by-products. The oven consists of a dome-shaped chamber about 11 feet in diameter and 7 to 8 feet high from the floor to the top of the dome. In front of the chamber is a doorway, which serves for the extraction of the coke and is built up with bricks and puddled clay during the coking process, whilst at the top of the dome is a hopper through which the charge is introduced, which can be closed with a damper whilst the charge is coking.

The ovens are built in batteries consisting of two rows back to back, with a flue running between them; from each oven there is a port opening into this flue which passes to the steam boilers and from thence to the chimney-stack. Sets of rails run along the whole length of each row of ovens, so that corves of slack can be run directly over the hoppers for the purpose of charging. Slack is filled into the oven to a depth of about 21 to 23 inches and levelled; a small opening is left in the brickwork of the door for the admission of air. In a short time the coal begins to decompose under the action of the heat retained in the masonry of the oven from the previous coking operations, assisted by the heat from adjacent ovens in full work, and in from half to one hour after charging the gases take fire. These gases burning in the dome of the oven heat the charge, which cokes gradually from the top downwards and swells up. When the coking is complete the hole in the door is closed and the charge kept at a red heat for some hours longer, when contraction takes place, which improves the hardness of the coke.

When once the charge is well alight the damper is placed over the hopper, and the partially burnt gases escape through the port into the gas flue and pass to the boilers, where they are used to generate steam. When the coking is complete the door is broken down and the charge quenched with water inside the oven, when the coke breaks up at right angles to the surface into columnar pieces. The cooled charge is then drawn. Sometimes the charge is withdrawn whilst red-hot and covered with coke dust to exclude the air while cooling. The time required for coking depends on the size of the charge and varies from 48 to 96 hours.

The process is somewhat wasteful; a certain quantity of the fixed carbon of the coke is burnt away by the air admitted to the oven, whilst certain valuable substances known as byproducts, which are contained in the gases, are entirely consumed either in the oven itself or under the boilers. The coke, however, is of excellent quality; it is hard, bears handling and carriage without breaking, and has a steel-grey colour. Owing to the practice of quenching in the oven, it usually contains only very small quantities of moisture.

Coking with Recovery of By-Products.

The great commercial value of some of the substances that are contained in the volatile products of the distillation of coal has led to the adoption of coking processes by which these bodies can be recovered. The process is carried out in the beehive oven, or in specially constructed ovens known as retort ovens.

Beehive Ovens with Recovery of By-Products.—Amongst ovens of this type are the Jameson, Aitken, Chambers, and Pernolet. In the first three ovens the coking is carried out by admitting air into the dome of the oven, as in the ordinary Beehive coking process; the oven, however, is fitted with channels or ports in its floor or base. These channels are connected by mains with exhausters, which cause the volatile substances to pass downwards through the coking mass, and to be conveyed to a special condensing plant for the recovery of the by-products. Certain residual gases which remain after the recovery of the by-products are either returned to the dome of the oven, where they are used to heat the coking mass as in the Aitken oven, or are used for generating steam by combustion under the boilers.

In the Pernolet oven no air is admitted into the oven, and the volatile products are removed through stand pipes in the roof of the oven. The ovens are heated externally by burning the residual gases from the recovery plant in flues built beneath the floor of the ovens. Coke breeze is also burnt in grates specially provided for the purpose.

Retort Coke Ovens.

The manufacture of coke in the retort oven resembles the distillation of coal in the gas retort inasmuch as it is carried out by distilling the coal in a closed chamber from which all air is excluded. The chief difference between these processes consists in the capacity of the coking chamber. Whilst the gas retort is small, holding only a few hundredweights of coal, the retort oven is large, capable of holding from 7 to 10 tons of coal.

The coking process in the retort oven may be carried out with or without the recovery of by-products. In the original retort ovens of Knab and Coppée by-products were not recovered, but very few retort ovens of that description are now erected.

The retort oven consists of a long, narrow chamber, which may be vertical or horizontal. In the former type the oven has openings at the top and bottom, whilst in the latter type the openings are at each end. The horizontal type of oven is the one most usually adopted. In this type the coking chamber (Fig. 85) is about 30 feet long, 6 to 7 feet high from the floor

to the crown of the arched roof, and from 15 to 22 inches wide. Each end is open and fitted with doors, which are closed and



FIG. 85.

Horizontal Retort Oven. Section through oven chamber.

well luted with puddled clay, technically known as "daub," during the coking process.

The chamber is surrounded with a series of flues; one runs



Horizontal Retort Oven. Section through side flues.

By permission, from the Trans. Inst. M. E.

beneath the floor of the oven, and is known as the sole flue, G (Fig. 85), whilst others, N (Fig. 86) called side flues are built in the side walls of the oven. The side flues may be either horizontal or vertical. In these flues gases for heating the oven are burnt, the air required for their combustion being supplied through a series of flues known as air flues, F (Fig. 86). The sole and side flues of the oven are connected by ports with a large flue known as the waste gas flue, P (Fig. 86), which carries the burnt gases under boilers, where they help to generate steam, and from thence to the chimney-stack.

In the roof there are three openings, A (Fig. 85), which serve for purposes of charging, and also one or two, B, through which the volatile products are removed. The latter are fitted with stand pipes, which communicate with the mains that carry the volatile substances to the by-product plant. These stand pipes are fitted with valves, which, when closed, shut off the connection between the oven and the by-product plant.

Retort ovens in which the by-products are not recovered, and also many in which they are, have a series of ports at the top of their side walls, which communicate directly with a horizontal flue, M (Fig. 86) placed over the side flues. When the byproducts are not recovered the volatile substances, instead of being removed through the stand pipes and conveyed to the recovery plant, pass through these ports into the side flues, where they burn and heat the ovens; but when the by-products are recovered the ovens are heated by residual gases from the recovery plant. These gases are conveyed in mains, known as return mains, C (Fig. 86), to the ovens, and burnt in the sole and side flues.

The ovens are built in batteries of thirty-five to fifty ovens. In front of the battery is a platform, or coke bench, which is level with the floor of the oven. The coke is received on the bench when the oven is drawn. From the back of the battery the oven is discharged by means of a mechanical ram, which, running on rails, is brought opposite the oven to be emptied, and pushed forward, so that it pushes the coked mass on to the platform in front.

The charging of the ovens may be carried out by hand, when the slack is introduced through the charging holes in the roof and levelled. In some modern plants, however, it is usual to charge the ovens with a compressed cake of slack. This cake is made in a machine called a "compressor," in which is a trough of the same length as the oven, but slightly narrower. Wet slack is run into the trough from a hopper, whilst a stamp

which travels the length of the trough compresses it into a cohesive cake. The cake is then pushed into the oven through the doorway.

Retort ovens may be divided into two classes—(1) ovens with horizontal side flues; (2) ovens with vertical side flues. These may be further sub-divided into ovens in which there is a single set of side flues between adjacent ovens, and ovens which have a double set of side flues between adjacent ovens. In the first class, which may be called single-flued ovens, each set of side flues has to heat two oven walls; in the second class, or double-flued ovens, each set of side flues has only one oven wall to heat.

The number of different ovens is legion, therefore it is only possible to mention a few of the more important.

Horizontal-Flued Ovens.

Single-flued Ovens. Simon Carvés. Huessener. Double-flued Ovens. Semet-Solvay. Colin.

Double-flued.

Brunck.

Vertical-Flued Ovens.

Single-flued. Otto Hoffmann. Otto Hilgenstock. Poetter. Kopper.

In some types of ovens the air for combustion is heated before it reaches the combustion flues. This is usually effected by causing the air to traverse a series of flues, which are heated by waste gases after they leave the combustion flues and before they reach the boilers. These ovens are known as regenerative ovens. In other types no special means are taken to heat the air.

The Coking Process.—In this process the ovens are always maintained at a red heat. As soon as an oven is discharged it is immediately recharged, either mechanically from the compressor or by hand. The doors are closed and well daubed with puddled clay, and the charging hoppers are covered with lids, which are also well daubed.

Distillation begins at once, and the products are removed by

exhaustion through the stand pipes. Coking is usually complete in from 36 to 48 hours, according to the width of the oven and the quality of the coal. When the process is completed the valve of the stand pipes is closed, the oven doors opened, and the red-hot mass pushed out on to the coke bench, where it is quenched with water. As soon as the oven is emptied the doors are closed, and recharging is commenced.

The temperature at which the coking takes place varies somewhat with the quality of the coal, but is usually between 1000° C. and 1300° C. The quality of the coke and the byproducts depends on maintaining as high a temperature as possible uniformly distributed over the whole oven, consequently great care and experience are required in burning the gases in the flues. The best results can only be obtained when the proportions of gas and air are properly regulated, and when both gas and air are properly distributed throughout the different flues.

A certain quantity of moisture in the coking slack used in retort ovens is necessary to prevent an excess of coal dust from entering the mains with the volatile products, and, where compressors are used, to enable a cake of slack to be formed strong enough to be pushed into the oven without breaking. The amount should not exceed 9 or 10 per cent.; any excess is exceedingly harmful, because its evaporation causes an unnecessary reduction in the temperature of the oven, thereby delaying the coking process, and also increases the amount of water to be dealt with in the by-product plant, thereby unnecessarily increasing the quantity of ammonia liquor and reducing its strength.

Charging and Discharging the Ovens.—A regular evolution of by-products is essential to the proper working of the coking process, and to effect this the ovens should be charged and discharged as systematically as possible, care being taken that adjacent ovens are not discharged at the same time, or an excessive cooling of the flues heating those ovens will take place.

Quenching the Coke.—As the coke is quenched outside the oven it is liable to contain excess of moisture when quenched by hand, unless care and intelligence be exercised in the process. The quenching will be more effective and the coke left drier, if large volumes of water are thrown over it when it first leaves the oven, smaller quantities being used later when the coke

ceases to glow. To avoid the use of excessive quantities of water and to more rapidly cool the coke, quenching machines are sometimes used, in which the coke passes through a box with open ends, and several tons of water are forced under high pressure, in the form of sprays, into the coke as it is pushed through.
CHAPTER XI

BY-PRODUCTS AND THEIR RECOVERY

THE recovery of the by-products from the volatile substances produced by the distillation of coal is essentially a chemical process requiring a knowledge of the properties of the substances to be dealt with.

The volatile products leaving the ovens are a complex mixture, which, in the recovery plant, is separated into—

Tar. Ammonia liquor. Benzol. Incondensable gases.

In addition to these there is a small quantity of cyanogen, which is not, as a rule, dealt with.

Tar.—The tar is a black fœtid-smelling liquid consisting of a mixture of definite chemical compounds, together with a large proportion of pitch. The compounds found in tar are as follows :—

1. Compounds of carbon and hydrogen—Hydrocarbons. These may be divided into two classes.

(1) Fatty hydrocarbons; (2) Aromatic hydrocarbons.

The fatty hydrocarbons may belong to either the paraffin, olefine, or acetylene groups.

The aromatic hydrocarbons usually belong to the benzene, naphthalene, and anthracene groups.

In some tars the hydrocarbons present chiefly belong to the fatty group, whilst in others they are replaced by aromatic hydrocarbons. Watson Smith calls the former "paraffinoid tars" and the latter "benzenoid tars."

2. Compounds of carbon, hydrogen, and oxygen.

These bodies may be acids, such as acetic acid, benzoic acid, &c.; or phenols, such as phenol (carbolic acid), cresol, naphthol, &c.

3. Compounds of carbon, hydrogen, and nitrogen, which may be bases, such as aniline, C_6H_7N , &c.; or neutral bodies, such as pyrrol, C_4H_5N , carbazol, $C_{12}H_6N$, &c.

4. Sulphur compounds, namely thiophene, C_4H_4S , &c.

5. Pitch containing a certain proportion of solid carbon.

The tar produced from most coals may be either paraffinoid or benzenoid in character, according to the temperature of distillation. At about 450° C. the tar produced contains chiefly paraffin and olefine hydrocarbons, but as the temperature rises the character of the hydrocarbons gradually changes, till at a temperature between 900° C. and 1100° C. aromatic hydrocarbons almost completely replace the fatty hydrocarbons. With cannel coal, however, a large proportion of fatty hydrocarbons is usually formed even at high temperatures.

Paraffinoid tars are usually lighter than water and more mobile than benzenoid tars. Among the oxygen compounds acetic acid is sometimes found, whilst phenol (carbolic acid) is absent, though more complex phenols are present. Paraffin wax is usually a constituent of a paraffinoid tar.

Benzenoid tars usually have a specific gravity from 1.1 to 1.2, and are thicker and more viscous than paraffinoid tars, owing to the presence of free carbon. Phenol is present in large quantities, to a certain extent replacing the higher phenols. Amongst the hydrocarbons the presence of naphthalene and anthracene and the absence of paraffin wax are special characteristics, whilst in many cases large quantities of pitch are present.

The tars obtained in the Jameson and Chambers ovens are paraffinoid tars, whilst those produced in the retort oven are benzenoid tars.

The benzenoid tars are more valuable than paraffinoid tars. The latter can be used for fuel, or are worked up into burning or lubricating oils and paraffin wax. The former, without further preparation, are used as fuel, for the manufacture of gas, for coating metals and building materials as a protection against the action of the atmosphere, in the preparation of building felt and lamp-black, and as an antiseptic.

Large quantities of benzenoid tar are subjected to a process

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of fractional distillation, when it is divided into fractions known as-

Specific Gravity.

| First runnings, boiling below 100° C. | | |
|---|---|------|
| Light oils, boiling between 100° C. and 150° C. | | 0.9 |
| Carbolic oils, " " 150° C. and 210° C. | • | 1.01 |
| Creosote oils, " " 210° C. and 270° C. | | 1.04 |
| Anthracene oils, boiling above 270° C | | 1.10 |
| Pitch, residue remaining in boiler. | | |

The light oils serve for the manufacture of solvent and burning naphthas, also of benzol, used in the manufacture of aniline dyes. From the carbolic oils phenol and naphthalene are obtained; creosote oil is used chiefly for pickling timber to protect it from decay, and also for the manufacture of sheep-wash; whilst from the anthracene oils anthracene is recovered and used for the manufacture of alizarin, the colouring matter of Turkeyred dye.

The quantity of tar generally obtained in the coking process amounts to about 4 to 5 per cent.

Ammonia Liquor.—The ammonia liquor is a solution of ammonia and ammonium salts, which is obtained partly by condensation in the mains and partly by washing the volatile products with water.

When coal is distilled only a certain proportion of the nitrogen in the coal is volatilised, and it is found in the volatile products as free nitrogen, ammonia, and certain nitrogenous carbon compounds such as cyanogen, aniline, &c. According to Schilling, when coal is distilled at 1100° C. to 1200° C. from 20 to 56 per cent of the nitrogen is volatilised, of which from 6 to 17 per cent. is obtained as ammonia. The table on page 200 showing the distribution of nitrogen in the products of coal distillation, is given by Knublauch as the result of his investigations on German coals.

The actual yield of ammonia depends primarily on the quality of the coal and on the temperature of distillation. C. R. A. Wright has shown that the maximum yield of ammonia is obtained at a moderate temperature, above or below which the yield diminishes. The actual temperature is not stated, but with the coal used the greatest yield of ammonia

was obtained when about 10,000 cubic feet of gas per ton of coal was produced by the distillation. Moisture in the coal is said to be favourable to a high yield of ammonia.

| Percentage | of | the | Total | Nitro | gen in | the | Coal | found | in | the |
|------------|----|-----|-------|--------|---------|-------|------|-------|----|-----|
| | | | Produ | cts of | Distill | ation | n. | | | |

| Volatilised Nitrogen. | Westpha | Saar Coal. | |
|---|--------------------------------------|---|-----------------------------|
| | I | II | |
| Gas Ammonia Cyanogen Tar Coke | $55.0 \\ 11.9 \\ 1.8 \\ 1.3 \\ 30.0$ | $\begin{array}{c} 47 \cdot 1 \\ 14 \cdot 1 \\ 1 \cdot 8 \\ 1 \cdot 4 \\ 35 \cdot 6 \end{array}$ | 16.1 15.9 4.1 63.9 |
| Percentage of nitrogen in the coal | 100 1.55 | 100 1·479 | 100 1·176 |

During the recovery process a large proportion of the ammonia is dissolved by the water which condenses in the mains and forms dilute ammonia liquor. In this way about 75 per cent. of the ammonia is recovered, the remaining 25 per cent. is subsequently removed by washing, for which process dilute ammonia liquor is used. The solution thus obtained is a complex mixture of ammonia and ammonium salts in which the ammonia is technically known as "free" and "fixed,"

The "free" ammonia is that which can be expelled from the solution by steam, and is present either as ammonia or salts of ammonium with weak acids which are decomposed by steam. The "fixed" ammonia is that which is present as ammonium salts, which are not decomposed by steam, but require the presence of an alkali to effect their decomposition. The proportion of the fixed ammonia in ammonia liquor is generally much greater than that of free ammonia and is shown in the following table :—

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| Coal. | Fixed. Per cent. | Free. Per cent. |
|---------------|--|---|
| Silkstone (1) | $ \begin{array}{r} 1.891 \\ 2.211 \\ 2.254 \\ 2.404 \\ 1.415 \\ 1.598 \\ \end{array} $ | $\begin{array}{c} 0.354 \\ 0.276 \\ 0.392 \\ 0.705 \\ 0.841 \\ 0.457 \end{array}$ |

Ammonia.

In the following table is given the analysis of ammonia liquor from the Leeds Gas Works :---

| | | | | Grammes |
|----------|--------------|-----|---|------------|
| | | | | Per Litre. |
| Ammonium | sulphide | | | 3.03 |
| ,, | mono carbon | ate | | 39.16 |
| ,, | chloride | | | 14.23 |
| 22 | thiocyanate | | | 1.80 |
| ** | sulphate | | | 0.19 |
| | thiosulphate | | | 2.80 |
| ,,, | ferrocvanide | | | 0.41 |
| 77 | | • | • | |

The liquor is subsequently treated for the preparation of ammonium sulphate. The process consists in first passing steam through the ammonia liquor to expel the free ammonia, and subsequently treating the liquor with lime to liberate the fixed ammonia—

 $2\mathbf{NH}_{4}\mathbf{Cl} + \mathbf{CaO} = 2\mathbf{NH}_{3} + \mathbf{CaCl}_{2} + \mathbf{H}_{2}\mathbf{O}.$

The ammonia is conducted into strong sulphuric acid of specific gravity 1.7, with which it combines—

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

forming ammonium sulphate, which separates out as a fine crystalline powder.

Ammonium sulphate, $(NH_4)_2SO_4$, forms colourless rhombic crystals, soluble in water, insoluble in alcohol, and having

an intensely bitter taste. It melts at 140° C. and decomposes at 280° C., when ammonia, nitrogen, and water are given off and acid sulphate of ammonium is sublimed.

The commercial ammonium sulphate is usually white in colour, though sometimes it has a grey or light brown colour due to the presence of tarry matters; occasionally the presence of iron ferrocyanide gives it a bluish tinge, whilst arsenic often causes a yellow colour. It is said that the addition of vitriol tar to the sulphuric acid assists in the production of a white salt by forming a scum on the surface of the sulphuric acid which retains the discolouring impurities.

In addition to the impurities already mentioned commercial ammonium sulphate contains traces of free sulphuric acid and sometimes traces of ammonium chloride. Ammonium sulphate is chiefly used as a fertiliser, its function being to supply nitrogen to the soil for assimilation by vegetation.

Valuation of Ammonia Liquor and Ammonium Sulphate. —The strength of an ammonia liquor is sometimes indicated by its specific gravity; this method is quite untrustworthy, because its specific gravity is affected not only by the ammonia and ammonium salts it contains, but also by any other substance, solid or gaseous, that may be dissolved in it.

The specific gravity is often measured by means of a Twaddell hydrometer, when it is expressed in degrees Twaddell. The relation between specific gravity and degrees Twaddell is expressed as follows :---

Specific gravity = (degrees Twaddell \times 5) + 1000.

The only satisfactory method for the valuation of ammonia liquor is to make a chemical determination of the ammonia it contains. The results of the analysis are sometimes expressed in ounces of sulphuric acid, specific gravity 1.845, which is neutralised by the ammonia contained in one gallon of liquor; thus a 10-ounce liquor contains sufficient ammonia in one gallon to neutralise 10 ounces of sulphuric acid of 1.845 specific gravity.

It is more usual in coke works to express the result in grammes of ammonia per 100 cubic centimetres of liquor or kilos per hectolitre, whilst these results may be converted into their equivalent of ammonium sulphate. To convert ounce liquor into percentage of ammonia by weight of liquor the ounces of sulphuric acid are multiplied by 0.2168. The method for estimating the strength of ammonia liquor usually adopted in coke works is as follows:—

Normal solutions of sulphuric acid and caustic soda are prepared. The former contains 49 grammes H_2SO_4 in 1 litre, and 1 cubic centimetre of this acid will neutralise 0.017 grammes of ammonia; the latter contains 40 grammes of NaHO per litre, hence 1 cubic centimetre of normal caustic soda will exactly neutralise 1 cubic centimetre of normal sulphuric acid.

To determine the total ammonia twenty-five cubic centimetres of ammonia liquor are placed in a 16-ounce flask, A (Fig. 87),

which is fitted with a tap funnel, B, and connected with the condenser, C, by means of the tube, The condenser consists of a D. spiral tube contained in a vessel through which cold water cir-The end of the spiral culates. tube dips into the beaker, E, which contains 50 cubic centimetres of normal sulphuric acid. Fifty cubic centimetres of caustic soda solution (10 per cent.) is placed in the funnel B, and when the apparatus is completely fitted up the caustic soda is run into the flask A, and



FIG. 87.

the mixture heated to boiling, which is continued until the solution is almost evaporated to dryness. The ammonia, both "free" and "fixed," is thus expelled and passes into the sulphuric acid, a portion of which it neutralises—

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

The number of cubic centimetres of sulphuric acid neutralised by the ammonia is determined by estimating the number of cubic centimetres of sulphuric acid that remain unneutralised and subtracting them from the 50 cubic centimetres originally taken.

To make this determination one or two drops of a solution of methyl-orange (2 grammes per litre) are added to the sulphuric acid, and normal caustic soda is run in from a burette until one drop of the caustic soda changes the colour of the acid from

pink to orange, at which point the acid is completely neutralised. The number of cubic centimetres of caustic soda run in is equal to the number of cubic centimetres of sulphuric acid unneutralised by the ammonia, hence the number of cubic centimetres of sulphuric acid neutralised by the ammonia = 50 cubic centimetres normal H_2SO_4 – number of cubic centimetres of normal caustic soda run in, and the grammes of ammonia in 100 cubic centimetres of the liquor = number of cubic centimetres H_2SO_4 neutralised by ammonia $\times 0.017 \times 4$.

The number thus obtained expresses grammes of ammonia per 100 cubic centimetres or the kilos per hectolitre (100 litres). Instead of calculating the result as grammes of ammonia per 100 cubic centimetres of liquor, it may be expressed as grammes of ammonium sulphate per 100 cubic centimetres. In this the number of cubic centimetres of normal sulphuric acid neutralised by the ammonia $\times 0.066 \times 4$ gives grammes of ammonium sulphate which can be obtained from 100 cubic centimetres of the liquor or kilos per hectolitre.

The grammes of ammonium sulphate per 100 cubic centimetres of liquor may be converted into lbs. per gallon as follows: There are 1000 ounces in 1 cubic foot of water, which is the same as the number of grammes in 1 litre; hence grammes per litre is equal to ounces per cubic foot.

Therefore grammes per 100 cubic centimetres $\times 10 =$

hence to convert grammes per 100 cubic centimetres into lbs. per gallon—

Let x = lbs. per gallon,

a = grammes ammonium sulphate per 100 cubic centimetres,

then
$$x = \frac{a \times 10}{16 \times 6.25} = \frac{a}{10}$$
.

To determine the "free" ammonia 50 cubic centimetres of ammonia liquor are taken, two drops of methyl-orange are added, and normal sulphuric acid is run in from a burette until one drop of the acid changes the colour of the solution from orange to pink. The number of grammes of "free" ammonia per 100 cubic centimetres or kilos per hectolitre is then obtained by multiplying the number of cubic centimetres of sulphuric acid used by 0.017 and by 2.

The quantity of "fixed" ammonia is obtained by subtracting the "free" ammonia per 100 cubic centimetres from the total ammonia per 100 cubic centimetres.

The strength of ammonia liquor used for working up into ammonium sulphate is usually about 3 to 4 per cent. of ammonia, and it hardly pays to work up liquors which contain less than 2 per cent.

The valuation of ammonium sulphate is carried out in a similar manner to the determination of the total ammonia in ammonia liquor; about 1 gramme of ammonium sulphate being carefully weighed into the flask, A (Fig. 87), and dissolved in about 50 cubic centimetres of water, caustic soda is then added. The solution is boiled and the gases passed into 50 cubic centimetres of normal H_2SO_4 and the ammonia estimated as described above. The percentage of ammonia (NH₃) in the ammonium sulphate is calculated as follows :—

$\frac{\text{c.c. }H_2\text{SO}_4 \text{ neutralised by ammonia} \times 0.017 \times 100}{\text{Weight of ammonium sulphate taken.}}$

Pure ammonium sulphate contains 25.75 per cent. of NH_g , but the commercial salt usually contains somewhat less than this quantity owing to the presence of impurities. The percentage of ammonia in the commercial product should never fall below 23 per cent., and usually it amounts to between 24 and 25 per cent.

Waste Gases from Ammonia Stills.—When ammonia liquor is distilled, sulphuretted hydrogen, hydrocyanic acid, and other noxious gases are carried over with the ammonia. These are not absorbed by the sulphuric acid, and if allowed to escape into the atmosphere are a source of considerable nuisance. The treatment of these gases is a matter of some importance. In some plants in Germany, for instance, they are conveyed into the mains which carry the gases to the ovens, and are burnt in the combustion flues. In England, however, it is usual to pass them through layers of hydrated ferric oxide, which retains both the sulphuretted hydrogen and the hydrocyanic acid. When

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ferric oxide it is oxidised, and certain sulphides of iron are formed according to the following equations:---

$$Fe_2O_3H_2O + 3H_2S = Fe_2S_3 + 4H_2O$$

 $Fe_2O_3H_2O + 3H_2S = 2FeS + S + 4H_2O$

whilst the hydrocyanic acid acts on the sulphide of iron, forming both cyanide of iron and sulphocyanide of iron. After a time the oxide ceases to act as a purifying agent, but this property can be restored by exposing it to the air, when the sulphides of iron become oxidised, thus:—

(1)
$$2 \text{FeS} + O_2 = 2 \text{FeO} + S_2$$

(2)
$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 3S_2$$

(3)
$$4 \text{FeO} + \text{O}_2 = 2 \text{Fe}_2 \text{O}_3$$
.

This process is technically known as "revivifying," and is usually carried out by spreading the spent oxide on the ground. The oxidation is accompanied by the heating of the mass, and care is necessary to prevent the material from becoming red hot. The "revivifying" process may be repeated about sixteen times, but eventually the oxide ceases to act as a purifying agent, when it may be sold and used for the manufacture of sulphuric acid or for the recovery of the cyanogen it contains.

Another method of dealing with the waste gases from the ammonia still has been devised by C. F. Claus. It consists in mixing the gases with a carefully regulated quantity of air, and passing the mixture into a kiln containing heated oxide of iron, when the sulphuretted hydrogen undergoes partial combustion according to the following equation, $H_2S + O = H_2O + S$. The sulphur volatilises, and, with the steam, is passed into flues fitted with baffle walls, where the sulphur condenses and is removed from time to time, being eventually used for the manufacture of sulphuric acid.

Waste Liquor from Ammonia Stills.—The waste liquor from ammonia stills contains in solution various lime salts and certain compounds, chiefly phenols, whilst insoluble lime compounds are in suspension. The liquor, which is either colourless or pale yellow, is run from the stills whilst hot into a series of settling tanks, which are divided by walls in such a manner that the liquor has to travel slowly up and down the length of the tank several times before reaching the discharging point. This allows the suspended matter to settle, and a clear liquid which has become dark-coloured from oxidation flows away.

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Owing to the presence of tarry substances the liquor usually smells of tar, and considerable objection is raised to the nuisance caused by its discharge into streams and sewers. These bodies may be removed by the addition of sulphate of iron (copperas) and lime to the effluent, but the quantity of lime added must only be sufficient to decompose the sulphate of iron. This process can be made automatic in action, but it is not usually adopted in collieries, where many devices are practised to dispose of the liquor, such as allowing the liquor to filter through beds of soil before reaching the stream, or pumping it on to spoilheaps which are on fire; or using it for quenching the coke. "Devil Liquor."—This is a liquor which condenses from the

"Devil Liquor."—This is a liquor which condenses from the gases which escape from the saturator. It contains sulphuretted hydrogen and hydrocyanic acid, which make it exceedingly offensive.

Benzol.

The benzol obtained in the recovery plant consists chiefly of a mixture of benzene and toluene which, owing to their comparatively low boiling-points, escape condensation in the tar. It is usually recovered by washing the gases with creosote oil, and subsequently distilling the solution. In some cases, however, it is separated by cooling the gases to -80° C.

Crude benzol is usually a brown or light yellow liquid of specific gravity varying from 0.87 to 0.89. Its actual composition varies with the quality, which may be greatly improved by rectification, but some idea of its constituents may be obtained from the following table :—

Composition of Benzol, 90 per cent.

| | | | | | | Per | cent. by | weight |
|-----------|--------|-------|-------|--------|-------|-----|----------|--------|
| Benzene | | | | | | | 85·1Ŏ | 0 |
| Toluene | | | | | | | 11.63 | |
| Xylene . | | | | | | | 1.54 | |
| Higher h | omolo | ogues | | | | | 0.09 | |
| Non-satu | rated | fatty | hydro | ocarbo | ons . | | 0.41 | |
| Bases . | | | | | | | 0.08 | |
| Phenols | | | | | | | 0.08 | |
| Thiopher | ie . | | | | | | 0.46 | |
| Carbon d | lisulp | hide | | | | | 0.01 | |
| Residue . | 1 | | | | | | 0.62 | |
| | | | | | | | | |

The most important hydrocarbons are benzene and toluene.

Benzene. C_6H_6 .

Benzene is a colourless mobile liquid of peculiar odour. It boils at 80.5° C., and, on cooling to 0° C., forms crystals which melt at 4.5° C. Its specific gravity is 0.984 at 15° C. It is very inflammable, burning with an exceedingly smoky flame, hence great care is necessary in storing it in quantity. It is very slightly soluble in water, but is readily dissolved by alcohol, ether, wood spirit, and acetone. It dissolves iodine, sulphur, and phosphorus, and is specially useful as a solvent of fats, resins, ethereal oils, and india-rubber. Large quantities of benzene are used in the manufacture of aniline and other dyes.

When the vapour of benzene is inhaled it produces an increase in the rate of breathing, which is followed by headache, giddiness, and inclination to vomit; large doses produce anæsthesia and subsequent death. Constant working with benzene produces a dryness of the skin owing to the secretions of the skin being dissolved.

Benzene is readily attacked by nitric acid, forming mononitroand dinitro-benzene—

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

 $C_6H_6 + 2HNO_3 = C_6H_4(NO_2)_2 + 2H_2O$

whilst, if heated with concentrated sulphuric acid, it forms benzene monosulphonic acid—

$$C_6H_6 + H_2SO_4 = C_6H_5HSO_3 + H_2O.$$

It is not readily attacked by oxidising agents.

Toluene. C₆H₅CH₃.

Toluene is a colourless mobile liquid with an odour somewhat resembling that of benzene. It boils at 110° C., and does not solidify on cooling to -20° C. It is insoluble in water, but readily soluble in alcohol, ether, and carbon disulphide. It burns with a smoky flame. Hot concentrated sulphuric acid dissolves toluene, forming toluene sulphonic acid—

 $C_6H_5CH_3 + H_2SO_4 = C_6H_4(HSO_3)(CH_3) + H_2O.$

Fuming nitric acid acts violently on toluene, forming trinitrotoluene; oxidising agents convert it into benzoic acid.

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The quality of benzol depends on the quantity of benzene and toluene it contains, and for trade purposes its quality is expressed as 90, 65, 50, 40, or 30 per cent. benzol, which numbers indicate the percentage by volume which distils below 120° C. The quality is sometimes expressed as 50/90 per cent., which means that 50 per cent. by volume distils over below 100° C. and 40 per cent. between 100° C. and 120° C.

The valuation of benzol for trade purposes is usually based on a distillation test, which consists in determining the percentage by volume which distils below 100° C. and between 100° C. and 120° C. This method is liable to give different



FIG. 88.

results at the hands of different operators, but, according to A. H. Allen, very constant results may be obtained when carefully applied according to the instructions given by him.¹ 100 cubic centimetres of benzol are placed in a tubulated retort of 200 cubic centimetres or 8 ounce capacity (Fig. 88), and the neck of the retort inserted into a Liebig's condenser from 15 to 18 inches long, well supplied with cold water. Before use, the retort and condenser should be rinsed with a little benzol and allowed to drain. A delicate thermometer, 14 inches long, with a small bulb and graduated in fifths of a degree from 70° to 130° C., is fixed in the tubulure of the retort, so that the bulb is $\frac{3}{8}$ of an inch distant from the bottom of the retort. The first graduation of the thermometer, 70°, should be at such a distance from

¹ Commercial Organic Analysis, 2nd ed., vol. ii. p. 496.

0

the bulb that it stands well out of the retort. The graduated cylinder used for measuring out the sample is placed under the farther end of the condenser, and the retort heated with the naked flame of a bunsen burner. The rate of distillation should be such that the distillate flows rapidly from the condenser in distinct drops, but not in a continuous stream.

When the distillation commences, the thermometer is carefully watched, and the temperature at which the first drop distils over noted, and as soon as it registers 85° C., the lamp is turned out, and after allowing sufficient time for the liquid in the condenser to drain into the receiver, the volume of distillate is noted. The lamp is again lighted and the distillation continued until the thermometer registers 100° C., when the flame is again extinguished and the volume of distillate noted after allowing time for drainage. The total volume of distillate gives the volume that distils below 100° C. The distillate is then continued up to 120° C., the distillate being collected in the graduated receiver containing the liquid that has already distilled over. At 120° C. the flame is extinguished, and after drainage has taken place, the total volume of distillate is noted as the percentage that distils below 120° C.

When the residue in the retort is cold its volume is measured. The total volume of the residue and distillate is usually less than 100 cubic centimetres; the deficiency, which amounts to 1 or 2 cubic centimetres, is supposed to be due to loss during distillation below 100° C., though it is by no means certain that the whole of the loss takes place below this temperature.

In stopping the distillations at 85° , 100° , and 120° , it is usual to turn out the lamp at $84 \cdot 5^{\circ}$, $99 \cdot 5^{\circ}$, and $119 \cdot 5^{\circ}$ C., because the thermometer always rises from half to one degree after the flame is extinguished, and this must be allowed for.

The Gases.—The gas which is left after the tar, ammonia, and benzol have been recovered is valuable as a heating agent and a source of power. It is a mixture having essentially the same composition as impure illuminating gas, but diluted with excess of nitrogen, which is caused by leakage of air into the coking chamber. The gases in the mixture may be divided into—

- (1) Heat-producing gases.
- (2) Illuminating gases.
- (3) Diluting gases.

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The Heat-producing Gases are: Hydrogen, marsh gas, and carbon monoxide.

The Illuminating Agents: Heavy hydrocarbons of the olefine series.

The Diluents : Carbon dioxide, nitrogen, and oxygen.

In the following table the composition of coke oven gas is compared with that of illuminating gas :---

| | Coke Ov | Illuminating | | |
|-----------------------|------------------------|-------------------------------|------|--|
| | Simon-Carvés Ovens. | Otto Hilgenstock Ovens. | Gas. | |
| Heat-producing gases- | | | | |
| Carbon monoxide . | 5.66 | 6 to 8 | 8.8 | |
| Marsh gas | 26.66 | 31 to 33 | 33.2 | |
| Hydrogen | 47.07 | 40 to 50 | 49.9 | |
| Illuminants- | | | | |
| Benzene | | | 0.5 | |
| Heavy hydrocarbons | 1.6 | 3 to 4 | 4.0 | |
| Diluents- | | | | |
| Carbon dioxide | 2.88 | 3 to 4 | 2.0 | |
| Oxygen | 0.91 | trace | 0.5 | |
| Nitrogen | 15.08 | 8 to 12 | 1.4 | |
| | | | | |

The quantity of nitrogen given in the above analyses probably represents the amount that may be obtained in gas from ovens in which the leakage is a minimum. In many cases far larger quantities of nitrogen are present, and analyses are quoted in which the nitrogen amounts to as much as 30 to 45 per cent. The quantity of carbon dioxide is higher than in illuminating gas because that impurity is not removed from coke oven gas.

The above analyses represent the composition of the gas obtained over the whole coking period, but the gas obtained from any single coke oven varies in composition at different periods of the coking time. During the first half of the coking time, when the temperature of the oven is the lowest, the gases,

marsh gas, heavy hydrocarbons, and carbon monoxide, are formed in the largest quantities; but in the second half of the coking time, when the temperature is higher, the quantities of these gases diminish whilst that of the hydrogen gradually increases until as much as 60 per cent. is present.

The primary use of coke oven gas is for burning in the oven flues, and from 30 to 75 per cent. of the gas is used for this purpose, the surplus is available either for lighting or power purposes. In burning the gas in the coke oven flues the temperature obtained by the combustion is the main consideration and depends on the proper regulation of the volumes of gas and air consumed, and whether the air used for combustion is heated The temperature that can be obtained by the comor not. bustion of coke oven gas when cold air is used is about 3300° C. to 1650° C., according to the quantity of air used for combustion, but a considerably higher temperature can be obtained if hot air be used, consequently in the latter case it is possible to obtain the same temperature as in the former case by the use of a smaller quantity of gas, and if the air for combustion be heated to 700° C. a saving of 20 per cent. of gas may be effected. If the surplus gas is to be used for illuminating or power purposes it is desirable to use all means to economise the quantity of gas required for combustion in the oven flues.

Gas for Illuminating Purposes.—The gas usually obtained from coke ovens has a low illuminating power on account of the removal of the benzol, which contributes very largely to the light-giving power of ordinary illuminating gas. If, therefore, the ordinary coke oven gas is used for lighting purposes, it is necessary to enrich it. It is further advisable to purify it from sulphur compounds by passing it through oxide purifiers after the manner in which the waste gases from the ammonia stills are purified.

It has, however, been pointed out that the gas obtained during the first half of the coking time is much richer in the heavy hydrocarbons which contribute to its illuminating power than the gas obtained during the second half of the coking time, and a method for supplying illuminating gas is now worked in America which takes advantage of this fact. The ovens are fitted with two mains, through one of which the gases given off during the first 19 hours are drawn and used for lighting purposes, whilst the gases obtained during the last 14 hours of the coking process are drawn off through the other main and used for heating the ovens.

Gas for Power Purposes.—The gas may be used to generate mechanical power either by burning it under the boilers to generate steam for use in steam engines or by using it directly in a gas engine. The former process is the more generally used in England, but on the Continent the latter process is rapidly being developed.

The value of the gas for power purposes depends on its calorific power. In coke oven gas it is very high and comparable with that of coal-gas.

B.T.U. per Cubic Feet, Gross. Description of Gas. Illuminating gas (London). 641 Retort oven gas-Semet Solvay 511 Otto Hoffmann (Lenz Colliery) 475 Simon-Carvés (Wharncliffe Silkstone Collierv) . 415 . . Producer gas-146 Dowson Mond . . . 145 150 Dynamic Wilson . 150 Blast furnace gas . 135

Calorific Power of Power Gas.

The horse-power to be obtained from any power gas depends on its calorific power and the quantity of gas supplied per minute. The theoretical horse-power of coke oven gas delivered at the rate of about 15,000 cubic feet per hour amounts to between 2000 and 3000 horse-power. Of this quantity only about 20 to 25 per cent. is available, and consequently the actual horse-power that can be obtained is something between 400 and 600 horse-power. Basing results on such assumptions, it requires about 30 to 35 cubic feet of gas per hour to give 1 brakehorse-power, or from 13 to 17 horse-power per oven.

| Description of Gas. | | | Cubi | c Feet per per B.H.P. | Hour |
|-----------------------|----|--|--------|--------------------------|------|
| Heathfield natural ga | IS | | | 12 - 15 | |
| Illuminating gas | | | | 20 - 25 | |
| Coke oven gases | | | | 30-37 | |
| Water gas | | | 19 A - | 60-80 | |
| Producer gas . | | | | 100-120 | |

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Volume of Gas required per Brake-Horse-Power.

If the gas is to be used in internal combustion motors, it is desirable that it be purified from sulphur compounds and any small quantities of tar that may be mechanically carried over in the gas. The tar is liable to cause sooting and to condense on the spindles of the valves of the engine and so prevent them from properly closing. It is said, however, that this difficulty may effectually be overcome by keeping the valves well lubricated with lard oil. The sulphur compounds produce sulphur dioxide by combustion, which in time will attack the cylinders and pistons. It is, however, believed by some that purification from sulphur compounds is not necessary because the "scavenging" of the cylinder takes place so quickly after the explosion that the products of combustion are removed before they have time to do any injury. This may be correct, but it is impossible to conceive that in course of time no injury must result.

Cyanogen.—This gas is usually formed during coal distillation, and a portion of it is condensed in the ammonia liquor, but a small quantity occurs in the coke oven gases. Its recovery is not usually undertaken in connection with by-product coking plants, but in some gasworks it is recovered. In gasworks the greater part of the cyanogen is retained in the oxide of iron purifiers, and is recovered from spent oxide as potassium cyanide; the gas is sometimes specially treated by washing it with water containing sodium carbonate in solution and oxide of iron in suspension. Sodium ferrocyanide, $Na_4FeC_6N_6$, is then obtained, which can afterwards be converted into potassium cyanide.

The Recovery Plant.

In every plant connected with coke ovens for the recovery of by-products the same processes are adopted, and one plant differs from another only in details of construction. The processes are :---

(1) Cooling for the condensation of the tar.

(2) Washing with water for the removal of the ammonia.

(3) Washing with creosote oil for the removal of benzol.

The products of distillation are extracted from the ovens by means of exhausters, which are usually placed between the cooling plant and the ammonia washing plant. Mechanical exhausters of the root-blower type are generally used, and serve as force-pumps for driving the gases through the ammonia and benzol washing plants. In some plants steam injectors are used instead of mechanical exhausters.

The volatile products pass out of the ovens through stand pipes, which are connected with a main (hydraulic), through which they are conveyed to the recovery plant. At the top of the stand pipes are valves, which are used to shut off the connection between the oven and hydraulic main when an oven is being discharged and refilled. In the earlier types of ovens the hydraulic main was placed about 1 foot to 2 feet 6 inches above the ovens, now it is usual to place it from 6 to 10 feet above the top of the ovens, in order to keep it as cool as possible.

The products passing into the hydraulic main have a temperature of about 260° C. (500° F.), and in their passage along the mains undergo considerable cooling, and large quantities of tar and some ammonia liquor condense. These mains all fall to a seal or trap, into which the tar and liquor flow, and from which they are syphoned off into a settling or distributing tank which is placed below the ground level. From this trap the mains, rising gently all the time, continue to the cooling plant, where the condensation of the tar is completed. The cooling plant may consist of a long horizontal zigzag or serpentine main built in the form of a pyramid, over which water is continually running; the gases enter at the bottom and flow backwards and forwards through the main until they pass out at the top. The more general plan, however, is to make the gases first pass up hollow towers containing a series of pipes through which the air can freely pass, and afterwards through similar towers in which cold water flows through the pipes, thus combining air and water cooling. In these coolers the condensation of the tar is completed, and a further quantity of ammonia liquor separates out. The tar and ammonia liquor condensed in the coolers are conveyed by mains to the distributing tank.

The gases should enter the coolers at a temperature of from 80° to 90° C., and should leave them at a temperature not exceeding 15° C. On the efficiency of the cooling depends the completeness with which the tar is condensed and the economical working of the subsequent washing process. Not-withstanding the most efficient cooling, a certain amount of tar, in the form of very fine globules, is carried away in suspension in the gases. This is removed by means of a special form of separator, generally the Pelouze-Audouin separator, in which the gases are made to pass through fine holes in baffle plates, to which the particles of tar adhere. The cooled gases then pass through the exhausters. If these are of the mechanical type, the gases become compressed after passing through them, which raises their temperature, and in many plants they pass directly through a cooling tower before entering the ammonia washing plant or scrubbers.

If steam injectors are used, at least two cooling towers are necessary after passing the injectors. In these towers the steam condenses and the water dissolves a certain quantity of the ammonia. After undergoing this subsidiary cooling, the gases enter the ammonia washing plant technically known as scrubbers. This consists of towers about 40 to 60 feet high, up which the gases pass, meeting a stream of water passing downwards. The towers may be filled with coke or pebbles, but often are packed with wooden grids arranged to cross one another, over these the water flows. In this way the gases are broken up into small streams and brought in contact with a large extent of wet surface. In some cases, however, the towers are fitted with a number of perforated iron shelves, over which the water flows in thin layers, and the gases, passing upwards, find their way through the perforations. Two and sometimes four of the scrubbers, placed in series, are used.

It is only in the final scrubber that pure water is used for washing. In the other scrubbers ammonia liquor is always used for the purpose of bringing it up to that strength which makes it profitable to use it for the manufacture of sulphate. The ammonia liquor used for washing is obtained by

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pumping all the liquor condensed in the cooling plant, together with that obtained by washing, into an overhead tank, from which it is made to circulate over and over again through the scrubbers. With proper cooling and careful washing the maximum quantity of ammonia which is left in the washed gas is about 4 to 5 grains per 100 cubic feet, but often only 1 grain per 100 cubic feet will escape. Assuming 1 ton of coal gives 10,000 cubic feet of gas, 1 grain per 100 cubic feet is equivalent to a loss of 0.057 lbs. ammonium sulphate per ton of coal coked. The ammonia liquor is subsequently treated in a separate plant (sulphate plant) for conversion into ammonium sulphate.

Benzol Washing.—The ammonia free gas passes to the benzol scrubbers, which are similar in construction to the ammonia scrubbers, and in them meets with a stream of creosote oil which circulates continually through the scrubbers, dissolving benzene, toluene, and other substances out of the gases. The creosote oil, saturated with benzol, subsequently undergoes a process of distillation for the recovery of the benzol. After the benzol has been recovered, the creosote oil is cooled and used again in the scrubbers. There is, however, a limit to the number of times the creosote oil can be used in this way, because it soon becomes thick from tar and coal dust mechanically carried over with the gases. The thickened creosote oil, however, can be distilled and the distillate used again for washing.

Benzol Recovery.—The distillation of the creosote oil for the recovery of the benzol may be carried out by (a) an intermittent process; or (b) a continuous process.

(a) Intermittent Distillation.—A large still made of boiler plates, capable of holding from 10 to 20 tons, is fitted inside with a coiled steam-pipe. At the top is a pipe through which the vapours of benzol pass; this is connected with a condenser consisting of a coiled lead pipe surrounded by a vessel through which cold water circulates. The still is filled with the creosote oil, and steam at a pressure of 70 lbs. is passed through the steam-coil. The benzol boils and passes as vapour into the condenser, where it is condensed. The liquid then flows into a trap in which any water that distils over settles at the bottom and the benzol at the top. The latter is drawn off by a syphon into tanks, whilst the former, which usually contains some ammonia, is syphoned off and added to the ammonia liquor.

The crude benzol thus obtained is usually either 30 or 65 per cent. benzol, and it may be submitted to a process of washing and rectification for the manufacture of the higher qualities.

(b) Continuous Distillation.-In this method the creosote oil charged with benzol is pumped continuously into a still divided into horizontal compartments like a Coffey still. The oil enters near the top and descends from chamber to chamber over overflow dams. Steam is blown in at the bottom of the still and passes through the creosote oil, carrying with it benzol vapours. The steam and benzol vapours leave the still at the top and pass into a condenser which is surrounded with cold water. The condensed liquids flow into a separator, where they form two layers, the benzol floating on the surface of the water. The benzol is syphoned off into store tanks, whilst the water flows away from the bottom. The creosote oil freed from benzol flows continuously from the bottom of the still into a cooler where its temperature is reduced to about 20° C. From the cooler it runs into a store tank from which it is pumped through the washing towers, where it absorbs more benzol. After a time the creosote oil becomes less efficient as an absorbent and too thick for easy circulation; it is then sold as thick oil.

The gases from which the benzol has been removed are conveyed by mains to the coke ovens, where they are used for burning in the oven flues and also under boilers.

Manufacture of Ammonium Sulphate .- The process for the manufacture of ammonium sulphate consists in expelling the ammonia from the liquor by steam and passing the gas into sulphuric acid. The plant consists of a still, A (Fig. 89); a saturator, E; a lime-mixer, B; a lime pump, H; and an econo-The manner of working is as follows: The liquor miser. flows from an overhead tank, a, into a worm in the economiser, where it is heated by hot waste gases coming from the saturator through the pipe K. From the economiser it flows into the upper part of the still, A, which is divided by shelves into compartments; on to these shelves the ammonia liquor flows, passing downwards from compartment to compartment through overflow pipes; in its passage downwards it meets with steam which removes the free or volatile ammonia. The liquor, freed from volatile ammonia, then enters the limemixer, B, and is mixed with lime; from the lime-mixer it passes

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into the still, C, and again meets with a current of steam which expels the fixed ammonia. The steam charged with this ammonia passes into A and is there used to remove the free ammonia. The liquor freed from ammonia runs away to settling tanks through the valve f. In most modern plants the still, C, is dispensed with.

The ammonia-laden steam passes through the pipe, i, to the saturator, which consists of a wooden tank, E, lined with lead containing the sulphuric acid. The pipe from the saturator is



FIG. 89.

covered with a lead bell, F, under which the foul gases liberated by the sulphuric acid collect and escape through a pipe K, to the economiser, where they surround the worm carrying the ammonia liquor to the still and heat it.

The ammonia is entirely retained by the sulphuric acid, and ammonium sulphate separates out in the form of fine crystals. Passing through the bell is a steam injector, and by its means the ammonium sulphate is, from time to time, elevated on to a sloping platform, where it drains, the excess of acid running back into the saturator. After draining, the sulphate is sent to the store, which usually is a brick chamber the sides of which

From Thorpe's "Dictionary of Applied Chemistry."

are lined with lead, the floor being of wood or some acid-proof cement. The waste liquor from the still, which usually contains a small trace of ammonia, runs from the still into settling ponds and eventually flows away.

The gases from the saturator, after leaving the economiser, pass through a condenser, where the "devil liquor" separates out. They are subsequently passed through oxide of iron purifiers from which they escape into the air, or they may be conducted to the combustion flues of the oven. The "devil liquor" is usually returned to the ammonia liquor and circulates again in the scrubbers.

Recently modifications have been made in by-product recovery plants whereby the ammonia is converted directly into ammonium sulphate, and the process of water-washing the gases for recovery of the ammonia avoided. One process designed by Koppers consists in cooling the gases for the condensation of tar, which causes the separation of ammonia liquor as in the old process. The cooled gases, which still contain some ammonia, after passing through a tar separator are heated to about 70° C. and passed directly into a saturator containing sulphuric acid with which the ammonia they contain combines and forms ammonium sulphate. From the saturator the gases, after cooling, pass to benzol scrubbers, and finally to the ovens.

To recover the ammonia from the ammonia liquor that condenses with the tar, the liquor is boiled with lime as in the ordinary ammonium sulphate plant, and the liberated ammonia is passed into the gases of the recovery plant just before they enter the saturator. By this and similar processes the amount of effluent coming from the ammonia stills is reduced.

In another process, the Otto process, the hot and moist gases coming direct from the ovens are freed from tar by bringing them, whilst at a temperature of 100° C., in contact with a hot tar spray. The tar-free gases charged with moisture are kept at a temperature of 70° C. and passed directly into the saturator, where the ammonia they contain unites with the sulphuric acid. The hot gases from the saturator, still charged with their original moisture, are conveyed directly to the oven flues where they are burnt. In this process no benzol is recovered and the gases are never cooled below 70° C., so that the condensation of waste liquor is avoided.

CHAPTER XII

EXPLOSIVES

Nature of Explosives.—An explosive is a body in which a large amount of potential energy is stored. The energy is chemical energy, that is, it can be set free by bringing about a chemical change in the body itself. This chemical change can usually be brought about by combustion, friction, shock, or blow. When the energy is set free it is converted into mechanical energy and heat.

When the chemical change takes place the explosive is usually converted into gases which, under the ordinary pressure, occupy a considerably larger volume than that of the explosive, but as the decomposition takes place with extraordinary rapidity, these gases, at the moment of their formation, are highly compressed; at the same time high temperatures are obtained owing to the rapid decomposition and highly compressed state of the gases.

The chief characteristics of explosives, therefore, are :--

(1) They contain a large amount of chemical energy.

(2) The energy is rapidly set free by chemical decomposition.

(3) The formation of large volumes of gases under very high pressure.

(4) The production of high temperature.

Bodies possessing these characteristics may be either gaseous, liquid, or solid mixtures or compounds. For blasting purposes only solids, or liquids carried in some absorbing medium so as to form a plastic body, are used.

Explosive Compounds.—Many chemical compounds possess the above characteristics. When such compounds are subjected to explosive decomposition heat is generated, and when once that decomposition is started it proceeds throughout the mass without the assistance of any external energy. Some explosive compounds are very sensitive to explosive decomposition and are unsuitable for use as blasting explosives, whilst others are

less sensitive and can be used for that purpose either alone or when mixed with non-explosive bodies.

The explosive compounds chiefly used for the manufacture of mining explosives belong to a large group of bodies generally called nitro-compounds. The nitro-compounds most frequently used are :---

| Nitro-glycerol ¹ | | $C_{3}H_{5}(NO_{3})_{3}$ |
|--------------------------------|---|---------------------------------|
| Nitro-cellulose or guncotton | | $C_{24}H_{29}O_{20}(NO_2)_{11}$ |
| Di-nitro-benzene | | $C_6 H_4 (NO_2)_2$. |
| Di-nitro-toluene | | $C_7 H_8 (NO_2)_2$. |
| Di-nitro-naphthalene . | | $C_{10}H_6(NO_2)_2$. |
| Tri-nitro-naphthalene . | • | $C_{10}H_5(NO_2)_3$. |
| Tri-nitro-phenol (picric acid) | | $C_6H_2OH(NO_2)_3$. |

All these bodies are combustible, and when small quantities are ignited in the air burn away quietly without any explosive violence, but under certain conditions will decompose with explosion.

Explosives used in blasting may be :---

(1) Mixtures of combustible but non-explosive bodies with suppliers of oxygen, as gunpowder, a mixture of charcoal, sulphur, and potassium nitrate.

(2) Explosive compounds, as nitro-glycerol in dynamite; or guncotton.

(3) Explosive compounds mixed with suppliers of oxygen, as tonite, a mixture of guncotton and barium nitrate; or bellite, a mixture of di-nitro-benzene and ammonium nitrate.

(4) Explosive compounds mixed with suppliers of oxygen and non-explosive bodies.

The suppliers of oxygen are usually nitrates or chlorates. Amongst the nitrates most commonly employed are potassium nitrate, barium nitrate, ammonium nitrate, and sometimes sodium nitrate; potassium chlorate and ammonium perchlorate are the chlorates chiefly used.

Explosive Decomposition in an explosive may be brought about by ignition or detonation. In the case of explosives which consist of mixtures of non-explosive but combustible bodies with suppliers of oxygen, such as gunpowder, the explosive decomposition proceeds by progressive combustion.

¹ Nitro-glycerol is the more correct name for nitro-glycerin.

They therefore can be fired by ignition, which proceeds with considerable rapidity from grain to grain, and they are independent of atmospheric oxygen, that gas being supplied by the nitrate or chlorate. The rapidity of combustion under ordinary atmospheric pressure is considerable, but it is greatly increased by increase in the surrounding gaseous pressure; hence when the explosive is confined, as in a shot-hole, the rapidity of combustion becomes very great.

In the case of explosive compounds explosive decomposition is not brought about by combustion. It is caused by the breaking up of the molecule itself for which the assistance of external oxygen is not necessary. The difference between combustion and explosive decomposition may be illustrated by guncotton, which, if ignited, burns away quickly but quietly, combining with the oxygen of the air forming carbon dioxide, water, and nitrogen; but if it be heated in a tube to a temperature of 180° C. it decomposes with explosive violence and a complex mixture of gases is produced. In the same way the explosive decomposition of nitro-glycerol is effected by the breaking up of the molecule in the following manner—

$$2C_{3}H_{5}(NO_{3})_{3} = 6CO_{2} + 5H_{2}O + 3N_{2} + O.$$

In order that explosive decomposition in an explosive compound may be developed to the greatest extent it must be propagated through the mass with a velocity so great that

| Unconfined. Feet per Second. | Confined. Feet per Second. |
|---|--|
| 19,800 16,500 to 23,000 23,500 23,500 6,600 to 12,000 12,000 5,280 6,900 | 13,000 9,900 11,900 |
| | Unconfined. Feet per Second. 19,800 16,500 to 23,000 23,500 23,500 6,600 to 12,000 12,000 5,280 6,900 |

Velocity of Explosive Wave.

¹ Bichel.

the molecules of the products of decomposition are set in violent agitation, vibrating backwards and forwards so rapidly that a series of shocks is produced on other undecomposed molecules causing their decomposition. These decomposed molecules also vibrate and decompose others, and so on. In this way the chemical decomposition is propagated through the entire mass in the form of a wave known as the *explosive wave*. The velocity with which the explosive wave is propagated is very great, and is greater when the explosive is confined than when unconfined. This is shown in the table on page 223.

Some explosive compounds are much more sensitive to this explosive decomposition than others—for instance, mercuric fulminate will decompose with explosive violence under the influence of heat, a slight blow, or friction, whereas nitro-glycerol, guncotton, and ammonium nitrate explosives require a much more powerful shock. This powerful shock is brought about by *detonation*, which consists in producing, in the interior of the cartridge, a powerful explosion which causes high pressure and temperature, and produces a shock sufficiently severe to set up the explosive wave. The explosive used for this purpose is mercuric fulminate with which caps or detonators are charged.

There are then two forms of explosive decomposition: Explosion of the first order, propagated by rapid combustion from particle to particle; explosion of the second order, or detonation, propagated in the form of the explosive wave.

Explosives exploding in the first manner, which can be fired by ignition, are called low explosives.

Explosives which explode according to the second manner, and can only be fired by detonation, are called high explosives.

Low explosives belong to Class I. mentioned on page 222, whilst Classes II., III., and IV. consist of high explosives. The chief characteristic of low explosives is the slowness of their decomposition; proceeding as it does by progressive combustion, the pressure of the gases produced gradually reaches a maximum, and so gives the resisting material time to yield along the lines of least resistance, thus producing a rending action which does not shatter the rock.

With high explosives, owing to the extremely rapid decomposition, the maximum pressure is reached almost instantly, and thus an intensely powerful blow is produced which pulverises the rock in the neighbourhood of the shot, and under the influence of which all lines of resistance are equally weak, so that the resisting material is broken down into small pieces and considerably shattered.

Strength of Explosives.

The strength of an explosive may be considered either from the point of view of the amount of mechanical work a unit weight is capable of performing, or from the view of the pressure produced by the explosion of a unit weight of explosive.

The maximum amount of mechanical work an explosive is capable of doing is obtained by multiplying the number of heat units produced by the decomposition of a unit weight of explosive by the mechanical equivalent of heat. Thus 1 lb. of nitroglycerol produces 1570 thermal units on explosion, which is equivalent to $1570 \times 1390 = 2,182,300$ ft. lbs. of mechanical energy.

The actual number of heat units produced by the decomposition of an explosive can be calculated if its heat of formation and the exact nature of its chemical decomposition are known. Most mining explosives are complex mixtures, and the exact character of their decomposition is not known, consequently the actual heat units evolved by their decomposition can only be accurately determined by experiment. But even results so obtained may not be those which are actually produced in the shot-hole, as the exact course of the chemical change may be considerably modified by differences in the conditions under which the explosion occurs.

Any numbers obtained experimentally under similar conditions will be comparative among themselves, and they will represent the maximum heat units that are liberated under those conditions. Assuming that these conditions are obtained in a shot-hole, and that the number represents the actual heat units produced, only a portion of them are converted into actual mechanical work, some being used to raise the temperature of the products of explosion and of the surrounding rocks.

Heat Units evolved by Explosion of certain Explosives experimentally determined (Heise).

| 1 lb. | Blasting gelatin | | | 1422 | thermal | units. |
|-------|------------------|---|---|------|---------|--------|
| ,, | Gelatin dynamite | • | | 1321 | " | >> |
| >> | Dynamite . | • | • | 1170 | | ,, |
| ,,, | Carbonite . | • | • | 576 | 22 | " |
| | | | | | | P |

The pressure produced by the explosion of a unit weight of explosive depends on—

(1) The volume and temperature of the gases produced ;

(2) The density of charge.

The volume of gas produced by the decomposition of a unit weight of explosive under atmospheric pressure and at 0° C. can be determined by experiment, or calculated if its decomposition can be expressed by a definitely known reaction. At the moment of generation in the shot-hole these gases, however, occupy a volume equal to, or only slightly greater than, that of the explosive itself, and consequently the pressure they exert is considerable. This pressure, however, is greatly increased by the high temperature at which they are produced.

The pressure also depends on the *density of the charge* or the weight of explosive contained in a unit volume. It is usually determined by dividing the weight of explosive in grammes by the volume of the space in which the explosion takes place in cubic centimetres.

If D = the density of charge,

- W grammes = the weight of explosive,
- V cubic centimetres = the volume of explosion space,

then

$$D = \frac{W}{V}.$$

To understand the effect of the density of charge consider a shot in a bore-hole completely stemmed, as shown in Fig. 90. The space in which the explosion takes place is exactly equal to the volume of the explosive, namely, *abcd*, and the density of charge $D = \frac{W}{abcd}$, but if for the same shot the stemming is not rammed down on the charge, but leaves an air space above the cartridge, the explosion space is *ef hg*, and the density of charge $D = \frac{W}{efhg}$.

In the former case D is greater than in the latter, and at the moment of firing the pressure will be greater, because the gases, at the moment of generation, will occupy a smaller volume.

EXPLOSIVES

Shattering Effect.

The shattering effect of an explosive is the breaking up and pulverising of the blasted material when the explosive is fired.

The action of high explosives, in this respect, is much more marked than that of low explosives. The shattering effect depends on the time required to develop the maximum pressure as well as on the actual pressure produced. The shorter the time required to produce the maximum pressure the



greater the shattering effect, and given two explosives which on explosion produce equal pressures, the one which explodes the more rapidly will produce the greater shattering effect.

All high explosives decompose more rapidly than low explosives, and produce a greater shattering effect. But in high explosives this effect is often reduced by adding nonexplosive bodies, such as wood meal, starch, &c., which reduces the rate at which the explosion takes place.

Measurement of the Strength of Explosives .- The relative



strength of explosives for blasting purposes is measured in various ways, amongst which are the Trauzl test and the ballistic pendulum test.

The Trauzl Test consists in measuring the expansion produced in a cylindrical cavity in a lead block by the explosion of a known weight of explosive. The blocks consist of cast lead cylinders 200 mm. in dia-

meter and 200 mm. high (Fig. 91). Along the axis a hole 125 mm. deep and 25 mm. wide is bored. The top of the hole is

countersunk to receive a steel plate in which is a central hole. Through this hole the wires or fuse for firing the shot pass. The capacity of the cylindrical hole is carefully measured, and the temperature of the lead cylinder, which should not be less than 15° C. or greater than 20° C., taken. A carefully weighed quantity of explosive is placed in a tinfoil case 120 to 125 mm. long and 70 mm. in diameter, and a cap containing 2 grammes of mercuric fulminate with fuse attached inserted. The tinfoil case is firmly tied round the neck to the fuse, and the whole placed in the cavity of the block. The cavity is filled to the bottom of the countersunk portion with dry sand which passes through a sieve of 0.34 mm. wires having 144 meshes to the square centimetre. A sheet of asbestos is then placed over the sand and the steel plate fitted into position over the asbestos. The whole is then tightly wedged in a frame and the shot fired, which enlarges the cavity. After carefully cleaning the cavity from sand it is accurately measured.

The comparison of the strength is made in two ways :---

(1) A fixed weight (10 grammes) of charge is used, and the size of the cavity produced measures the relative strength.

(2) The weight of the charge is varied so as to produce a cavity equal in volume to that produced by 10 grammes of 75 per cent. dynamite. The relative strength is in the inverse ratio of the weight.

The latter method is probably more accurate, as the larger the cavity produced the less the resisting power of the walls of the block; hence in the former method there is a tendency to exaggerate the strength of the stronger explosive and to underestimate that of the weaker. The strengths of high and low explosives cannot be compared by this method.

The Ballistic Pendulum Test.—This test is used at the testing station at Woolwich. The apparatus consists of a mortar weighing 5 tons and of 13 calibre, which is mounted on friction wheels in an iron frame and hangs from a beam so that it can swing like a pendulum. The explosive is fired from a cannon, which is placed at a fixed distance from the mortar. The weighed charge is placed in the cannon and stemmed with a weighed quantity of clay, a small plug of cotton wool being placed between the charge and the stemming. When the cannon is fired the mortar swings and the extent of the swing is measured on a fixed scale. In this test large charges of

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explosives can be used, as much as 113 grammes (4 ounces) of dynamite being used at Woolwich. The strengths of all kinds of explosives can be compared by this test.

Shattering Power.—Attempts have been made to determine the shattering power by Heise, using the Trauzl test. Instead of taking a weight of explosive which will produce a fixed expansion in the lead block he uses a weight of explosive which is capable of producing on explosion 2500 kilogrammetres of work, and measures the cavity thus produced. It is assumed that the more rapid the explosion the greater the proportion of this energy that will be expended in enlarging the cavity, therefore the larger the cavity the greater the shattering power.

Explosive Compounds used in the Manufacture of Blasting Explosive.

(1) Nitro-glycerol, $C_8H_5(NO_8)_{3^3}$ is obtained from glycerol by the action of nitric acid—

$$C_{3}H_{5}(HO)_{3} + HNO_{3} = 3C_{3}H_{5}(NO_{3})_{3} + 3H_{2}O.$$

It is a colourless and odourless liquid, with a somewhat sweet burning taste. Its specific gravity is 1.6 at 15° C. It freezes to a solid at about 8° C. It is insoluble in water and soluble in ether, wood-spirit, benzene, chloroform, and hot alcohol. It is poisonous, and may be absorbed by the skin when handled, producing headache. It can be evaporated at 185° C., when it undergoes decomposition; it takes fire at 217° C.; when it undergoes decomposition; it takes fire at 217° C.; when ignited in very small quantities it burns away quietly, but larger quantities after burning for a short time explode violently. Small quantities detonate if heated at 217° C., but larger quantities explode at 180° C. The decomposition takes place according to the following equation—

$2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 3N_2 + O.$

Liquid nitro-glycerol is very sensitive to explosive decomposition by heat, a blow, or friction, but is less sensitive to decomposition when frozen.

(2) Nitro-cellulose, or guncotton, is obtained by acting on cellulose with a mixture of strong sulphuric and nitric acids; the nitric acid alone acts on the cellulose. The form of cellulose

generally used is cotton or sawdust. Several varieties of nitrocellulose are known, and they are classified as soluble and insoluble varieties according as they are or are not dissolved by a mixture of 1 volume of alcohol and 2 volumes of ether. Insoluble nitro-cellulose is known as guncotton, whilst the soluble varieties are often called collodion cotton.

Guncotton unless reduced to pulp has the same appearance as the original fibre, but it is rougher to the touch. It has neither taste nor smell, and is soluble in acetic ether, but insoluble in ether-alcohol and water. Ignited in small quantities in the air it burns rapidly without explosion, but if ignited in a closed vessel it eventually explodes. It decomposes with explosive violence when briskly heated at 150° C. (Abel). If perfectly pure, guncotton can be kept for any length of time without undergoing decomposition; but if it contains the slightest trace of free acid, decomposition takes place; at first slowly, but eventually the whole mass explodes. When dry and compressed it is easily detonated with a cap of fulminate of mercury, but when wet it cannot be exploded by a cap alone. Wet compressed guncotton can, however, be exploded by the explosion of a small quantity of dry guncotton. In the fibrous and uncompressed state it is usually blown about and scattered by the explosion of the cap without exploding itself.

Soluble guncotton is a less highly nitrated compound than guncotton; it is readily soluble in alcohol-ether and nitroglycerol. It is used in the manufacture of blasting gelatin.

(3) Di-nitro-benzene, $C_6H_4(NO_2)_2$, is a pale yellow solid obtained by the action of strong nitric acid on benzene—

$$C_6H_6 + 2HNO_3 = C_6H_4(NO_2)_2 + 2H_2O_1$$

Three varieties of di-nitro-benzene are known, namely, ortho, meta, and para-di-nitro-benzene. That used in the manufacture of explosives is chiefly meta-di-nitro-benzene mixed with small quantities of the ortho and para varieties. Pure meta-di-nitrobenzene melts at 91° C., but that used in explosive manufacture generally melts between 85° to 87° C. It is odourless, poisonous, and by itself is not readily explosive, though if suddenly heated it decomposes violently. Mixed with nitrates it forms a powerful explosive.

(4) **Di-nitro-toluene**, $C_7H_6(NO_2)_2$, is obtained from the hydrocarbon toluene by the action of strong nitric acid. Several varieties are known, and that used in explosive manufacture melts at 71° C. It crystallises in needles, which are soluble in hot water and alcohol. It decomposes when heated at 300° C., and forms powerful explosives when mixed with nitrates.

(5) Di-nitro-naphthalene, $C_{10}H_6(NO_2)_2$, is obtained by the action of the strongest nitric acid mixed with twice its volume of strong sulphuric acid on naphthalene. It forms brilliant yellow needles, which melt at 185° C. It is chiefly used in the manufacture of ammonite.

(6) Picric acid or tri-nitro-phenol, $C_6H_3(OH)(NO_2)_3$, is derived from phenol or carbolic acid, C_6H_6O . It crystallises in brilliant yellow needles, which melt at 122.5° C., and if suddenly heated explode. It is sparingly soluble in water, and dyes silk, wool, and other animal tissues a fast yellow colour. It has an intensely bitter taste. When ignited it burns with a smoky flame, but does not explode. In the compressed state or in the lump solidified it explosive lyddite, used at one time for filling shells, consisted of solidified picric acid. It forms a powerfully detonating mixture with certain metallic oxides and nitrates. When acted on by metallic bases it forms salts, known as picrates, all of which are more or less explosive and have, from time to time, been used in the manufacture of ammunition.

(7) Fulminate of mercury, HgC, N,O, is prepared by dissolving 5 parts of mercury in 12 parts of nitric acid (specific gravity 1.4), heating the solution to 70° C. and adding 11 parts alcohol (98 per cent.). After a short time a violent reaction takes place, which can be moderated by cooling, and eventually the fulminate separates out as a grey powder, which, after decanting the acid and well washing with cold water till all traces of acid are removed, can be purified by crystallisation from hot water, when it is obtained in yellowish white crystals. It has a sweetish, acid, metallic taste, and like all mercury compounds is highly poisonous. It explodes with extreme violence under the influence of a moderate blow or slight friction. When slowly heated it explodes at 152° C., but if rapidly heated it explodes at 187° C. Small quantities ignited with a flame decompose with slight detonation. Pure fulminate of mercury can be compressed under very high pressure without exploding. Wet fulminate of mercury does not explode so easily as dry; but wet fulminate, even though entirely under water, can be exploded by a blow or by friction. It is chiefly used for the manufacture of detonators, when it is mixed with 20 per cent. of potassium chlorate.

Low Explosives.

Gunpowder is an intimate mixture of charcoal, sulphur, and potassium nitrate. It is used as ammunition and for sporting and blasting purposes. It is usually obtained in loose grains of a black colour with a grey lustre. The grains should not adhere to one another and should not leave a mark when rolled on paper.

The purpose for which gunpowder is required determines the property that is most important. For blasting purposes the production of large volumes of gas at high temperature is essential. The proportion of the various ingredients in blasting powder is determined to obtain this object, and the following table, according to Guttmann, gives the composition of blasting powders in various countries :—

| | Austria- Hungary. | France. | Germany. | Great Britain. | Italy. | Russia. |
|-------------------|----------------------|---------|----------|-------------------|--------|---------|
| Potassium nitrate | 60.19 | 72.0 | 70.0 | 75.0 | 70·0 | 66.6 |
| Sulphur | 18.45 | 13.0 | 14.0 | 10.0 | 18.0 | 16.7 |
| Charcoal | 21.36 | 15.0 | 16.0 | 15.0 | 12.0 | 16.7 |

Gunpowder may be fired by ignition, or if confined, as in a bore-hole, by detonation. The rate at which it decomposes depends upon the pressure of the surrounding atmosphere. In a vacuum it will not ignite, and only with difficulty under a pressure of 20 inches (Abel), whereas at the ordinary atmospheric pressure inflammation is complete in a few seconds. The size of the grains also influences the rate at which combustion takes place, the coarse-grained blasting powder burning more slowly than the fine-grained rifle powder. The products of combustion consist of solids and gases. In blasting powder, the former amount to about 49 per cent. and the latter to 51 per cent. by weight of the powder. The following results were obtained by Noble and Abel :—
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Gaseous Products.

Solid Products.

| Carbon dioxide . | 22.79 | Potassium carbonate | | 19.45 |
|-----------------------|--|-----------------------|---|-------|
| Carbon monoxide . | 15.22 | Potassium sulphate . | | 0.28 |
| Nitrogen | 8.28 | Potassium sulphide . | | 17.45 |
| Sulphuretted hydrogen | 3.89 | Potassium thiocyanate | | 1.39 |
| Ethylene | 0.20 | Potassium nitrate . | | 0.04 |
| Hydrogen | 0.17 | Ammonium carbonate | • | 0.84 |
| | | Sulphur | | 6.64 |
| | | Carbon | | 0.95 |
| | | | | |
| | 51.35 | | | 47.04 |
| | the second s | | | |

Gunpowder for blasting purposes is sometimes compressed into bobbins.

There are many substitutes for gunpowder, such as argus powder, elephant brand, oxalate powder, bobbinite, &c. The chief of these is bobbinite, of which there are two varieties, having the following composition :---

| 1 | | 1st Variety. | 2nd Variety. |
|--|-------|--|---|
| Potassium nitrate . Charcoal Sulphur Ammonium sulphate Copper sulphate } Moisture Rice or maize starch Paraffin wax | · · · | $\begin{array}{c} 65.0 \text{ to } 62.0 \\ 19.5 \\ ,, 17.0 \\ 2.5 \\ ,, 1.5 \\ 17.0 \\ ,, 13.0 \\ 2.5 \\ \dots \\ \dots \end{array}$ | 66.0 to 63.0 20.5 ,, 18.5 2.5 ,, 1.5 3.0 9.0 to 7.0 3.5 ,, 2.5 |

High Explosives.

High explosives for blasting purposes consist of some explosive compound alone or mixed with other substances.

The substances used are of three kinds :---

(1) Substances used to reduce the strength of the explosive, whilst at the same time increasing the volume of gases produced, such as wood meal, starch, and similar combustible but nonexplosive bodies.

(2) Substances used to reduce the temperature produced by the decomposition. These are generally substances containing water of crystallisation, such as magnesium sulphate, $MgSO_4 + 7H_2O$, copper sulphate, $CuSO_4 + 5H_2O$, &c., which, at high temperatures, decompose and absorb heat, thereby reducing the temperature; at the same time the evaporation of the water and its conversion into steam adds to the volume of gases produced.

(3) Suppliers of oxygen, which serve to supply the deficiency of oxygen in the explosive compound and also to add the amount required for the combustion of the bodies included under division 1. For this purpose nitrates are chiefly used, the most important being potassium nitrate, barium nitrate, ammonium nitrate. Occasionally potassium chlorate (KClO₃) and potassium perchlorate (KClO₄) are used, and ammonium perchlorate is now being introduced.

High explosives for blasting purposes may be divided into the following classes :---

- (1) Nitro-glycerol explosives.
- (2) Guncotton explosives.
- (3) Blasting gelatin explosives.
- (4) Ammonium nitrate explosives.

(1) Nitro-glycerol Explosives are explosives in which nitroglycerol is used as the explosive compound. A very large number of these explosives are known.

Nitro-glycerol, being a liquid, cannot be used for blasting purposes, unless it is mixed with some absorbing material.

Dynamite.—The chief of all nitro-glycerol explosives is dynamite. It consists of 75 per cent. of pure nitro-glycerol absorbed in 25 per cent. of an infusorial earth called kieselguhr. A plastic mass of the consistency of somewhat hardened putty is thus formed, having a colour which varies from buff to reddish brown. Sometimes special colouring matters are added.

Dynamite has most of the physical properties of nitro-glycerol; it is odourless, highly poisonous, freezes at 8° C. (46° F.). When frozen, dynamite cannot be exploded in the ordinary way, even strong detonators are not sufficient. Frozen dynamite must therefore be thawed before being used. The thawing is carried out in special cans at a temperature of about 70° C. or 160° F. The cans (Fig. 92) consist of jacketed sheet zinc vessels, A, B, the space between which contains warm water at 70° C. The whole is then surrounded with non-conducting material, C, such as felt or hair packing, which is securely fastened by lagging. The cartridges are placed in A and

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allowed to remain until thoroughly thawed. It is important that sufficient time be allowed for this to take place completely throughout the cartridge, otherwise a core of frozen dynamite

will remain, which is a source of considerable danger. On emergency a single cartridge may be thawed by carrying it in the pocket, from which all metallic substances, matches, &c., have been removed. On no account must frozen cartridges be exposed to the heat from a fire.

The cartridges should not show any trace of liquid nitro-glycerol on the surface, nor should there be any "grease spots" on the cartridge

cases. Such indications show that the nitro-glycerol is exuding from the cartridge. Exudation of nitro-glycerol from dynamite is often caused by repeated freezing and thawing.

Dynamite made with perfectly pure nitro-glycerol can be stored for an indefinite time without fear of decomposition.

Dynamite explodes at 180° C. if slowly heated and at 230° C. if rapidly heated. If exposed to heat for some time, especially to the direct rays of the sun concentrated at one point, chemical decomposition may take place, and eventually an explosion will occur. Strong electric discharges, such as a flash of lightning, can explode dynamite.

If a dynamite cartridge be immersed in water for some time, the water will entirely replace the nitro-glycerol; therefore, in blasting under water, the cartridges should always be encased in waterproof bags.

The number of explosives containing nitro-glycerol which are available for use in coal mines is very large. For their composition the Explosives in Coal Mines Orders, which are issued periodically by the Home Office, must be consulted. They all partake more or less of the properties of dynamite, are poisonous and odourless; they readily freeze, and the precautions to be observed in thawing dynamite refer equally to them. Their shattering power and sensitiveness to explosive decomposition are, in most cases, less than those of dynamite.

(2) Guncotton Explosive.—Guncotton alone compressed into slabs is used only for military blasting. For ordinary commer-



FIG. 92.

cial purposes the chief guncotton explosives are tonite and potentite. The former consists of 50 per cent. of guncotton mixed with 50 per cent. of barium nitrate, whilst the latter contains 50 per cent. of guncotton and 50 per cent. of potassium nitrate. Neither of these explosives is suitable for blasting in coal mines.

(3) Blasting Gelatin Explosives.—Blasting gelatin is a mixture of that variety of guncotton known as soluble guncotton or collodion cotton, with nitro-glycerol. An amber-coloured or dark brown coloured jelly-like mass is obtained, which can easily be cut, bent, or pressed.

The composition of blasting gelatin varies slightly according to the country in which it is made.

Composition of Blasting Gelatin.

| | Collo | dion Cotton. | Nitro-glycerol. |
|----------------------|-------|--------------|-----------------|
| Great Britain | | 9 to 10 | 91 to 90 |
| Austria and Germany. | | 7 | 93 |
| Italy | | 8 | 90 ¹ |
| Switzerland | | 9 | 91 |

Like the nitro-glycerol explosives, blasting gelatin freezes at 8° C., but is more sensitive to explosion by shock when frozen than when unfrozen. Repeated thawing and freezing do not cause the exudation of nitro-glycerol.

It requires a powerful detonator to explode it, and its sensitiveness to detonation is considerably decreased by the addition of camphor. Blasting gelatin can be kept under water without causing the nitro-glycerol to separate out. When slowly heated it begins to decompose at 60° C. and explodes at 204° C. (Hess); when rapidly heated it explodes at 240° C.

Gelatin Dynamite or Gelignite.—Blasting gelatin is only used in the case of extraordinarily tough rock. For ordinary purposes it is converted into gelignite or gelatin dynamite by the addition of absorbing powders.

Various mixtures have been used under the name of gelatin dynamite, but, according to Guttmann, its composition is :---

¹ To which are added 2 parts methyl-alcohol.

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| | | Per cen | t. | Per cent. |
|--------------|----------|--------------|---------------|------------|
| 65 per cent. | blasting | f 96.15 | nitro-glycero | = 62.50 |
| gelatin | | 3.85 | soluble cotto | n = 2.50 |
| | | (75.0 | sodium nitra | te = 26.25 |
| | | $\{ 24.0 \}$ | wood meal | = 8.40 |
| | | 1.0 | soda | = 0.35 |
| | | | • | |
| | | | | 100.00 |
| | | | | |

In some countries ammonium nitrate is used, but in Great Britain it is thought that this substance impairs the stability of the explosive.

A large number of explosives for use in coal mines contain blasting gelatin. For a list of these and for their composition the Explosives in Coal Mines Orders must be consulted.

(4) Ammonium Nitrate Explosives.—The use of ammonium nitrate in the manufacture of blasting explosives for use in coal mines largely arose from the results of the French Commission on the use of explosives in mines. It was determined that the temperature of detonation was much lower when ammonium nitrate was added to nitro-glycerol explosives than when any other nitrate was used. Sprengel also pointed out that bodies, such as nitro-benzene, nitro-naphthalene, &c., when mixed with nitric acid or nitrates, produced violent explosives, and hence appeared a large number of explosives, at one time miscalled flameless explosives and afterwards safety explosives, which, at the time, were said to be incapable of igniting mixtures of fire-damp and air or coal dust and air. Although this has not been found to be correct, many of these explosives are suitable for use in coal mines. One great advantage possessed by them is that they are completely converted into gases, and there is no solid residue to be projected in a red-hot condition into the mine's atmosphere. It must be remembered that they all produce flame on explosion, though the size of the flame produced varies greatly with different explosives.

Another advantage possessed by ammonium nitrate is its property of decomposing with explosive violence under certain conditions. The conditions are difficult to achieve in ammonium nitrate alone, but if a small quantity of a combustible body be mixed with it explosive decomposition is more easily brought about.

Ammonium nitrate explosives are not sensitive to a sudden

shock or blow, and no danger arises from sparks or flame if no caps or other explosives are near. They usually burn with difficulty, and generally only if some external flame remains in contact with them. There is little danger even when large quantities are set on fire.

One great disadvantage attending the use of ammonium nitrate is the readiness with which it attracts moisture from the atmosphere; it is therefore necessary to pack the explosive in hermetically sealed cartridge cases of lead or tin-foil, or to coat the cartridge cases with special waterproof preparations. Owing to this property ammonium nitrate explosives in paper cartridge cases are apt to deteriorate if stored for a long period in damp magazines.

It would appear that ammonium nitrate explosives are more easily detonated when in the form of a fine, dry, loose powder than when compressed, and instances are on record of cartridges, in which the powder has become more or less caked by keeping, missing fire.

Permitted Explosives.—With regard to blasting in coal mines, explosives are divided into non-permitted and permitted explosives. Permitted explosives are those which have passed certain tests in an experimental gallery at Woolwich Arsenal. The gallery consists of a metal tube about 25 feet long and $2\frac{1}{4}$ feet in diameter. One end of the gallery is covered with a metal plate, in the centre of which is a circular hole made to receive the muzzle of a cannon from which the shots are fired. The cannon is carried on a trolley, which enables it to be pushed up against the closed end of the gallery. Along the axis of the cannon is a bore-hole or barrel, from which the shots are fired. The test is described in the Twenty-fourth Report of H.M. Inspectors of Explosives (1899) as follows :—

"(1) The test will be carried out by H.M. Inspectors of Explosives with the testing apparatus at the Home Office Testing Station, Woolwich Arsenal.

(2) The charges of explosives will be determined as follows: 1—

¹ If, in any case that may arise, it is shown to the satisfaction of the Secretary of State that neither of these methods is applicable to the explosive, the method of determining the equivalent will be specially considered. (The author believes that the ballistic method described on page 228 has been substituted for the lead-block method of testing.)

"(a) In the case of explosives intended to be fired by a detonator, and commonly called 'High Explosives,' the charge will be taken as the equivalent of a given charge of dynamite No. 1 (containing 75 per cent. of nitro-glycerol) as determined by the enlargement obtained on firing the same in a lead cylinder tamped with loose sand.¹

"(b) In the case of gunpowder, or any explosive not intended to be fired by a detonator, the charge will be taken as the equivalent of a given charge of R.F.G. powder, as determined by the enlargement obtained on firing the same in a lead cylinder tamped with loose sand and heavily weighted with a mass of metal.

"(3) Each explosive will be subject to the following test:—Ten shots with charge equivalent to 3 ozs. of dynamite, or 9 ozs. R.F.G. gunpowder, and 9 inches of stemming. Ten shots with charge equivalent to 4 ozs. of dynamite, or 12 ozs. R.F.G. gunpowder, and 12 inches of stemming.

"(4) Every shot will be fired electrically, and in the case of high explosives the size of the detonator recommended by the manufacturer or the person submitting the explosive will be used.

"(5) All charges will be stemmed with dry clay well rammed.

"(6) Each shot will be fired in the case or wrapper in which it is proposed to be employed in actual use.²

"(7) Each shot will be fired into a mixture consisting of or equivalent to 85 per cent. of air and 15 per cent. of the coal gas now supplied from the Royal Arsenal Gasworks.

"(8) An explosive will be considered to have passed the test if in the series of twenty shots mentioned above no single shot has ignited the gaseous mixture or left an appreciable amount of charge unexploded.

"(9) A shot may be repeated at the discretion of the officer in charge of the testing station if, in his opinion, there is reasonable ground to believe that a failure was due to any cause unconnected with the explosive."

¹ In cases where an explosive differs very much in power from dynamite the charge fired in the lead cylinder will be varied so as to give an enlargement approximate to that given by dynamite.

² In the event of an explosive passing the test it will be permitted for use only with a detonator or detonators, and in a case or wrapper similar to those with or in which it has been tested. No alteration in the detonator or case may be made without the special sanction of the Secretary of State.

The use of permitted explosives in coal mines is regulated by orders made by the Secretary of State for the Home Department under Section 6 of the Coal Mines Regulation Act 1896, and known as the Explosives in Coal Mines Orders. In these orders the names and compositions of the permitted explosives are given, and the size of cap or detonator to be used with each explosive stated. For the conditions under which the use of permitted explosives is authorised the Explosives in Coal Mines Orders must be consulted.

The Firing of Explosives.

Low explosives may be fired with a straw or fuse, and, if confined, with a cap or detonator. High explosives can only be fired with a detonator.

A straw consists of a long paper case of narrow diameter which can be filled with fine meal powder.

A fuse consists of a core of fine meal powder, which is covered with layers of jute, tape, or waterproof material. A special variety of fuse is made by Messrs. Bickford & Co. The fuse is



lighted by a match or by use of a Bickford's patent safety igniter, which consists of a tube, A (Fig. 93), closed at one end. At the closed end is a small hermetically sealed glass bulb, B, containing strong sulphuric acid, placed in contact with a pellet, C, of potassium chlorate

and sugar, not exceeding 100 milligrams in weight. If the bulb containing sulphuric acid be broken the acid comes in contact with the potassium chlorate and sugar, and a flame is produced. To use the igniter the free end of the fuse is inserted in the igniter till it touches the pellet C, and the igniter is securely fastened to the fuse. The closed end of the igniter is then squeezed with special pliers, and the bulb, B, broken; the acid, coming in contact with the pellet, produces flame, which ignites the fuse. Owing to the end of the fuse being enclosed in the tin tube the flame of the burning fuse does not come in contact with the external atmosphere. Bickford's patent safety igniter is sanctioned for use in coal

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mines under the following conditions :- The fuse to which it is attached shall consist of a core of gunpowder, in weight not exceeding 6 grammes per metre, traversed by two threads, and enclosed by (1) a layer of jute yarn; (2) a layer of jute yarn in the contrary direction; (3) a layer of tape; (4) a layer of tape in the contrary direction; (5) a layer of jute yarn secured by a suitable varnish (the three outer layers being specially treated with a fire-proofing composition). The igniter must be securely fastened to the fuse, and the joint cemented with a special tape marked with the outline of the crown and the letter P.1

Detonators or caps consist of copper cylinders closed at one end, containing a certain quantity of a mixture of 80 per cent. mercuric fulminate and 20 per cent. potassium chlorate. The detonators are made in different sizes, which are numbered from 1 to 10, according to the weight of mixture they contain.

| Number . | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|--------------------|-------------|-----|-----|------|------|----|------|----|------|----|
| Charge in grains . | 4 ·5 | 6.0 | 8.1 | 9.75 | 12.0 | 15 | 22.5 | 30 | 37.5 | 45 |

Weight of Detonating Mixture in Detonators.

The detonator may be fired—(1) by a fuse; (2) electrically. To fire a detonator with a fuse the fuse is cut to the required length. The end to be ignited is cut on the slant, whilst the other end, which is to be inserted in the cap, is cut square. The square end of the fuse is inserted

in the cap as far as it will go without using any undue force, and when it touches the fulminate the cap is securely fastened to the fuse by



FIG. 94.

squeezing the open end with special pliers. If the explosive is being used in wet ground, it is advisable to smear the top of the cap with a little tallow or vaseline to prevent water from entering the cap. The cap is then inserted in the primer so that the upper

¹ Since this was written an Explosives in Coal Mines Order has been issued removing the fuse and igniter from the permitted list of explosives.

part of the cap projects above the explosive, and then the cartridge case is securely tied round the fuse. If the cap is inserted



so far into the primer that the fuse becomes embedded in the explosive, the burning fuse mayignite the explosive before the flame reaches the fulminate in the cap.

It is safer to use caps which are fired by electric means. These are known as electric detonators or electric fuses. Electric de-

tonators are of two kinds, namely, low-tension detonators and high-tension detonators.

Low-tension Detonators (Fig. 96) are fired by a current of low voltage but large in quantity; they consist of the

usual cap containing a mixture of fulminate of mercury and potassium chlorate. The open end of the cap is fitted with a cap or plug through which the ends of the leads, carefully insulated, are passed. The bared ends of the leads are separated from one another, and bridged across with a piece of fine platinum wire. This bridge is either wrapped round with a small wad of guncotton or embedded in some priming composition. This guncotton, or priming composition, rests above the mercuric fulminate. The embedded leads are continued outside the cap for various lengths suitable to different depths of bore-holes.

The cap is fired by passing a current of electricity from an ordinary voltaic cell or low tension exploder through the leads. This current makes the platinum bridge red hot, which fires the guncotton or priming composition, which, in its turn, fires the cap.

High-tension Detonators.—The parts of the high-tension detonator (Fig. 97) are similar to those of the low-tension detonator, and they are similarly put together in every respect except one.

FIG. 97.

Fig. 96.



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The bared ends of the leads which are embedded in the priming composition are not joined by a bridge, but separated from one another by a small gap. These detonators are fired by a current of high tension from a frictional machine or high-tension exploder. This current is of sufficient tension to jump the gap between the ends of the wires, and in so doing fires the priming composition, which, in its turn, fires the fulminate mixture.

Priming Compositions.—For high-tension detonators priming mixtures of the following composition are used :—

| (1) | Antimony | sulph | ide | | 44 | per cent. |
|-----|-----------|--------|-----|---|----|-----------|
| . , | Potassium | chlora | ite | | 44 | - ,, |
| | Graphite | • | • | • | 12 | >> |
| (2) | Antimony | sulph | ide | | 44 | ,, |
| | Potassium | chlora | ate | | 44 | ,, |
| | Potassium | nitrat | е | | 6 | ,, |
| | Charcoal | | | | 6 | > > |

In the case of the second composition, a current of lower tension is required to fire the cap than in the case of the first.

For low-tension detonators the following mixture is used :---

| Copper subphosphide | | 14 | per cent. |
|---------------------|--|----|-----------|
| ,, subsulphide | | 64 | - ,, |
| Potassium chlorate | | 22 | 22 |

Advantages and Disadvantages of High and Low Tension Detonators.—The chief advantage of high-tension detonators is the small effect that external resistance has on the current, consequently considerable length of cable can be used, and the wires of the cable may be of small diameter. One disadvantage is the necessity for perfect insulation of the cable and leads. If the insulation becomes damaged or reduced by moisture, short circuiting will occur and give rise to a miss-fire. Another disadvantage is the impossibility of testing the detonators to ascertain if they are perfect before using them.

With low-tension detonators there is not the same necessity for such perfect insulation, as the current will not jump across gaps of high resistance, hence they are of advantage in blasting in wet places and under water where the insulation may be affected by moisture. It is also considered an advantage that

they can be tested before use, and the chances of miss-fires from the use of imperfect caps avoided; this is true if the bridge be



broken, as the test applied will detect a broken bridge. But a defective cap may arise from the ends of the wires embedded in the priming mixture coming in contact and so forming a short circuit. In this case the test would show a perfect cap, but the cap would miss-fire. The disadvantage of lowtension detonators is that the external resistance has considerable effect, and cables of comparatively thick copper wires must be used.

The Test for Low-tension Detonators.—This consists in passing a low-tension current, so weak that it cannot ignite the cap, through the leads with a

galvanometer in the circuit. If the needle of the galvanometer shows that a current passes the cap is taken to be perfect, but if the galvanometer gives no indication of the passage of any current, the bridge is broken. In making the test, the cap must be enclosed in an iron tube, so that if it were to explode anaccident would be avoided.

The Safety of Mining Explosives.—The safety of an explosive for mining purposes may be considered



FIG. 99. Davis's Galvanometer for testing Low-tension Detonators. Bu permission of Messrs. Davis & Sons.

from two points of view: (1) with regard to transport and handling; (2) with regard to its ability to ignite explosive mixtures of fire-damp and coal dust.

Safety of an Explosive for Transport and Handling.—All English explosives are manufactured by licence granted under the Explosives Act of 1875, which guarantees that their composition is sufficiently safe for transport and handling in the usual

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way; but an explosive is a dangerous body and requires careful handling. Rough and careless usage may at any time cause it to explode.

Safety of Explosives for Use in Coal Mines.—The chief danger arises from the possibility of igniting mixtures of firedamp and air, or coal dust and air, and so causing a colliery explosion.

A great number of experiments and researches have been carried out to discover the exact conditions under which explosives can bring about ignition of gas and dust.

The chief danger arises from the occurrence of blown-out shots or badly placed shots, in which the explosive does not do its full share of work when fired. But no explosive, however well placed the shot may be or however well stemmed, is absolutely free from this danger.

The ease with which explosives can bring about the ignition of gas and dust varies greatly, and one of the most dangerous in this respect is gunpowder.

It would appear from the researches of Berthelot, Le Chatelier, Lohmann, Winkhaus, Heise, Watteyne and Denoël, and others that the safety of explosives, so far as the ignition of gas and dust is concerned, depends on—

- (1) Temperature of detonation.
- (2) Amount of flame.
- (3) Weight of explosive used.
- (4) Shattering power.

Temperature of Detonation.—This is the maximum temperature produced by the explosive decomposition of the explosive, and, provided no mechanical work is performed by the explosive, would represent the temperature of the products of decomposition at the moment of explosion. The temperature of detonation of the explosive can be calculated from thermo-chemical considerations, provided the chemical composition of its components and the exact nature of the chemical change it undergoes on explosion are known. Only in the case of a few explosives are these known. Many explosives are complex mixtures containing substances whose chemical composition is uncertain, and when they decompose with explosive violence it is equally uncertain what compounds are produced. In these cases the temperature of detonation can be experimentally determined, or a probable temperature calculated, by making certain assumptions.

The following table gives the temperature of detonation of certain explosives :---

Calculated Temperatures of Detonation in degrees Centigrade.

| Nitro-glycerol | 3150 | Carbonite . | | | | 1845 |
|---------------------------|--------------|-----------------|--------|-------|-----|------|
| Blasting gelatin | 3090 | Coal-carbonite | II. | | | 1821 |
| Gelatin - dynamite (gel- | | Westphalite | | | | 1806 |
| ignite) | 2 984 | Köln-Rottweiler | r safe | ety (| ex- | |
| Dynamite (75 per cent.) . | 2940 | plosive . | | | | 1774 |
| Bellite No. 1 | 2124 | Bellite No. 3 | | | | 1689 |
| Dahmenite A | 2064 | Roburite I. | | | | 1616 |
| Wetter dynamite | 1970 | Ammonium nits | rate | | | 1130 |
| Coal-carbonite I | 1868 | | | | | |

Although these temperatures are not actually produced in practice, because some of the heat produced is converted into the mechanical work of blasting, yet gases at temperatures far higher than 750° C.—the temperature of ignition of marsh gas—are set free. It is a peculiarity of marsh gas that it does not ignite instantaneously, but must be in contact with a steady flame for a certain time before ignition takes place.

Experiments conducted by the French Commission on the safety of explosives seem to show that, under the influence of a high explosive fired by detonation, a temperature of 2200° C. must be reached before the ignition of marsh gas would take place. It was decided by that Commission, therefore, that any explosive could be used with safety for blasting in rock if its temperature of detonation was below 1900° C., and for blasting in coal if below 1500° C.

With the object of reducing the temperature of detonation, inert bodies which contain large quantities of water of crystallisation such as magnesium sulphate, $MgSO_4 + 7H_2O$, and sodium carbonate, $Na_2CO_3 + 10H_2O$, are mixed with the explosive. These bodies decompose at high temperatures with the absorption of large quantities of heat, thereby lowering the temperature of the resulting gases. The use of ammonium nitrate is also effective in reducing the temperature of detonation, as its temperature of detonation is lower than that of most explosive compounds used in the manufacture of blasting explosives.

The following table shows the effect of ammonium nitrate on the temperature of detonation :---

| | Composi | ition. | Weight Igniting : | | |
|---------------------------------|----------------------|-----------------------|---------------------------|-------------------------------------|--|
| Temperature of Detonation. | Ammonium Nitrate. | Di-nitro- Benzene. | Dust. | Dust and 7 per Cent. of Pit Gas. | |
| 2200° C. | Per cent. 83 | Per cent. 17 | Ounces. 7.93 | Ounces. - 1.76 | |
| 2047° C. 1870° C. 1696° C | 86 89 92 | 14 11 0 | 10.58 17.64 17.64N* | 3.03 5.29 19.35 | |
| 1482° C. | 95·25 | 8 4·75 | 17.64N* | 17.64 | |

* N=Non-ignition.

Flames from Explosives .- Every explosive on detonation produces a flame, or, if not actual flame, white hot and incandescent gases. The flames given by exploding 100 grammes (3.53 oz.) of explosives, either suspended in the air or as blownout shots unstemmed from the bore-hole of a steel mortar, have been photographed by Siersch.¹ His results show that— (1) Every explosive on detonation gives a characteristic flash both as regards size and shape, whether fired freely suspended or as blown-out shots. (2) The smaller the flame the greater the relative safety of the explosive. (3) The size of flame increases with the weight of explosive fired. (4) The size of the flame increases with the diameter of the cartridge and decreases with the density. (5) The size of the flame given by any ammonium nitrate decreases as the quantity of ammonium nitrate is increased. (6) The use of water or wet moss for stemming very considerably reduces the quantity of flame given by any explosive.

The flames given by explosives are either large and spreading or small and compact, and a comparison between the results obtained by exploding various explosives in mixtures of firedamp and air and the flames given by them leads to the conclusion that those explosives which give large spreading flames are not so safe as those giving smaller and less spreading. It seems reasonable to suppose the larger the flame the larger the amount of gas and dust it will come in contact with, and the greater the ease with which ignition will occur. It is therefore

¹ Trans. Inst. M. E., vol. xi. p. ii.

possible to conceive that a large flame of low temperature lasting for a comparatively long time may produce ignition, whereas a smaller flame of much higher temperature but lasting a much shorter time may not.

The Weight of Explosive Used.—It has been shown by the German experimenters, Winkhaus, Heise, and others, that the safety of an explosive decreases as the weight of the charge increases. According to Winkhaus, there is for every explosive a certain weight of charge which cannot be exceeded without producing danger of ignition of gas and dust. This weight decreases as the percentage of gas in the air increases. A greater weight is required to produce ignition of dust alone than dust mixed with fire-damp. The following table compiled from Winkhaus's ¹ results will give some idea of the weights that will give rise to ignition :—

| | | Pit | | Dust. | | |
|--------------------|-----------------|---------------------|----------------|----------------|---------|---------------------------------|
| Explosive. | 21 per Cent. | 6 to 7 per Cent. | 8 per Cent. | 9 per Cent. | Alone. | +6 to 7 per Cent. of Gas. |
| | Ounces. | Ounces. | Ounces. | Ounces. | Ounces. | Ounces. |
| Blasting gelatin . | 2.65 | 1.76 | 1.33 | 0.32 | 5.3 | 1.58 |
| Dynamite | 2.65 | 2.05 | | | | 1.06 |
| Stonite | 3.92 | 2.86 | | | | |
| Roburite | 5.36 | 2.40 | 3 | | | 4.59 |
| Roburite No. I. | | | 14.12 | 8.82 | 21.88N | 21.88 |
| Wetter dynamite | 7.05 | 5.43 | | | | 1.08 |
| Westphalite . | 10.58 | 8.85 | | | | 8.82 |
| New Westphalite | | | 17.65 | 5.30 | 21.18 | 21.18N |
| Dahmenite | 12.35 | 8.85 | | | | 8.82 |
| Dahmenite A | | 0.00 | 14.12 | 3.53 | 19.4 | 17.65 |
| Progressite | 14.11 | 19.4 | | | | 19.76 |
| Carbonite | 15.88N | 21.17N | 21.18N | 21·18N | 35.3N | 29.64N |
| | | | | 1 | | |

N = Non-ignition, the experiments not being continued beyond these weights.

So convinced are the German investigators of the effect of weight of charge on the safety of explosives that in testing explosives for safety the charge fired into an explosive mixture of fire-damp and air or dust and fire-damp is gradually increased by 50 grammes (1.76 oz.) until a weight is obtained which will

¹ Trans. Inst. M. E., vol. ix. p. 250; vol. xii. pp. 32 and 33.

produce ignition in five shots. These are the weights given in the preceding table.

The Shattering Power.—According to Heise, the safety of an explosive decreases as its shattering power increases, the shattering power being defined according to the explanation given on page 229. When a shot is fired in a shot-hole a compression wave travels through the air; the amount of compression produced will depend upon the suddenness of the initial shock, which will also depend upon the maximum pressure produced and the rapidity with which that maximum pressure is reached.

The temperature of the air in the compression wave is raised, and according to the law which governs the rise of temperature according to pressure. Heise has calculated that under a pressure of 60 atmospheres the temperature in the wave would be 670° C., under 100 atmospheres 820° C., and under 200 atmospheres 1060° C. By the explosion of a detonated explosive in a shot-hole Heise points out that a momentary pressure of from 6000 to 8000 atmospheres may be produced, and in the neighbourhood of the shot-hole a compression wave in which the pressure is 100 atmospheres might easily be produced. In this compression wave the temperature reached would be above the temperature of ignition of fire-damp, and if that gas were present in the atmosphere its ignition would result. He therefore concludes that the less shattering an explosive the safer it is for use in coal mines.

The results given on the next page, obtained by Heise, bear out his contention.

In blasting, the safe use of explosives can, to a certain extent, be controlled by the exercise of proper care in the choice of explosives, in the manner of placing the shot, and in the charging of the hole. The weight of the charge should be carefully proportioned to the work it has to do, so that the greatest proportion possible of the energy of the shot may be used in doing mechanical work. When this is the case the temperature of the escaping gases is reduced as low as possible. The length of the charge should be regulated by the depth of the shot-hole, as the longer the length of stemming the greater the safety. The stemming should consist of non-inflammable material, preferably well-puddled moist clay; under no circumstances must coal dust or bituminous shale or bind be used, because these

| Explosive. | Strength deter- mined with 10 Grammes Explo- sive, Carbonite being 100. | Weight e 2500 Kild metres of | qual to ogram- Work, | Shattering Power corresponding to these Weights, Car- bonite being 100. | Limiting Charge of Safety in Dusty Atmosphere con- taining 8 per Cent. Pit Gas. |
|-----------------|---|------------------------------------|----------------------------|--|---|
| | | Grammes. | Ounces. | | Ounces. |
| Carbonite . | 100.0 | 10.82 | 0.382 | 100.0 | 31.77N |
| Carbonite I. | $112 \cdot 2$ | 10.46 | 0.369 | 105.5 | 25.60N |
| Carbonite II | 119.4 | 10.78 | 0.380 | 121.8 | 25.90N |
| Köln - Rott- | | | | | |
| weiler | 166.0 | 9.40 | 0.331 | 143.0 | 8.82 |
| Dahmenite A . | 230.0 | 7.33 | 0.258 | 137.3 | 17.65 |
| Do., granulated | 164.1 | 7.33 | 0.258 | 109.0 | 24.71N |
| Roburite I | 155.8 | 11.36 | 0.401 | 157.9 | 12.35 |
| Westphalite . | 188.8 | 9.12 | 0.321 | 157.9 | 12.35 |
| | | 1 | | | |

N signifies non-ignition, and that the explosive was not tested beyond this weight.

substances will give off gases that will ignite and increase the amount of flame. Above all, the size of the cap used should be sufficient to bring about the most complete explosive decomposition, and thus ensure the development of the greatest amount of energy. The use of too small a cap may give rise to a miss-fire or a blown-out shot, but if these do not occur the decomposition produced may not be that which gives rise to the development of the greatest amount of energy, and the charge may behave as an under-loaded shot.

CHAPTER XIII

EXPLOSION IN GASES

WHEN a combustible gas burns the relation between the volume of gas burnt and the volume of oxygen required for the combustion is constant so long as the products of combustion are always the same. If the gas be burnt in air the volume of air required is that which contains the necessary quantity of oxygen.

The combustion of all gases containing carbon, except carbon monoxide, may be complete, when carbon dioxide is formed, or incomplete, when carbon monoxide is produced. In the latter case a smaller quantity of oxygen is required than in the former, but the relation between the volumes of combustible gas and oxygen is definitely fixed in each case.

For example, when the combustion of marsh gas is complete and carbon dioxide and water are formed the relation between the volumes of marsh gas and oxygen is 1 to 2, but if air containing 21 per cent. by volume of oxygen be used the relation becomes 1 to 9.52, because 9.52 volumes of air contain 2 volumes of oxygen. If, however, the combustion of marsh gas be incomplete and carbon monoxide and water formed, then the relation between the volumes of marsh gas and oxygen becomes 1 to 1.5, or, when air is used, 1 to 7.14.

The table on page 252 shows the relations between the volumes of combustible gases and oxygen or air when combustion is complete and incomplete, and the volumes of gas produced by the combustion.

If these gases are ignited as they issue from a jet into the air they burn quietly, and the quantities of oxygen given in the table are consumed for every volume of gas burnt, but if the gases are mixed with oxygen or air before ignition then on starting the ignition at any point in the mixture the combustion spreads throughout the mass of gases with extreme rapidity, and

Volumes of Oxygen and Air required for Combustion of One Volume of Combustible Gas.

| Combustible Gas. | Oxygen. | Air containing 21 per cent. Oxygen. | Volume of Products of Combustion. | | | | | | | |
|--|----------------------------|--|--|--|--|--|--|--|--|--|
| Hydrogen Carbon monoxide Marsh gas Ethylene | $0.5 \\ 0.5 \\ 2.0 \\ 3.0$ | 2·38 2·38 9·52 14·28 | $\begin{array}{l} 1 \ \text{vol.} \ H_2O \ (\text{gaseous}). \\ 1 \ ,, \ CO_2. \\ 1 \ ,, \ CO_2, \ 2 \ \text{vols.} \ H_2O \ (\text{gaseous}). \\ 2 \ \text{vols.} \ CO_2, \ 2 \ \text{vols.} \ H_2O \ ,, \end{array}$ | | | | | | | |
| Incomplete Combustion. | | | | | | | | | | |
| Marsh gas Ethylene | 1·5 2·0 | 7·14 9·25 | $\begin{array}{l} 1 \mbox{ vol. CO, 2 vols. } H_2O(gaseous). \\ 2 \mbox{ vols. CO, 2 vols. } H_2O ,, \end{array}$ | | | | | | | |

the mixture is said to undergo explosive change, whilst the change is called explosion.

The following are characteristic of explosion in gases :---

(1) The sudden liberation of large amounts of energy.

(2) The rapidity with which the change takes place.

(3) The peculiar manner in which the combustion is propagated throughout the mass of gas.

Heat of Combustion.—When any gas burns energy is liberated which is generally measured in the form of heat. The amount of heat liberated when a unit weight of any gas is burnt in oxygen is known as its heat of combustion. If the amount of mechanical energy corresponding to the heats of combustion is calculated, it will be realised how great an amount of energy is set free by the combustion.

The table on the next page shows the heat of combustion of different gases measured in the lbs. of water raised 1° C. by the combustion of 1 lb. of the gas, and the foot-lbs. of mechanical energy corresponding to the heat of combustion.

Rapidity of Combustion.—The amounts of energy given in the table are always liberated by the combustion of a unit weight of the gas, and in the ordinary combustion are set free slowly. Each gas burning quietly in the air has to seek the oxygen for its combustion, takes it up as it requires it and sets the energy free regularly and quietly. But if the gases are mixed the combination between the molecules takes place suddenly and the whole of the energy is set free in an exceedingly short space of time. How quickly the change may take place is seen from the results obtained in photographing the progress of the flame in an explosive mixture of hydrogen and oxygen, from which it has been estimated that the change is completed in less than one-thousandth part of a second.

The actual velocity with which the flame travels in an explosive mixture of gases was first measured by Bunsen and estimated to be 34 metres (109 feet) per second in a mixture of 2 volumes of hydrogen and 1 volume of oxygen, whilst in the

| Gas. | Lbs. of Water raised 1° C. by Com- bustion of 1 lb. of Gas. | Estimated Foot- lbs. of Mechanical Energy. |
|-----------------|--|--|
| Hydrogen . | . 34,500 | 47,955,000 |
| Carbon monoxide | 2,435 | 3,384,650 |
| Marsh gas . | 13,344 | 18,548,160 |
| Ethylene | 12,183 | 16,934,370 |

Heat of Combustion.*

* NOTE.—English units are used in this table in order to make the comparison with the English unit of mechanical energy.

case of carbon monoxide, marsh gas, and coal gas, it was about 1 metre (3.2 feet) per second. Later investigations by Berthelot and Mallard and Le Chatelier have shown that the velocity of explosion ultimately reached is very much greater than those measured by Bunsen, and their results have been fully confirmed and added to by the researches of Dixon and others.

The general results arrived at by these researches are that when an explosive mixture of gases is ignited in a tube (1) the flame travels for a certain distance at a uniform velocity. This distance depends on the diameter and length of the tube. (2) At a certain point the character of the flame changes and assumes a vibratory motion. The flame swings backwards and forwards with oscillations of increasing amplitude, whilst the velocity with which the vibrating flame travels through the mass gradually increases.

(3) Finally a maximum velocity is reached which remains constant throughout the remainder of the explosion. In some cases, however, the flame goes out before the maximum velocity is reached.

The propagation of the explosion with the maximum velocity constitutes "detonation," and has been called by Berthelot the "explosive wave" (*l'onde explosive*). This is transmitted throughout the entire mass of the exploding gas by a series of shocks among the gaseous molecules which have been brought into a state of violent vibration in consequence of the heat set free by the chemical change. The maximum velocity, which is constant for each explosive mixture, is only set up after the flame has travelled a certain distance, and is independent of the nature of the material of the tube in which the explosion takes place and of its length, provided the critical length sufficient for the explosive wave to be established is exceeded.

The actual velocities established in explosive mixtures have been measured by Berthelot and Dixon, and their results in metres per second are given in the following table, in which are also given velocities calculated from certain theoretical considerations enunciated by Berthelot :---

| Gaseous Mixture. | Berthelot. | Dixon. | Calculated. |
|--|-------------|-------------|-------------|
| <pre>1 vol. hydrogen +0.5 vol. oxygen 1 ,, marsh gas +2 ,, ,, 1 ,, ethylene +3 ,, ,, 1 ,. carbon monoxide+0.5 vol.</pre> | M. per sec. | M. per sec. | M. per sec. |
| | 2810 | 2821 | 2831 |
| | 2287 | 2322 | 2487 |
| | 2210 | 2368 | 2517 |
| | 1090 | 1264 | 1940 |
| | | 1738 | |

Further investigations of Le Chatelier and Dixon have shown that from the point where detonation starts a wave is thrown back through the still burning gases; this has been called a wave of "*retonation*." The burning gases through which the retonation passes are probably still in the initial stages of inflammation in which the flame is propagated with a much slower velocity than when detonation takes place. The retonation wave passing through these layers increases the rate of their combustion. If mixtures of coal gas and air and fire-damp and air are ignited they show phenomena of the first and second kind. Ignited at the open end of the tube the flame travels quietly for a certain distance with uniform velocity, then it begins to vibrate. The vibrations travel with increasing velocity and growing intensity, according to the composition of the mixtures and conditions of the experiment, but the uniform maximum velocity is not set up. In narrow tubes the flame dies out.

The combustion of gaseous compounds of carbon to carbon dioxide may take place in one stage only, $C + O_2 = CO_2$, or in two stages, carbon monoxide being the first product, C + O = CO, and this gas may subsequently burn with the excess of oxygen, forming carbon dioxide, $CO + O = CO_2$. This has an important bearing on the propagation of explosions of fire-damp and the formation of after-damp. Dixon has pointed out that, if the burning takes place in one stage, the rate of the explosive wave should correspond with the velocity for the complete reaction; whereas, if the combustion takes place in two stages, the explosive wave should correspond with the velocity for the formation of carbon monoxide. By experiment Dixon has shown that when the oxygen is present in sufficient quantity only to form carbon monoxide the velocity of explosion is greater than when there is sufficient oxygen to form carbon dioxide, which is in favour of the view that carbon monoxide is the direct product of the explosion and that the carbon dioxide is subsequently formed by the combustion of that gas.

The above is only a mere outline of some of the more important facts relating to explosion in gases that have been obtained by the investigators of the subject, and when they are applied to the results of an explosion of the magnitude of a colliery explosion they help to explain them.

In a colliery explosion the ignition of the explosive mixture is accompanied by (1) a loud report; (2) a considerable expansion of the gases followed by a contraction with an inrush of air into the mine; (3) a large amount of mechanical damage; (4) a residual atmosphere, known as after-damp, which is highly poisonous owing to the presence of carbon monoxide.

The sudden transformation of energy consequent on the rapid chemical change produces the report and gives rise to high temperature and pressure. Although, owing to the formation of carbon monoxide, the volume of the products of combustion may, at the moment of explosion, be slightly greater than that of the exploding gases, this does not account for the large expansion, which is chiefly due to the high temperature.

After the explosion the temperature falls and the heated gases contract; this contraction is rendered greater by the condensation of the steam produced by the combustion as soon as the temperature falls below 100° C. The contraction is followed by an inrush of air.

The destruction is one of the chief features; falls of roof, blown-out props, tubs overturned and hurled for distances along the roadways, are found along the track of the explosion. The forces required to effect this damage are very great, but when account is taken of the large amount of energy that is brought into play by the combustion and the manner in which the explosion is propagated, it is easy to realise that so much damage is possible in spite of the small mass of the exploding gases. The manner of propagation is described by Professor Dixon in a paper read before the Institution of Mining Engineers in 1892, as follows :---

"If a mixture of coal gas and air, or of fire-damp and air, in free communication with the atmosphere, is ignited, the flame at first would do little damage; but passing along a gallery of a mine, would begin to vibrate, and then, gathering impetus, would produce enormous oscillations of heated gas, which would smash everything in its way."¹

In this way the extent of the damage is easily explained, but the results of the experimental researches offer an explanation of the intermittent character of the damage.

It is well known that frequently little damage is done at the seat of ignition, and that evidence of the violence of the explosion does not occur till some 50 to 80 yards from that point, also, that in travelling along the course of an explosion, the amount of damage varies, places of great damage are separated by intervals of comparatively little damage.

The small amount of damage that is done in the neighbourhood of the seat of the ignition is probably due to the comparatively quiet form of combustion that takes place previously to the setting up of the vibratory condition. In this region only charring of timbers and burning of brattice will take place. The damage begins when the vibratory motion is set up in a column of gas; the column is divided into regions of active vibration separated by periods of comparative or complete rest. As the vibratory motion is propagated through the roadways of the mine, the greatest damage will occur where the masses of gas are in most active motion, whilst comparatively little or no damage will be produced where the intervals of rest exist.

Colliery Explosions.

A colliery explosion may result from an ignition of (1) firedamp, or (2) coal dust.

(1) **Explosions of Fire-Damp**.—An explosion caused by the ignition of fire-damp may be confined to the gaseous mixture, or, after initiation in the gaseous mixture, it may be continued through the agency of coal dust.

There are certain features which indicate whether an explosion has been a purely gaseous explosion; amongst these are (1) the extent of the explosion, (2) the roadways affected, and (3) evidence of alarm on the part of the victims. No explosion can be carried on without the necessary fuel, consequently a purely gas explosion must be confined to those parts of the mine in which the atmosphere is fouled with fire-damp in sufficient quantity to form an explosive mixture. It is therefore characteristic of a purely gas explosion that the length of roadways affected is usually short, and that it is confined within the district in which it starts, except in cases of sudden outbursts of gas of large extent. The explosion, once started, continues in the direction of those districts in which an explosive mixture exists with a force which depends on the proportion of gas in the mixture. Finally it expends its violence and ceases when it reaches an atmosphere in which there is no explosive mixture.

The extent to which the atmosphere of a mine will be fouled by gas so as to become explosive will generally be confined within the limits of the roadways in the neighbourhood of the place of escape, whether it be from the coal face or from the goaf or old workings; hence the comparatively small extent of a purely gas explosion.

The roadways chiefly affected are return air-ways; only intake air-ways in the immediate neighbourhood of the seat of explosion are, as a rule, affected, and then to a smaller extent than the return air-ways. Very seldom does a purely gas explosion pass into the main intakes unless they are dusty. It is easy to understand this, for, as the ventilating current passes through the mine, the fire-damp accumulates in the return airways, and in this air the explosion is more likely to find the necessary fuel than in the intake air; therefore the tendency is for the explosion to traverse the return air and only pass into the intake air so far as that air has become fouled in the immediate neighbourhood of the place of ignition.

It is further characteristic of a gas explosion that some alarm has been experienced before the explosion occurred. The men working in the district have been warned of the existence of large quantities of gas by the jumping of the flames of their lamps, and have left their working places. The bodies of the victims are usually found some distance from the seat of ignition, they having been overcome by the poisonous gas, or killed by the violence of the explosion in their attempt to escape. Frequently there is oil in the lamps of the victims, because the lamps have been extinguished either by the men, when alarmed by the presence of the gas, or by the gas itself firing in them.

These features of an explosion confined to fire-damp are well illustrated by the explosion that occurred at the Whitehaven Colliery on April 25, 1882, which is described by W. N. and J. B. Atkinson in their book on "Explosions in Coal Mines."

The explosion originated in a working-place at G (Fig. 100), at the bottom of a drift 208 yards long which passed through a 32 yards down-throw fault and connected the two parts of the same seam. The drift was connected through the place, C, with a passage driven back to the fault, where a staple, E, made connection with the workings above. At the top of the drift was a staple, H. When the staple at E was completed, air was taken down the drift into the workings below and returned up E; but, before the completion, the drift and workings were bratticed. and air was taken down one side of the brattice and returned up the other to the staple at H. About two months before the explosion a fall took place in the staple at E, completely blocking it, and the ventilation by means of bratticing was again resorted to, the air being taken down the drift on one side of the brattice into G, then returning by way of D to the staple at H.

Large quantities of gas had been met with whilst the work was being carried out; before the explosion it was frequently found at the face at G, and four days before the explosion it



From "Explosions in Coal Mines." By permission of Messrs. W. N. and J. B. Atkinson.

was seen in lamps in the intake 15 yards from C towards D, whilst the return air escaping at H was nearly explosive. At the time of the explosion there were 10,800 cubic feet of air passing down the drift. Seven men were working in the district, a driver at M, a pumper at K, three pumpers who were working at the pump at the bottom of the drift, and two hewers at the face, all having safety lamps. It appears that when the hewers prepared to begin work at G, the "flames of their lamps lifted." They seized their lamps and hurried out, but when they were in the place C they were knocked down by the force of the explosion.

The explosion passed up the drift, but did not extend into the return air-way beyond the top of the staple H. The brick brattice in the drift was blown over from the return into the intake, and the force of the explosion expended itself at the top of the drift where doors at 1, 2, and 3 were blown down, and stoppings at 4, 5, and 6 were blown out. A light stopping 1700 yards away was forced. The lamps of the hewers were found at L_1 and L_2 . Four men were killed—the three pumpers and one hewer. Their bodies were found at the top of the drift at X. The workings were wet and there was no dust. It was estimated that 32,800 cubic feet were filled with explosive mixture, and that the explosion passed along the return side of the brattice up to the top of the drift and passed into the intake by blowing down the brattice.

The characteristics of this explosion are :---

(1) Its fixed limits; it did not continue beyond the area fouled with gas. (2) The workmen at the face were alarmed and left their places before the explosion occurred, whilst the pumpers at O would appear to have been alarmed and to have been retreating at the time the explosion took place. (3) The explosion passed along the return air-way and only passed into the intake because the force of the explosion blew down the brattice which separated the intake from the return.

Coal Dust.—More important than fire-damp is coal dust. The part it plays in colliery explosions is twofold: (1) It can influence an explosion originated by fire-damp; (2) it is itself capable of forming an explosive mixture with air in the entire absence of fire-damp.

The Influence of Coal Dust on a Gas Explosion.—Coal dust can influence a gas explosion in the following ways :—

(1) When dust is present in the air the proportion of firedamp required to form an explosive mixture with air is very much reduced. (2) The amount of flame which accompanies the explosion is considerably increased.

(3) The area affected by the explosion is greatly extended.

(4) The amount of carbon monoxide which is formed is probably greater than when fire-damp alone explodes.

(1) The Proportion of Fire-Damp which is rendered Explosive by the Presence of Coal Dust.—In dustless air 6 per cent. of fire-damp is generally accepted to be the smallest quantity that will burn with explosive violence, but Mr. W. Galloway concluded, from experiments made with the dust from the Llwynypia Colliery, that as small a quantity as 0.892 per cent. of fire-damp, equal to 1 of fire-damp to 112 of air, was rendered explosive by the presence of that dust. Sir Frederick Abel brought about explosions in mixtures containing 2 to $2\frac{1}{2}$ per cent. of fire-damp in presence of dust from the Seaham Colliery, and these results were confirmed by experiments made for the Prussian Fire-Damp Commission, which came to the conclusion that so small a proportion as 2 to 3 per cent. of marsh gas in the air gives rise to the danger of an explosion with the great majority of German dusts.

(2) Influence of Coal Dust on the Amount of Flame.—In experiments made for the Prussian Fire-Damp Commission it was estimated that from 10 to 13 feet of flame are produced when a blown-out shot of half a pound of gunpowder is fired into gas-free air from a shot-hole stemmed with clay, and that the flame increases to 16 feet when the hole is stemmed with stone dust and coal dust, whilst if coal dust alone is used the flame increases to 31 to 52 feet.

In experiments on flameless explosives made by the North of England Institute of Mining Engineers it was proved that considerably more flame was produced when shots were fired into dusty atmospheres than when fired into gaseous atmospheres without dust.

When a gas explosion takes place it may be compared with a blown-out shot, and if it occurs in a dust-free atmosphere the amount of flame produced is that due to the volume of gas that is burnt; but if the air be charged with coal dust the heat of the flame causes some of the dust to distil, with the production of gases which take fire and add to the volume of flame, whilst the atmosphere becomes charged with red-hot particles of coke dust.

(3) Influence of Coal Dust on the Extent of a Gas Explosion. —By far the most important effect is the manner in which coal dust will carry on a gas explosion beyond the limits of the gasfouled area. Many gas explosions have taken place which have traversed very considerable lengths of roadways, in some cases amounting to thousands of yards. The extent of the explosion in these cases is so great that it is difficult to account for it by the explanation that the atmosphere throughout the course of the explosion was fouled with gas in sufficient quantity to form an explosive mixture. If this were so, there would be evidence of alarm all along the course, but in most cases this is wanting. It is also improbable from the fact that generally the roadways are main intake air-ways, which could only be fouled by gas coming from some sudden outburst.

These main intakes are generally dry and dusty with coal dust which forms tolerably thick layers on the roadways, timbers, and walls, and in its finest form floats in the air itself. The dust in such an atmosphere produces just the conditions necessary to continue an explosion of gas when started, for, when the explosion takes place, the flames not only shoot forward into the dusty atmosphere and ignite the dust in suspension, but the vibrating masses of burning gas blow up clouds of dust in front of them, which become ignited, and they in turn blow up and ignite further clouds and the explosion is continued along the dusty roads as long as there is coal dust in sufficient quantity capable of being blown up into the air by the force of the exploding mass.

In these explosions it is a well-known fact that their course is stopped by roadways that are wet, from which the dust cannot be blown up in clouds, or roadways dusty with a noninflammable stone dust, or coal dust largely mixed with stone dust, which proves that coal dust and not gas causes the propagation of the explosion. If the explosion were continued in an atmosphere fouled with gas along its whole course the wetness of the coal dust or the presence of stone dust would make no difference to the explosion, which would continue so long as there was gaseous fuel, and only the absence of gaseous fuel would stop it, whereas in an explosion propagated by coal dust it is the absence of inflammable dust that stops the explosion.

A very good example of a gas explosion continued by dust is

that of Trimdon Grange, which took place in 1882, and is fully described by Messrs. W. N. and J. B. Atkinson in "Explosions in Coal Mines," from which the following résumé is taken :---

The explosion took place in the Harvey seam, and was confined to districts on the north side of the downcast shaft (Fig. 101). There were three principal districts-the Headways, the Cross Cut, and the Pit Narrow Board. At the end of the Pit Narrow Board was an engine landing, beyond which were some old drowned-out workings. At the engine landing was a pump used to pump the water from these old workings. The pump was working on the day of the explosion, and was tended by a boy. The probable cause of the explosion was the ignition of gas, which escaped from these workings owing to the lowering of the water, and the fact that the barometer was low. The explosion passed along the Pit Narrow Board main intake for 1757 yards, where 12,560 cubic feet of air were passing, also up the horse level and along the first and second southways, and from them reached the face and passed into the return for a short distance. From the Pit Narrow Board it passed up the roadway leading to the Cross Cut and Headways districts. At the junction of the main haulage road of these two districts it passed along the Headways intake for 1045 yards, along which 10,971 cubic feet of air were passing; from this intake it reached a small portion of the face, and entered for a short distance into the return. It did not pass into the Cross Cut Way. The most distant parts affected by the explosion were 2800 yards apart along the roads traversed by it. Seventy-four men and boys and eleven horses were killed. The explosion traversed main intake and haulage roads, which were dry and dusty. It did not traverse the Cross Cut Way, which was damp for a distance beyond the junction with the Headways Way. Little or no damage was done to the returns except where the force of the explosion had blown out the doors; where it did enter the return it soon died out. Coked dust was found in large quantities at the extremities of the explosion. The survivors said they were under no apprehension at the time of the explosion.

All these facts point to the continuance of the original gas explosion by coal dust. The extent makes it impossible to believe that the air along the whole course was fouled with gas, and further evidence of this is to be found in the fact that the air which ventilated the Headways and Cross Cut Ways districts

came from the same source, and was split at the junction of the two haulage roads, but the explosion only traversed the dusty



FIG. 101.—From "Explosions in Coal Mines." By permission of Messrs. W. N. and J. B. Atkinson.

Headways road and did not pass into the Cross Cut Way which was wet for some distance up. The conclusion arrived at by Messrs. W. N. and J. B. Atkinson was that "the wave or movement of air accompanying the ignition of a mixture of firedamp and air in the landing had raised a cloud of dust, and that the flame from the fire-damp had passed into this cloud, causing ignition of the dust; the ignition of the dust thus started became self-propagating, and continued with force and flame over those parts of the pit where a sufficient quantity of dust existed."

(4) Increase in the Amount of Carbon Monoxide.-There is no direct evidence to show that the amount of carbon monoxide formed is greater in proportion to the fuel burnt in an explosion continued by coal dust than in one that is not, but it is held by some authorities that this must be the case, because the proportion of carbon in a dust explosion is probably greater than in a gas explosion, which will tend to the production of carbon monoxide, and, in addition, the red-hot particles of carbon coming in contact with carbon dioxide will help to reduce that gas to carbon monoxide. It has been shown by Dixon that when marsh gas and other gases containing carbon explode, carbon monoxide is the direct result of the explosion, but whether this is the case when carbonaceous dusts explode has yet to be proved. So far as the action of coal dust in increasing the proportion of carbon monoxide is concerned, it probably depends on whether carbon monoxide is the direct result of the explosion or not.

Coal Dust Explosions.

That coal dust could take part in a colliery explosion was pointed out as early as 1803. On 8th September in that year an explosion took place at the Wallsend Colliery. In a report written after an examination of the scene of the disaster it was stated that "the workings were dry and dusty, and the survivors who were most distant from the point of explosion were burnt by the showers of red-hot sparks of the ignited dust which were driven along by the force of the explosion."

In 1845 a further reference was made by Professor Faraday and Sir Charles Lyell in a report on an explosion at the Haswell Colliery which took place in 1844. The following is an extract from the report :---

"In considering the extent of the fire from the moment of

the explosion it is not to be supposed that fire-damp was its only fuel; the coal dust swept by the rush of wind and flame from the floor, roof, and walls of the works would instantly take fire and burn if there were oxygen enough present in the air to support its combustion; and we found the dust adhering to the faces of the pillars, props, and walls in the direction of, and on the side towards, the explosion, increasing gradually to a certain distance as we neared the place of ignition. This deposit was, in some parts, half an inch, in others almost an inch thick. It adhered together in a friable coked state; when examined with the glass it presented the fused round form of burnt coal dust, and when examined chemically and compared with the coal itself reduced to powder was found deprived of the greater portion of the bitumen and, in some instances, entirely destitute of it. There is every reason to believe that much coal gas was made from this dust in the very air itself of the mine by the flame of the fire-damp which raised and swept it along, and much of the carbon of this dust remained unburnt only from want of air. At first we were greatly embarrassed by the circumstance of the large number of deaths from choke-damp, and in the evidence that that had been present in very considerable quantities compared with the small proportion of fire-damp which, in the opinion of those in and about the works just before, must have occasioned the explosion. But on consideration of the character of the goaves and reservoirs for gaseous fuel and the effect of dust in the mine, we are satisfied that these circumstances fully account for the apparent discrepancy."

Further reference was made to the same subject by Professor Faraday at a discussion at the Royal Institution. But these significant references were passed by till MM. Verpilleux and Vital in France and Professor W. Galloway in England drew attention to the importance of the subject. Professor Galloway supported his views by experimental evidence. He was one of the first to hold prominently the view that coal dust when suspended in air that contained no fire-damp was explosive and could be ignited by a blown-out shot. He was led to this conclusion when considering the much greater violence and extent of explosions that occurred in South Wales collieries in comparison with those that occurred in Scotch collieries, and stated that "the usual attempted explanation by supposing sudden outbursts of gas to have taken place was quite untenable, and there must be some other cause which had not been discovered." Following the publication of his views and the results of his experiments a controversy arose as to whether coal dust alone was explosive, or the presence of fire-damp was necessary to cause ignition.

The evidence of experiment was brought to bear on the subject, but the results were most conflicting. Various commissions in England and abroad conducted experiments and collected evidence, but differed in their conclusions.

It is quite impossible to refer to all the experimental evidence, and only some of the more important can be mentioned. Amongst some of the earlier experiments those of the Chesterfield and Midland Counties Institution of Engineers were carried out in a wooden gallery 82 feet long, 12 inches wide, and 18 inches deep. 134 experiments were made with dust alone, and ignition occurred in 36 cases, equal to 27 per cent.; whilst in 46 experiments with dust and gas ignition occurred in 21 cases, or about 46 per cent. The conclusion arrived at from these results was that "in no instance, even in the presence of 6 per cent. of gas, was anything that could be called explosion produced, the only result being ignition."

In 1876 experiments on a larger scale were made by Sir Henry Hall, then H.M. Inspector of Mines, in an adit 45 yards long. Coal dust was strewn on the floor of the adit and shots were fired in the face. The dust ignited, the flame travelled the whole length, and the blast was so violent that it would have proved fatal to any one struck by it.

Later, in 1891, Sir Henry Hall carried out two series of experiments on a scale comparable with working conditions. The first series of experiments were confined to dusts from the Lancashire coal : seams and carried out in three different sets.

First Set.—A cannon, 2 feet 6 inches long with a 2-inch bore, was suspended, muzzle upwards, at the bottom of a disused shaft 50 yards deep and 7 feet in diameter, which acted as the upcast shaft for a pumping shaft about half a mile away. Two to three hundredweights of fine dust from the Arley seam were thrown down the shaft and charges of 1 to $1\frac{1}{2}$ lbs. of gunpowder fired into the dusty atmosphere from the cannon; out of 5 experiments 4 ignitions occurred.

Second Set .- The experiments in this set were carried on in

a similar manner to those in the first set, in a pit in the process of sinking and 130 yards deep. At a depth of 100 yards there was a cut through to another shaft, also in the process of sinking; at this point the cannon was suspended. In 6 experiments with dust from the Arley seam no ignition occurred, but in this case the shaft was very wet.

Third Set.—These experiments were carried out at the Big Lady Pit in a shaft 210 yards deep and 8 feet in diameter, which acted as an upcast for a pumping shaft 21 yards away, and in it air was travelling at the rate of 100 feet per minute. The cannon was suspended at a depth of 180 yards. Seventeen experiments were made, in all of which the air was tested for fire-damp, which was found to be absent. Nine ignitions occurred.

The second series of experiments, which were made in 1893 in a disused shaft at the White Moss Colliery, Skelmersdale, were much more extensive. Dusts from most of the coal fields in Great Britain were tested.

The shaft was 50 yards deep and 7 feet in diameter. It was ventilated by a current of 750 feet of air per minute. Struts of timber, 6 feet long, 7 inches broad, were fixed at intervals of 6 feet down the shaft to represent the timbers in a roadway. The experiments were carried out in a similar manner to those of the first series; various intervals of time, from 3 to 25 minutes, were allowed to elapse after throwing the dust down the shaft before firing the cannon.

Dusts from 36 different seams were tested in 128 experiments, and 71, or 55 per cent. of, ignitions occurred. The ignitions were accompanied by large volumes of flame, which shot out 30 to 60 feet above the pit mouth, and in some instances the head gear from which the cannon was suspended was blown down.

There were 57 experiments, or 44 per cent., in which no ignition took place; in 11 of these experiments high explosives were used.

The following table gives the details of the dusts tested and the results obtained :---
| County. | No. of Experiment. | Dust tested. | No. of Ignitions. |
|------------------|-----------------------|-------------------|----------------------|
| Northumberland | 2 | Beaumont | 1 |
| 11 | 3 | Cambois | 3 |
| Durham | 9 | Hutton | 6 |
| ,, | 5 | Maudlin | 3 |
| ,, | 4 | Harvey | 0 |
| ,, | 3 | 5/4 or Jet | 3 |
| ,, | 3 | Busty | 3 |
| ,, | 1 | Main Coal | 1 |
| Yorkshire | 7 | Parkgate | 2 |
| ,, | 4 | Beeston | 3 |
| ,, | 2 | Barnsley Bed . | 2 |
| Derbyshire . | 5 | Silkstone | 4 |
| ,, | 3 | Deep Hards . | 1 |
| Nottinghamshire | 2 | Top Hards | 2 |
| Staffordshire . | 3 | Great Row. | 0 |
| ,, | 2 | 7 feet Banbury . | 2 |
| ,, | 2 | Cockshead | 2 |
| ,, | 2 | Shallow | 0 |
| » · · · | 3 | Bulhurst | 0 |
| Lancashire | 2 | Park | 1 |
| ,, | 4 | Arley | 3 |
| ,, | 3 | Big Mine | 0 |
| ,, | 2 | Crombouke . | 0 |
| »» · · | 6 | Trencherbone . | 4 |
| Glamorganshire . | 2 | Cribbar | 2 |
| ,, | 10 | Aberdare 4 feet . | 7 |
| ,, | 4 | No. 3 Rhondda . | 3 |
| ,, | 4 | Big Vein | 0 |
| Monmouth | 3 | Black Vein | 2 |
| | 2 | Meadow | 0 |
| Somersetshire . | 2 | No. 6 | 0 |
| Forest of Dean . | 6 | Rocky | 0 |
| Scotland | 4 | Splint | 3 |
| »» · · | 2 | Ell Coal | 2 |
| »» · · · | 3 | Kilsyth | 3 |
| »» • • | 2 | Main Splint . | 2 |
| »» · · | 2 | Bannockburn | |
| | | Main Coal . | 1 |
| | 128 | | 71 |
| | | | |

Experiments of a similar character, though not on so large a scale, carried out in Germany for the Prussian Fire-Damp Commission, and in Austria on behalf of the Austrian Fire-Damp Commission, led to similar results.

The most conclusive experiments are those which are being conducted by Mr. W. E. Garforth, on behalf of the Coalowners' Association of Great Britain, in an experimental gallery erected at the West Riding Collieries at Altofts, in Yorkshire.

The gallery consists of a series of boiler shells, 7 feet 6 inches to 8 feet in diameter, bolted together to form a tube about 900 feet long. This length is divided into one straight length, called the intake, about 600 feet long, and another, at right angles to it, which is 295 feet long, and made zig-zag to break the force of the explosion. This length is called the return, and at the end of it is a fan capable of circulating 80,000 cubic feet of air per minute through the gallery with a 3-inch water-gauge. The gallery is fitted with pit props throughout the length of the intake, and wooden shelves are placed along its sides to act as ledges on which coal dust can rest. There is also a concrete floor laid with rails, so that tubs can be run into the gallery. The gallery is fitted with a series of safety valves; these consist of wooden doors bolted to baulks of timber. The area of the intake is 41 square feet, and that of the return 28 square feet. There is a firing station, which is fitted with instruments for recording the pressure, velocity, temperature, &c., produced by the explosion.

The dust used is obtained by crushing the coal in a disintegrator, and its fineness is measured by passing through sieves containing 200, 150, and 100 meshes to the lineal inch. The character of the fineness is shown from the results with a sample of Silkstone dust :—

| 80 | per cent. | passed through | 200 | mesh | sieve |
|----------|-----------|-----------------|-----|-----------------------|-------|
| 6 | - ,, | | 150 | ,, | |
| 9 | | 33 | 100 | ,, | |
| 5 | 39 | failed to pass. | | | |

The shot is fired from a cannon charged with 24 ozs. of gunpowder, and stemmed with 8 inches of dry clay.

The method of carrying out the experiments is as follows :---Dust is strewn on the props, the floor, and sides of the gallery along the intake at the rate of 1 lb. of dust per lineal foot; the cannon, charged with powder, is placed at a certain point in the dusty zone, the muzzle being inclined upwards. Tufts of cotton wool are hung from the roof of the gallery at intervals throughout the length of the intake, and small tufts of guncotton are similarly fixed on the sides; these serve to indicate how far the flame of the explosion has travelled. A tub is usually placed on the roadway of the gallery. The various instruments for recording the pressure, temperature, velocity, &c., being adjusted for making the necessary measurements, the fan is started and about 60,000 cubic feet of air per minute drawn through the gallery. At a given signal the cannon is fired.

A large number of experiments have been made with lengths of dust-strewn roadways, varying from 100 feet to 540 feet, and now a standard length of 367 feet is generally adopted.

The usual result on firing the shot is that, first, black clouds of dust and smoke are seen rolling from the mouth of the gallery, followed by flames which shoot out with much greater violence, succeeded by large clouds of dust and smoke. In a short time after the explosion has taken place large clouds of black smoke are expelled from the Evasée chimney of the fan. When the smoke has cleared away the tub is usually found to be blown to pieces, and its parts hurled some 300 or 400 feet away, whilst the ground in front of the gallery is strewn with a confused mass of props and lids. Inside the gallery is a confusion of blown-down timbers, whilst in some cases the massive safety-valves are blown to pieces.

The following are results of individual experiments described in the *Colliery Guardian* of August 28, 1908 :---

(1) A coal-dust zone, 369 feet long, ended at a distance of 175 feet from the intake of the gallery; 50,000 cubic feet of air per minute were circulating. The result of the explosion was that two sections of boiler shells, 60 feet from the intake, were wrecked, the tub was blown 136 feet into the open, the valves were blown off, and one hurled for a distance of 426 feet.

(2) In a similar experiment with 367 feet of coal-dust zone the flame was projected for 150 feet into the return, the tub was broken, and parts of it hurled for a distance of 337 feet outside the gallery.

(3) In this experiment 540 feet of coal-dust zone was fired, when three boiler shells at the intake end of the gallery were wrecked, and pieces hurled into the air at various heights and

distances, whilst the report and vibration were felt seven miles away.

These experiments are most conclusive experimental proof of the explosibility of coal dust *per se*.

Evidence of the Explosibility of Coal Dust from Colliery Explosions.—The amount of evidence afforded by colliery explosions in favour of the explosibility of coal dust *per se* is so great that it is only possible to refer to one or two of the more striking examples.

The great difficulty in the case of colliery explosions is to prove, without any possibility of contradiction, the absence of any trace of fire-damp at the moment of ignition.

There is one example on record of an explosion of dust that took place in a coal hopper at the Brancepeth pit in 1889, under conditions that preclude the presence of gas. This hopper formed a store for dry coking slack, and advantage was taken of the fact that it was empty to clean it out. The hopper was 24 feet by 31 feet and $31\frac{1}{2}$ feet high; inside it was divided into four stages or platforms, and the whole structure tied together with iron rods. It was covered with a roof which was not sufficiently tight to prevent the escape of gas if any had been given off by the coal. Six men entered the hopper with naked torch lights which were hung on the iron tie rods near to the bottom. Three of the men remained at the bottom whilst three went on to the upper platforms and began to throw the dust down. Tn about three minutes a violent explosion took place, part of the roof was blown off, and the sides were covered with charred coal dust.

This explosion was caused by the fine coal dust falling in clouds on the naked lights. The absence of any gas in this case is proved by the fact that the man who superintended the machinery had been in the top of the hopper with a naked light only a few minutes before the cleaners went in.

Another example in which the absence of gas was proved almost beyond the possibility of a doubt was the explosion that took place on November 13, 1893, at the New Pit of the Cammerton Colliery. Although this pit had been worked for over a hundred years no gas had ever been reported, and naked lights were used. On the night of November 13, a man and a boy were ripping the roof in a main haulage road; two shots were fired, the second about two hours after the first. It was

EXPLOSION IN GASES

an overcharged and badly placed shot, and caused an explosion



FIG. 102.—Plan of Altofts Colliery, showing course of the explosion. By permission of the Controller of H.M. Stationery Office.

which extended 1260 yards along the road, which was particularly dusty on account of the coal in the tubs grinding against

the roof. To obtain some evidence as to the presence of firedamp at the moment of ignition, the ventilation of the pit was stopped for a fortnight, when the members of the Coal Dust Commission visited the colliery and made careful tests for gas in the intake and return air-ways with the Clowes, Stokes, and other delicate gas detectors, but failed to find a trace. It can hardly be denied that fire-damp played no part in the explosion.

One of the most pronounced examples of a dust explosion is the one that took place at Altofts Colliery in 1885. This explosion was caused by shot-firing in the West Chain haulage road (Fig. 102), one of the main intakes of the mine. Three shots were fired, two at one time, and a third some little time after. The third shot was overcharged, and caused the explosion. This shot was situated 970 yards from the face in one direction, and from 1800 to 1900 yards in the other direction. The course of the explosion followed the dusty haulage roads; starting from the point of ignition it passed along the West Chain haulage road in the direction of the shaft, and crossed three intake roadways which were haulage roads, and two return air-ways, one being the Main West return.

The explosion traversed the three intake air-ways, but missed the return air-ways. The former were dusty with coal dust, whilst the latter were not. As the explosion passed the slit leading to the Main West return, the force of the blast must have entered the slit, for two bodies were found 40 yards in bye in Roper's drift, which at this point joined the Main West return. The Main West return, however, was practically untouched by the explosion.

As the explosion passed along the No. 1 Chain haulage road it passed three cross-cuts which led up to the face, but did not pass along them. In them the coal dust was smothered in dirt dust, and no damage at all was done at the face.

The course of the explosion was confined to the haulage roads, which were dry and dusty through the grinding of the coal that falls from the tubs, and the dust which is swept from the tubs as they travelled against the air current. The explosion was caused by the ignition of dust by the firing of an overloaded shot after two other shots had been fired, the shock of which had blown up a cloud of dust into the atmosphere. It may be asked what proof there is that no gas was present. In the first place, 50,000 cubic feet of air per minute were passing the point where the shots were fired. The timbers supporting the roof at this point were tightly packed up to the roof, leaving no cavities where gas could accumulate, and when a hole was bored down to the lower seam immediately below where the shot was fired no gas escaped from it. These facts point to the absence of gas when the shot was fired. The explosion was a dust explosion, which traversed roads dusty with dry coal dust for a distance of 1900 yards, and gradually died away on dirt dusty roads which could not supply the necessary fuel for its continuance.

Courrières Explosion.-The most disastrous explosion in the annals of coal-mining occurred at the Courrières Collieries on March 10, 1906. These are among the most extensive collieries in the Pas de Calais coalfield ; there are thirteen pits working ten seams. The workings of the different pits and districts communicate with one another by staples and drifts, so that the pits and seams are more or less joined up across the whole extent of the concession. The explosion caused the death of 1100 men and boys, four pits were wrecked, nine seams were affected, in five of which the explosion entered, whilst into four others the after-damp penetrated. It was thought at first that the explosion was caused by a fire that existed in one of the seams-the Cécile seam; that gas from the distillation of the coal had penetrated into the roadways, and by leaking through stoppings and crevices had found its way into a seam 138 feet below-the Josephine seam-where it was ignited by a naked light. There was evidence, however, that the explosion was a coal-dust explosion; dry and inflammable dust existed throughout all the roadways traversed by the flames. The explosion stopped at places where the roads were wet, or covered with shale dust, or were not dusty. Deposits of charred and coked coal dust were plentiful all along the course of the explosion.

All this pointed to a dust explosion, and it was discovered that it had originated in a heading—the Lecœuvre heading in the Josephine seam, where three brothers, named Lecœuvre, were probably engaged in cutting out a shot which had missed fire, and, striking the detonator with their pick, had caused the charge to explode and ignite the dust in the heading, and the

explosion was carried on by the dust which lay in great quantities along the roadways.

Many other examples might be quoted, but those given above, together with the experimental evidence, establish conclusively the explosibility of coal dust alone.

The explosibility of coal dust would seem to depend on :--

(1) Its fineness.—It is the very fine particles of dust which float for a long time in the atmosphere and gradually settle as a velvety pile on the timbers and ledges of the walls, that readily ignite.

(2) Its dryness.—It is the dust that accumulates on dry roads that carries on the explosion. Roads which are wet or damp are seldom affected.

(3) Its purity.—If largely mixed with incombustible stone dust, the coal dust cannot propagate the explosion, for it _ becomes, as it were, so diluted that its particles are separated sufficiently from one another to prevent the propagation of flame from one to another.

(4) The thorough mixing with air.—As with gaseous mixtures explosion is impossible unless the combustible gas is intimately mixed with air, so explosion of dust cannot take place unless the cloud of dust is blown up into the air and thoroughly mixed with it.

For some time it was thought that an explosion could only take place through the application of a powerful flame, such as that from a blown-out shot, but it was shown as long ago as 1878, by Professor Marreco and Mr. Morrison, that dust could be ignited by allowing it to fall on a Bunsen flame. The experience of the Brancepeth hopper shows that it is not only possible to ignite dust with a small naked flame, but that, if the volume of dusty air be sufficient, the ignition is followed by a powerful explosion.

Prevention of Dust Explosions.—The following precautionary measures have been suggested to reduce the danger arising from the presence of dust in coal mines: (1) Watering; (2) sprinkling or mixing the dust with calcium chloride; (3) removal of the dust from certain lengths of roadways so as to divide them into dusty and dustless zones; (4) separating the dusty zones by zones of stone dust.

(1) Watering.—Under this head are included (a) the sprinkling of the tubs with water as they leave the face, to prevent the

dust from being blown off the coal by the ventilating current; and (b) the watering of the dusty roads so as to thoroughly moisten the dust and prevent it from being blown up into the air. This can only be effective if the dust on the floor, timbers, and sides is kept wet. In some instances, there is a serious objection to watering the roadways. In some pits the strata above and below the coal are readily disintegrated by water, and watering occasions large falls of roof. Where watering can be adopted, however, it is effectual in confining the limits of an explosion. This was the case in the explosion that took place at Maclaren Colliery in 1902. Reporting on this explosion, Mr. Martin, at that time H.M. Inspector of Mines, says :—

"The workings, although in a few places a little water may be found in a few places dripping from the roof, are of a dry and dusty nature and require artificial watering.

"Good use seems to have been made of this arrangement (for watering), and to it may be attributed the limited loss of life which has occurred, as had the main level been dry and dusty, not only would the men who were in the rise workings have been more seriously affected, but also those on the dip side, and not improbably the effects of the explosion would have traversed the east side workings, where men were also employed.

⁶ This is perhaps the first practical proof of artificial watering limiting the effects of what would otherwise have proved a very widespread and much more disastrous affair."

(2) Use of Calcium Chloride.—Calcium chloride is a very deliquescent solid, which, on exposure to moist air, becomes wet and eventually liquefies. Its efficacy depends on this property, for, if finely ground calcium chloride be mixed with the dust, it will absorb moisture from the air and not only make the dust damp but keep it damp for a considerable time. Or if the dust be watered with a solution of calcium chloride, it will remain damp for some time, because, although some of the water may evaporate, it will not do so completely, as the calcium chloride will always retain some.

Experiments have been made with calcium chloride by Sir Henry Hall. In one case a roadway on which the dust was 3 inches thick was watered with a solution of calcium chloride of 40° to 65° Twaddell at the rate of 8 gallons per 30 feet. The dust was not damped underneath, but the

roadway could be travelled in comfort for a period of three months after watering.

In another case 225 feet of roadway were cleared of dust and watered with 90 gallons of the solution. The effect of the calcium chloride was visible four months afterwards.

To try the effect of solid calcium chloride, 330 lbs. of the finely ground substance were scattered over 249 feet of dusty roadway without removing the dust. The road was reported wet the next day and without any dust rising, whilst the effect remained after six weeks or two months.

A similar result was obtained when 448 lbs. of calcium chloride were strewn over 282 square feet, from 60 square feet of which the dust had been removed.

(3) The Removal of Dust to form Dustless Zones.—The complete removal of dust from the roadways would, if it were possible, prevent the danger, but as this is impossible, it has been proposed to remove the dust from certain lengths of roadway at intervals, and so interpose dustless zones between dusty zones, with the idea that when an explosion takes place in a dusty zone it will expend its force in the dustless zones on either side without penetrating into the dusty zones beyond. How far dustless zones will act in this way depends on their length, which will be determined by the violence of the explosion they are intended to stop.

Some important experiments were made by Mr. Garforth to test the efficacy of the dustless zone. In one, 275 feet of the gallery at Altofts were strewn with dust, leaving 150 feet in front of it quite free from dust. On exploding the dust the flames shot out 16 feet beyond the end of the gallery, showing that 166 feet of flame penetrated beyond the coal-dust zone.

What really happens in the case of dustless zones is that when the explosion occurs a cloud of dust is projected into the dustless zone, which then ceases to be dustless. This fine dust continues the explosion to a distance which will depend on the quantity of dust and the violence with which it is thrown forward. It is reasonable to suppose that the more violent the explosion the larger the cloud of dust that is formed and the farther it will be projected into the dustless zone.

(4) The Use of Stone Dust.—This remedy was suggested to Mr. W. E. Garforth from the experience of the Altofts explosion, which failed to penetrate roads which were dusty with stone dust. The proposal is to either separate coal-dust zones by zones of stone-dust or to cover completely the dusty roads with fine stone dust without removing the coal dust. Experiments made in the Altofts gallery point to the efficacy of the proposal.

In one case stone dust was laid for 150 feet from the mouth of the gallery, and beyond this 275 feet of coal dust. On firing the dust, clouds of stone dust and smoke issued from the open end, but no flame. On examining the gallery for evidence of flame it was found that the flame had only extended 55 feet into the stone-dust zone. In another experiment in which the respective lengths of stone-dust and coal-dust zones were 100 feet and 275 feet, the flame only penetrated 23 feet into the stone-dust zone.

To test whether the flame would pass over a stone-dust zone and ignite dust beyond, a length of 50 feet from the mouth of the gallery was strewn with coal dust, beyond this stone dust was laid for 100 feet, and then a coal-dust zone of 275 feet. This zone was fired, when the flame penetrated 54 feet into the stone-dust zone, and did not ignite the 50 feet of coal dust at the mouth of the gallery.

As a rule, about 140 to 170 feet of flame are produced when the 275 feet of coal dust explodes, but when the flame is projected into stone dust the flame is extinguished in from 20 to 50 feet. This may be explained as follows: The force of the explosion blows up a cloud of stone dust which mingles with the burning coal dust in increasing quantity as the flame travels along, until at last so much stone-dust becomes mixed with the coal dust that it extinguishes the flame.

The efficacy of this method seems to be established so far as experimental evidence is concerned, and it would appear to be all the more effective as it is believed that it is unnecessary to remove the coal dust, but simply sufficient to smother it in a layer of fine stone dust.

CHAPTER XIV

THE EFFECT OF TEMPERATURE AND PRESSURE ON THE DENSITY AND VOLUME OF GASES, AND DIFFUSION OF GASES

ALL gases expand with increasing temperature and contract with decreasing temperature, thereby producing a change in their density. The actual increase or decrease in volume and density produced by an alteration of one degree of temperature is comparatively large.

The density and volume of gases are affected to a far greater degree by an alteration in the pressure. It is consequently very necessary to note carefully the temperature and pressure whenever dealing with either the density or volume of gases.

Co-efficient of Expansion.—The increase which a unit volume of gas at 0° C. or 0° F. undergoes when its temperature is raised 1 degree under constant pressure is called its *co-efficient of expansion*. It is the same for all permanent gases.

When the temperature is measured on the Centigrade scale the co-efficient of expansion is $\frac{1}{273}$, or 0.003665, that is, a gas expands $\frac{1}{273}$ of its volume at 0° C. for each degree Centigrade it is heated.

| Thus | 273 | cubic feet | of gas | \mathbf{at} | 0° C. |
|--------|-----|------------|--------|---------------|----------------|
| become | 274 | ,, | ,, | ,, | 1° C. |
| 22 | 275 | 22 | ,, | ,, | 2° C. |
| 33 | 276 | ,, | ,, | ,, | 3° C. |
| ,, | 277 | 22 | ,, | ,, | 4° C. |
| ,, (2 | 73+ | t) ,, | 37 | " | <i>t</i> ° C. |

A careful examination of this table shows that 273 cubic feet of gas at 0° C. expand 1 cubic foot, or $\frac{1}{273}$ of their volume, on heating to 1° C., also that 274 cubic feet at 1° C. become 275 cubic feet at 2° C., that is, they expand 1 cubic foot, which is not $\frac{1}{273}$ of 274 cubic feet but $\frac{1}{273}$ of 273 cubic feet, the volume which 274 cubic feet at 1° C. assumes at 0° C.; likewise for each increase of 1° in temperature the volume increases 1 cubic foot, which is $\frac{1}{213}$ of the original volume at 0° C.

The co-efficient of expansion of a gas is $\frac{1}{450}$, or 0.002118, when the temperature is measured on the Fahrenheit scale, which means that a gas expands $\frac{1}{450}$ of its volume at 0° *F*. for each degree Fahrenheit that its temperature is raised.

| Thus | 459 | cubic feet | of gas | at | 0° F. |
|--------|-----|------------|--------|----|----------------|
| become | 460 | ,,, | " | " | 1° F. |
| " | 461 | 33 | ,, | ,, | 2° F. |
| ,, | 462 | ,,, | " | ,, | 3° F. |
| ,, | 463 | , | ,, | " | 4° F. |
| ,, (4 | 59+ | t) ,, | ,, | " | t° F. |

Here again it will be seen that 459 cubic feet of gas at 0° F. increase 1 cubic foot for each degree the temperature is raised, which is $\frac{1}{459}$ of the volume at 0° F. and not of the volume at any other temperature.

Absolute Temperature.—The measurement of temperature is usually made by the ordinary thermometer, but there is a method of measuring it which is based on the law of expansion of gases. The temperature so measured is called the absolute temperature. Supposing either 273 cubic feet of a gas at 0° C. or 459 cubic feet at 0° F. were cooled instead of being heated, they would contract 1 cubic foot for each degree Centigrade or Fahrenheit they were cooled, that is, 273 cubic feet of gas at 0° C. would become 272 cubic feet at -1° C., 271 cubic feet at -2° C., and so on; similarly 459 cubic feet of gas at 0° F. would become 458 cubic feet at -1° F., 457 cubic feet at -2° F., and so on. If these volumes were cooled to -273° C. and -459° F. respectively, their volumes would theoretically be 273 - 273 = 0 and 459 - 459 = 0. What would actually happen to the volume of a gas if these low temperatures were reached is not of importance; theoretically, no gas can exist at these temperatures. The temperatures, -273° C. or 273° below 0° C., and -459° F. or 459° below 0° F., are known as the absolute zero on each scale.

Temperatures measured from the absolute zero are called absolute temperatures, and temperatures indicated by the ordinary thermometers are easily converted into absolute temperatures by adding 273 to Centigrade degrees and 459 to

Fahrenheit degrees. The ordinary temperature is generally represented by t° and the corresponding absolute temperature by T^{\circ}.

 $t^{\circ} C. = (273 + t)^{\circ} C.$ on the absolute scale, and $t^{\circ} F. = (459 + t)^{\circ} F.$, , , , ,

Effect of Temperature on the Density of a Gas.—The density of a gas has been defined as the mass per unit volume, and, seeing that a gas expands on heating and contracts on cooling, it is evident that the weight of a fixed volume must decrease as the temperature rises and increase as the temperature falls. There is a very simple numerical relation between the alteration in the density of a gas and the rise and fall of temperature. This relation is expressed by the law which states that The density of a gas is inversely proportional to the absolute temperature, the pressure remaining constant.

Let d_1 be the density of a gas at temperature t_1° C., and d_2 its density when the temperature changes to t_2° C.; then, to find how the density changes, it is necessary first to find the absolute temperatures corresponding to t_1° C. and t_2° C.

Absolute Temperature.

 $t_1^{\circ} C. = (273 + t_1)^{\circ} C.$ $t_2^{\circ} C. = (273 + t_2)^{\circ} C.$

Then the densities are *inversely* proportional to the absolute temperatures, hence—

$$\frac{d_2}{d_1} = \frac{(273 + t_1)}{(273 + t_2)} \text{ or, } \qquad d_2 = d_1 \frac{(273 + t_1)}{(273 + t_2)} \tag{1}$$

If t_1 and t_2 are measured on the Fahrenheit scale, then—

Absolute Temperature. $t_1^{\circ} \text{ F.} = (459 + t_1)^{\circ} \text{ F.}$ $t_2^{\circ} \text{ F.} = (459 + t_2)^{\circ} \text{ F.}$ $\frac{d_2}{d_1} = \frac{(459 + t_1)}{(459 + t_2)} \text{ or,}$ $d_2 = d_1 \frac{(459 + t_1)}{(459 + t_2)}$

(2)

and

The Effect of Pressure on the Density of a Gas.—It has been pointed out that the atmosphere exerts a pressure which is measured by means of the barometer. The pressure exerted by the atmosphere is not a property peculiar to the air, but one which is possessed in common by all gases. A gas is like a coiled-up spring which is always trying to stretch itself out, and so exerts a pressure on the bodies with which it is in contact.

It is the gas itself which exerts the pressure, and this pressure is dependent on the density of the gas, or the mass contained in a unit volume. The greater the density or mass in a unit volume the greater the pressure it exerts. There is a very simple numerical relation between the pressure of a gas and its density. The law expressing this relation is: The pressure of a gas is directly proportional to its density, the temperature remaining constant; so if d_1 is the density of a gas when its pressure is p_1 and d_2 its density when its pressure changes to p_{2} , then—

$$\frac{d_2}{d_1} = \frac{p_2}{p_1}$$
 or, $d_2 = \frac{d_1 p_2}{p_1}$ (3)

The above formulæ allow us to calculate a change in the density when the temperature changes but the pressure remains constant, and when the pressure changes but the temperature remains constant.

In most cases both the temperature and pressure alter at the same time; under such circumstances both the laws act independently of one another, and the change in density is the combined result of the operation of both laws.

Let d_1 be the density of a gas when its pressure is p_1 and its temperature t_1 , and let d_2 be its density when its pressure changes to p_2 and its temperature to t_2 .

Here it is necessary to apply both laws. In the case of the alteration of the density with the temperature, it is necessary to determine the absolute temperatures. Let $t_1 = T_1$ on the absolute scale, and $t_2 = T_2$ on the absolute scale—

then
$$d_2: d_1 = \begin{cases} T_1: T_2 \\ p_2: p_1 \end{cases}$$

$$d_2 = d_1 \times \frac{T_1}{T_2} \times \frac{p_2}{p_1}$$

and

If t_1 and t_2 are degrees Centigrade, then

 $T_1 = 273 + t_1$ and $T_2 = 273 + t_2$.

Substituting these values for T_1 and T_2 ,

$$d_2 = d_1 \times \frac{(273 + t_1)}{(273 + t_2)} \times \frac{p_2}{p_1}.$$
 (4)

If t_1 and t_2 are Fahrenheit degrees,

 $T_1 = 459 + t_1$ and $T_2 = 459 + t_2$,

then by substitution we get the formula-

$$d_2 = d_1 \times \frac{(459 + t_1)}{(459 + t_2)} \times \frac{p_2}{p_1} \tag{5}$$

The formulæ (4) and (5) are perfectly general and apply to any gas, so that if the density at any temperature and pressure is known, the new density may be calculated when the change in temperature and pressure is known.

For purposes of ventilation in colliery work it is often necessary to calculate the weight in lbs. of a cubic foot of air at any temperature and any pressure. This can be easily done by a special formula, which was first stated by Atkinson in his book, "Gases met with in Mines," and is generally known as Atkinson's formula. The formula there given and generally accepted is—

$$\mathbf{W} = \frac{1 \cdot 3235 \times \mathbf{I}}{459 + t}$$

where I is the height of the barometer in inches, t the temperature on the Fahrenheit scale, and 1.3235 the weight in lbs. of 459 cubic feet of air at 0° F. and 1-inch pressure.

The weight of 1 cubic foot of air at 32° F. and 30 inches pressure is usually taken to be 0.0807 lbs., and if this weight is correct there would appear to be some slight error in the number 1.3235 lbs., for, on calculating the weight of 1 cubic foot of air at 32° F. and 30 inches pressure by Atkinson's formula, the number 0.08086 lbs. is obtained. The error is not very great, only about 1.6 in 800, or about 0.2 per cent., and for practical purposes is probably unimportant; but the correct weight of 459 cubic feet of air at 0° F. and 1-inch pressure, on the assumption that 1 cubic foot of air at 32° F. and 30 inches pressure weighs 0.0807 lbs., is 1.32079, and Atkinson's formula then becomes—

$$\mathbf{W} = \frac{1 \cdot 32079 \times \mathbf{I}}{459 + t}.$$

The formula is obtained in the following manner: 459 cubic feet of air at 0° F. and 30 inches pressure become 459 + 32 =491 cubic feet at 32° F. and 30 inches pressure, 1 cubic foot of air at 32° F. and 30 inches pressure weighs 0.0807 lbs., therefore 491 cubic feet of air at 32° F. and 30 inches pressure weigh 491 $\times 0.0807 = 39.6237$ lbs., and this is the weight of 459 cubic feet of air at 0° F. and 30 inches pressure. When the pressure is reduced to 1 inch the weight of 459 cubic feet of air at 0° F.

becomes
$$\frac{39.6237}{30} = 1.32079$$
 lbs.

If I be the height of the barometer in inches the weight of 459 cubic feet of air at 0° F. and I inches pressure becomes

$1.32079 \times I$ lbs.

But let the temperature be t° F. instead of 0° F., then the 459 cubic feet become 459 + t cubic feet, hence the weight, W, of 1 cubic foot at I inches and t° F. will be

$$W = \frac{1 \cdot 32079 \times I}{459 + t}$$
 lbs.

A similar formula can be obtained for calculating the weight of 1 cubic foot of air at any pressure and any temperature on the Centigrade scale. In this case the weight of 273 cubic feet of air at 0° C. and 1 inch pressure is calculated. This is 0.73437 lbs., and the formula obtained is

$$W = \frac{0.73437 \times I}{273 + t}$$
 lbs.

where I is the height of the barometer in inches and t is the temperature on the Centigrade scale.

The Effect of Change of Temperature on the Volume of a Gas.—The expansion and contraction of the volume of any gas under the influence of a change in temperature takes place according to a definite law, which expresses the numerical relation between the change in volume and the change in temperature. The law is: The volume of a gas is directly proportional to its absolute temperature, the pressure being constant.

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If v_1 be the volume of any gas at t_1° C., and v_2 the volume it becomes when the temperature changes to t_0° C.,

then
$$\frac{v_2}{v_1} = \frac{(273 + t_2)}{(273 + t_1)}$$
 or, $v_2 = \frac{v_1(273 + t_2)}{(273 + t_1)}$. (1)

If the temperatures are measured on the Fahrenheit scale the formula becomes

$$\frac{v_2}{v_1} = \frac{(459 + t_2)}{(459 + t_1)} \quad \text{or,} \quad v_2 = \frac{v_1(459 + t_2)}{(459 + t_1)}.$$
 (2)

This law follows from the law of expansion of a gas, namely, that a gas expands $\frac{1}{273}$ of its volume at 0° C. or $\frac{1}{459}$ of its volume at 0° F. for each degree Centigrade or Fahrenheit its temperature alters.

| For let v_0 | be the volume | of any | gas at 0° (| J., |
|---------------|---------------|-------------------|------------------|------------------------------|
| and v_1 | ,, | that v_0 | becomes at | t_1° C., |
| and v_2 | >> | ,, v ₀ | ** | $\overline{t_2^{\circ}}$ C., |
| | a (n. 1 a | $t_1 \rangle_{-}$ | $v_0(273 + t_1)$ |) |

then

$$v_{2} = \left(v_{0} + v_{0}\frac{t_{2}}{273}\right) = \frac{v_{0}(273 + t_{2})}{273}$$
(4)

(3)

and

Now divide equation (4) by equation (3)-

$$\frac{v_2}{v_1} = \frac{\frac{v_0(273 + t_2)}{273}}{\frac{v_0(273 + t_1)}{273}} \quad \text{or,} \quad \frac{v_2}{v_1} = \frac{(273 + t_2)}{(273 + t_1)}.$$

Since v_0 at 0° C. becomes v_1 on heating to t_1° C. and v_2 on heating to t_2° C., then if v_1 at t_1° C. be heated to t_2° C. the volume will become v_2 ; therefore the volume of any gas v_1 at t_1° C. is to the volume v_2 which it becomes on heating to t_2° C. directly as the absolute temperature.

In the same way the law can be proved for temperature measured on the Fahrenheit scale.

The Effect of Change of the Pressure of a Gas on its Volume. -When the pressure of a gas increases its volume decreases, and vice versa, and there is a very simple numerical relation between the change of pressure and the consequent change of volume. This relation is expressed by Boyle's Law, namely,

The volume of a gas is inversely proportional to its pressure, the temperature being constant.

If v_1 be the volume of a gas whose pressure is p_1 , and v_2 be the volume it becomes when pressure changes to p_2 , then—

$$\frac{v_1}{v} = \frac{p_2}{p_1} \text{ or, } v_1 p_1 = v_2 p_2 \text{ and } v_2 = \frac{v_1 p_1}{p_2}.$$
(5)

This law was experimentally proved by the Hon. Robert Boyle by the following experiment: A glass tube, ABCD, bent into the form of the letter

J (Fig. 103), has one end, D, closed, and the other end, A, open; a small quantity of mercury is poured into the bend of the tube so that the height of the liquid in both limbs of the tube is the same as shown at B and C. There is now enclosed in DC a certain volume of gas at atmospheric pressure. Let this volume be called v_1 , and let the height of the barometer be h inches; then if p_1 be the pressure of the volume v_1 , $p_1 = h$ inches.

Now pour mercury in at A, the open end of the tube. The mercury rises slowly in DC, compressing the gas in DC, whilst it quickly rises in AB. Continue to pour mercury in

at A until the volume DC is compressed to one-half and the mercury in DC stands at E; the mercury in AB now stands at F.

The original volume v_1 has been compressed to v_2 , and v_2 is $\frac{v_1}{2}$.

It remains now to find the pressure of the gas that is compressed to half its original volume. To measure this pressure we must consider the pressure in each limb of the tube. The mercury in the tube is at rest, therefore the total pressure in each limb is equal, otherwise the mercury would move towards the side of the smaller pressure.

The total pressure in the limb DC is equal to the pressure of the gas DE and the pressure of the mercury column EC, whilst the total pressure in the limb AB is equal to the



pressure of the atmosphere and the pressure of the column of mercury, AB.

The pressure of the column of mercury, EC, will balance the pressure due to a column of mercury of equal height in AB, namely, GB, therefore the pressure of the gas in DE balances the pressure of the atmosphere and the pressure of the column of mercury, GF.

Let p_2 be the pressure of the gas in DE, then

 p_2 = the pressure of the atmosphere and the pressure of the mercury column GF.

Measure the height of the column GF, that is, the height of **F** above E, the level of the mercury in DC. This height will be found to be equal to h inches, the height of the barometer, and therefore

$$p_2 = h + h = 2h$$
 inches,
 $p_2 = 2p_1$, whilst $v_2 = \frac{1}{2}v_1$,

so that

or, whilst the volume of the gas has been reduced to one-half its pressure has been doubled; this proves that the volume of a gas is inversely proportional to its pressure, the temperature being constant.

When the temperature and pressure vary together both of these laws act together, and the final volume is the resultant of their combined action; therefore to find the change in volume when both temperature and pressure change the two laws must be combined.

Let v_1 be the volume of a gas at temperature t_1° C. and pressure p_1 , and v_2 be the volume it becomes when the temperature changes to t_2° C. and the pressure to p_2 ,

then
$$v_1: v_2 = \begin{cases} (273 + t_1): (273 + t_2) \\ p_2: p_1 \end{cases}$$

and

$$\frac{v_2}{v_1} = \frac{(273 + t_2)}{(273 + t_1)} \times \frac{p_1}{p_2}$$

 $v_2 = v_1 \times \frac{(273 + t_2)}{(273 + t_1)} \times \frac{p_1}{p_2}.$ (6)

If t_1 and t_2 be measured on the Fahrenheit scale the formula becomes

$$\frac{v_2}{v_1} = \frac{(459 + t_2)}{(459 + t_1)} \times \frac{p_1}{p_2}$$

DENSITY AND VOLUME OF GASES

and

$$v_2 = v_1 \times \frac{(459 + t_2)}{(459 + t_1)} \times \frac{p_1}{p_2} \tag{7}$$

Diffusion of Gases.

When two gases are brought together they will become intimately mixed in course of time in spite of a difference in their relative densities. For instance, if a jar of hydrogen be inverted with its mouth over a jar of oxygen, although oxygen is 16 times heavier than hydrogen, it will pass upwards into the hydrogen, whilst the hydrogen will pass downwards. In course of time the two gases will become intimately mixed. The process by which gases become mixed under these conditions is called diffusion. When once gases are mixed together they cannot be separated by allowing the mixture to stand at rest, but remain permanently mixed.

By the same process gases which are separated from one another by some porous partition pass through the pores and mix with one another. If a box (Fig. 104) be divided into two compartments by a partition of unglazed earthenware, and one compartment contains air whilst the other contains marsh

gas, the air will pass through the partition into the marsh gas, and at the same time the marsh gas will pass through into the air, so that a mixture of the two gases will be found in both compartments.



FIG. 104.

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When gases escape out of the goaf or old workings into the atmosphere of a mine it must not be mistaken for diffusion; this is due to an increase in the volume of gas in the goaf or old workings owing to fall of pressure or some other cause, which causes the gas to force its way into the roadways. Diffusion takes place when the gases are at the same pressure, still and unagitated.

Let us imagine, for instance, a heading into which no ventilating current passes and where the atmosphere is still, and that fire-damp escapes from the coal in large quantities into the air. This gas will rise to the roof and collect there, whilst the air on the floor will be free from it. If the air in the heading remains undisturbed, in course of time the fire-damp will diffuse downwards into the air and the air upwards into the fire-damp, and

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eventually fire-damp will be found near the floor. If the atmosphere remains undisturbed for sufficient time the gas and air will become uniformly mixed. In the same way, if a layer of carbon dioxide forms on the floor of a roadway and the atmosphere remains undisturbed, the heavy carbon dioxide will diffuse into the air above it, whilst the air will pass downwards into the carbon dioxide.

When the air is in motion the gases become mixed by the agitation.

The rate at which gases mix by diffusion is not equal for all gases but depends on their relative densities. A gas of small



FIG. 105.

density diffuses more quickly than a gas of high density. The following experiments show this :---

A porous cell, A (Fig. 105), is connected with the Woulf's bottle, B, by a tube which does not dip into the liquid in B, whilst the tube, C, dips below the surface of the liquid. A glass vessel, D, is placed over A, and hydrogen from the flask, E, is passed up into D. The porous cell, A, contains air and becomes surrounded with hydrogen, which is 14.4 times lighter than air. The two gases begin to diffuse, air passing out of A into D, and hydrogen from D into A, but the hydrogen diffuses into the

air more quickly than the air into the hydrogen, hence the volume of gas inside the cell, A, increases, causing increased pressure which forces the water to flow in a jet from B through the short tube, C.

A similar experiment may be made by surrounding the cell with carbon dioxide, which is 1.53 times as heavy as air, in the apparatus shown in Fig. 106. A bent tube coming from the porous cell, A, dips into water in the beaker, B, carbon dioxide is passed into the beaker, C, and surrounds the porous cell.

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When the diffusion begins the air passes out of the cell A more

quickly than the heavier carbon dioxide passes in, and the volume of gas in A diminishes, causing the water to rise in the tube showing the reduction in the volume.

The rate at which gases diffuse into each other has been measured, and a numerical relation established between the relative density of gases and their rates of diffusion. The



FIG. 106.

relation is expressed by the following law:-

The rate of diffusion of gases is inversely proportional to the square root of their relative densities.

> Let d_1 be the relative density of a gas A, and d_{o} be the relative density of a gas B;

the rate of diffusion of A into B the rate of diffusion of B into A = $\frac{\sqrt{d_2}}{\sqrt{d_1}}$ then

The relative densities may be the specific gravities, or the vapour densities of the gases. In the first case the rate of diffusion of air becomes the standard, and in the second case the rate of diffusion of hydrogen.

So far as mining problems are concerned it is sufficient to consider the rates of diffusion into air and take the specific gravities of the gases.

Example:

To find the rate of diffusion of marsh gas into air-

let d_1 be the specific gravity of air = 1

and d_2 be the specific gravity of marsh gas = 0.559. The rate of diffusion of air into marsh gas = 1.

$$\frac{\text{rate of diffusion of air}}{\text{rate of diffusion of marsh gas}} = \frac{\sqrt{\overline{d}_2}}{\sqrt{\overline{d}_1}}$$
$$\frac{1}{\text{rate of diffusion of marsh gas}} = \frac{\sqrt{0.559}}{\sqrt{1}}$$

or

rate of diffusion of marsh gas = $\frac{1}{\sqrt{0.559}}$

 $=\frac{1}{0.747}=1.3375.$

This number means that 1.3375 cubic feet of marsh gas will diffuse into air *in the same time* that 1 cubic foot of air will diffuse into marsh gas.

How many cubic feet of carbon dioxide will diffuse into marsh gas whilst 100 cubic feet of marsh gas diffuse into carbon dioxide?

$$\frac{\text{rate of diffusion of carbon dioxide}}{\text{rate of diffusion of marsh gas}} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

$$d_1 = \text{specific gravity of carbon dioxide} = 1.529$$

$$d_2 = \text{specific gravity of marsh gas} = 0.559$$

$$\therefore \frac{\text{rate of diffusion of carbon dioxide}}{\text{rate of diffusion of marsh gas}} = \frac{\sqrt{0.559}}{\sqrt{1.529}}$$

$$= \frac{0.747}{1.2365} = 0.604$$

that is, whilst 1.2365 cubic feet of marsh gas diffuse into carbon dioxide, 0.747 cubic foot of carbon dioxide diffuses into marsh gas, or whilst 1 cubic foot of marsh gas diffuses into carbon dioxide, 0.604 cubic foot of carbon dioxide diffuses into marsh gas; so that the quantity of carbon dioxide that diffuses in the same time as 100 cubic feet of marsh gas is equal to $0.604 \times 100 = 60.4$ cubic feet.

CHAPTER XV

CHEMICAL CALCULATIONS

1. To calculate the percentage composition of any compound :---

Take the formula of the compound and its molecular weight. Multiply the relative weight of each element present in the molecule by 100, and divide by the molecular weight.

- Let m be the molecular weight of any compound;
 - a the relative weight of any element in the molecule of the compound;
 - p the percentage of that element, then

$$p = \frac{a \times 100}{m}.$$

Example: Find the percentage composition of carbon dioxide.

 $CO_{2} = 12 + 32 = 44 = m.$

Percentage of carbon,

$$a = 12.$$

$$p = \frac{a \times 100}{m} = \frac{12 \times 100}{44}.$$

$$p = 27.27.$$

Percentage of oxygen,

$$a = 32.$$

 $p = \frac{a \times 100}{m} = \frac{32 \times 100}{m}.$
 $p = 72.73.$

Percentage composition,

$$C = 27 \cdot 27$$
$$O = 72 \cdot 73$$
$$100 \cdot 00$$

2. To calculate the simplest formula of a compound from its percentage composition :---

(a) Divide the percentage of each element by its atomic weight to obtain the atomic relation between the quantities of the elements present in 100 parts by weight of the compound.

(b) Select the smallest number thus obtained and divide each of the others by it.

(c) Multiply each of these numbers by the smallest number that will convert them all into whole numbers.

Example : The percentage composition of nitro-glycerol is

$$C = 15.86. H = 2.20. N = 18.50. O = 63.44.$$

Find its simplest formula.

(a) C
$$\frac{15\cdot86}{12} = 1\cdot32$$
. (b) $\frac{1\cdot32}{1\cdot32} = 1$.
H $\frac{2\cdot20}{1} = 2\cdot20$. $\frac{2\cdot20}{1\cdot32} = 1\cdot66$.
N $\frac{18\cdot50}{14\cdot1} = 1\cdot32$. $\frac{1\cdot32}{1\cdot32} = 1$.
O $\frac{63\cdot44}{16} = 3\cdot96$. $\frac{3\cdot96}{1\cdot32} = 3$.

(c) Multiply each of these numbers by 3, which is the smallest number that will convert them all into whole numbers :---

```
\begin{array}{ll} C & 1 \times 3 = 3 \\ H & 1 \cdot 66 \times 3 = 4 \cdot 98 \\ N & 1 \times 3 = 3 \\ O & 3 \times 3 = 9 \end{array}
```

4.98 is practically 5, and the formula becomes $C_3H_5N_3O_9$.

3. To calculate the molecular formula of a compound being given its percentage composition and its vapour density:—

(a) Multiply the vapour density by 2 to obtain the molecular weight.

 (\bar{b}) By simple proportion calculate the weight of each element present in the molecular weight of the compound.

(c) Divide the numbers thus obtained by the atomic weight of each corresponding element to obtain the number of atoms of each element in the molecule.

Example: The vapour density of benzene is 39, and its percentage composition is C = 92.31. H = 7.69, calculate its molecular formula.

(a) Molecular weight of benzene = $39 \times 2 = 78$.

(b) Weight of carbon in 78 parts by weight of benzene,

 $\frac{92.31 \times 78}{100} = 71.98$, practically 72.

Weight of hydrogen in 78 parts by weight of benzene,

$$\frac{7.69 \times 78}{100} = 5.99$$
, practically 6.

(c) $\frac{72}{12} = 6 =$ number of carbon atoms in the molecule of benzene.

 $\frac{6}{1} = 6 =$ number of hydrogen atoms in the molecule of benzene.

Hence molecular formula of benzene = C_6H_6 .

4. To find the weight of any substance that is produced by a chemical change from a given weight of material :---

This can be done if the substance is formed by a definite chemical change which can be represented by a chemical equation.

Write out the equation that represents the change and the relative weights of the various substances involved in the change. As these weights are relative, they may represent pounds, tons, grammes, &c., and show how much of the given substance would be produced from a weight of material equal to the weight given in the equation. By simple proportion the

weight to be obtained from any other weight of material can be calculated.

Example: What weight of di-nitro-benzene can be obtained from 10 tons of benzene ?

78 tons of benzene give 168 tons of di-nitro-benzene; how much di-nitro-benzene will 10 tons of benzene yield?

$$\frac{168 \times 10}{78} = 21.54 \text{ tons.}$$

5. To calculate the weight of material required to produce a given weight of any substance by a definite chemical change :----

Write out the equation and work the example by simple proportion in a similar manner to the previous case.

Example: What weight of potassium chlorate is required to produce 23 lbs. of oxygen?

| KClO3 | = | KC | 1 | + | О ₃ . | |
|------------|---|------|------|---|------------------|------------|
| K = 39 | | K = | = 39 | | $O_3 =$ | 4 8 |
| Cl = 35.5 | | Cl = | 35•5 | | | |
| $O_3 = 48$ | | | | | | |
| | | | | | | |
| 122.5 | : | = | 74.5 | | + | 4 8 |

48 lbs. of oxygen are obtained from 122.5 lbs. of potassium chlorate; how much potassium chlorate will give 23 lbs. of oxygen?

 $\frac{122.5 \times 23}{48} = 58.7$ lbs. potassium chlorate.

6. To find the volume of any gas at the freezing-point of water and under a pressure of one atmosphere that can be produced from a given weight of any material when the gas is formed by a definite chemical change that can be expressed by an equation.

(a) When the volume is measured in *litres*, the weight of material in *grammes*, and the temperature and pressure are 0° C. and 760 mm.

Write the equation representing the change which gives rise to the gas, and add the molecular weights of the substances. Then the molecular weight in grammes of any gas occupies $22\cdot32$ litres at 0° C. and 760 mm. Multiply $22\cdot32$ litres by the number of molecules of gas produced by the chemical change and it gives the number of litres at 0° C. and 760 mm. pressure if the weights of the substances represented by the equation are taken in grammes. A simple proportion sum then gives the required weight in grammes to produce the given number of litres of gas at 0° C. and 760 mm. pressure.

Example: Calculate the number of litres of marsh gas at 0° C. and 760 mm. that can be obtained from 40 grammes of sodium acetate—

| $NaC_2H_3O_2 +$ | NaHO = | CH_4 + | Na_2CO_3 |
|-----------------|--|-----------|--|
| Na = 23 | Na = 23 | C = 12 | $Na_2 = 46$ |
| $C_2 = 24$ | H = 1 | $H_4 = 4$ | C = 12 |
| $H_3 = 3$ | 0 = 16 | | $O_3 = 48$ |
| $O_2 = 32$ | | | , in the second s |
| | - | | |
| 82 | 40 | 16 | 106 |
| | The second s | - | Concession of the local division of the loca |

From 82 parts by weight of sodium acetate 16 parts by weight of marsh gas are formed. 16 represents the molecular weight of marsh gas, hence 16 grammes of marsh gas occupy 22.32 litres at 0° C. and 760 mm. Hence 82 grammes of sodium acetate will yield 22.32 litres of marsh gas at 0° C. and 760 mm. pressure; how many litres of marsh gas at the same temperature and pressure will 40 grammes of sodium acetate give?

$$\frac{40 \times 22.32}{82} = 10.88$$
 litres.

Similarly the number of grammes of any substance required to yield a given number of litres of a gas at 0° C. and 760 mm. pressure can be calculated.

Example : How many grammes of marble will yield 10 litres of carbon dioxide at 0° C. and 760 mm.?

| + 2] | HC1 | = | $CaCl_2$ | + | CO_2 | + | H_2O |
|------|----------------------|--|--|--|--|--|--|
| Η | = 1 | | Ca = 40 | | C = 12 | | ${ m H}_2 = 2$ |
| Cl | = 35.5 | | $Cl_2 = 71$ | | $O_2 = 32$ | | $0^{-} = 16$ |
| | (36.5) | $\overline{)} \times 2 =$ | | | | | |
| | | | | | | | |
| + | 73 | = | = 111 | + | • 44 | + | 18 |
| | + 2] H Cl + | + 2HCl H = 1 Cl = 35.5 (36.5) + 73 | + 2HCl = H = 1 Cl = $35 \cdot 5$ ($36 \cdot 5$) × 2 = + 73 = | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$ | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$ | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$ | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$ |

100 grammes of marble give 44 grammes of carbon dioxide. 44 is the molecular weight of carbon dioxide, therefore 44 grammes occupy 22:32 litres at 0° C. and 760 mm. 100 grammes of marble will give 22:32 litres of carbon dioxide; how many grammes will give 10 litres?

$$\frac{10 \times 100}{22 \cdot 32} = 44.8$$
 grammes.

(b) When the volume is measured in cubic feet, the weight of material in lbs. and the temperature and pressure at 0° C. and 760 mm. or 32° F. and 30 inches.

The molecular weight in lbs. of any gas occupies 356.88 cubic feet at 0° C. and 760 mm. or 32° F. and 30 inches pressure. Consequently if the weights represented by the equation be taken in lbs. every molecule of gas produced occupies 356.88 cubic feet. By substituting 356.88 cubic feet for 22.32 litres in the above calculations, the cubic feet of gas yielded by a given number of lbs. of material can be calculated, or the number of lbs. of material that will yield a given number of cubic feet.

Example : Find the number of cubic feet of marsh gas at 32° F. and 30 inches pressure that can be obtained from 40 lbs. of sodium acetate—

$$\begin{array}{c} {\rm NaC_2H_3O_2 + NaHO = CH_4 + Na_2CO_3}\\ {\rm 82} & {\rm 40} & {\rm 16} & {\rm 106}\\ {\rm (356\cdot88)} \mbox{ cubic feet.} \end{array}$$

From the equation given above 82 lbs. of sodium acetate yield

CHEMICAL CALCULATIONS

16 lbs. marsh gas or 356.88 cubic feet at 32° F. and 30 inches pressure—

$$\frac{356.88 \times 40}{82} = 174$$
 cubic feet.

Find the weight of marble that will yield 10 cubic feet of carbon dioxide at 32° F. and 30 inches pressure—

$$\begin{array}{rl} {\rm CaCO}_3 + 2{\rm HCl} = {\rm CaCl}_2 + {\rm CO}_2 + {\rm H}_2{\rm O} \\ {\rm 100} \, + \, 73 \, = \, 111 \, + \, 44 + \, 18 \\ {\rm (356\cdot88) \ cubic \ feet.} \end{array}$$

100 lbs. of marble yield 44 lbs. of carbon dioxide, or 356.88 cubic feet at 32° F. and 30 inches pressure; how many lbs. of marble will yield 10 cubic feet of the gas?

$$\frac{44 \times 10}{356.88} = 1.23$$
 lbs.

If the volume of the gas is measured at any other temperature and pressure than 0° C. and 760 mm. pressure, or 32° F. and 30 inches pressure, the volume must be reduced to these temperatures and pressures, and the reduced volume used in the calculations.



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APPENDIX I

TABLE OF APPROXIMATE ATOMIC WEIGHTS

Note.—The atomic weights given in the following table are sufficiently accurate for practical purposes of ordinary chemical calculations. More exact numbers, which are universally accepted, are published annually by the Chemical Society of London; these are printed in tables, which can be obtained from Messrs. Jackson & Gurney, 10 Paternoster Row, E.C.

| | | | | | Symbol. | Approximate Atomic Weights. |
|--|------------------|---|--------------------------------------|---------------------------------------|--|---|
| Aluminium Antimony Argon Arsenic Barium Bismuth Boron Bromine Cadmium Cæsium Calaium | a • • • | | • • • • • • • • | · · · · · · · · · · · · · · · · · · · | Al Sb A As Ba Bi B Br Cd Cs Cs | $27 \\ 120 \\ 39.5 \\ 75 \\ 137 \\ 208 \\ 11 \\ 80 \\ 112.5 \\ 133 \\ 40$ |
| Carbon | : | | : | : | Č | 12 |
| Cerium | | | | | Ce | 140 |
| Chlorine | • | • | • | | Cl | 35.2 |
| | | | | | | |

APPENDIX I

| | | | | Symbol. | Approximate Atomic Weights. |
|-------------|---|---|---|---------|--------------------------------|
| Chromium | | | | Cr | 52 |
| Cobalt . | | | | Co · | 59 |
| Columbium | | | | Cb | 93.5 |
| Copper . | | | | Cu | 63.5 |
| Dysprosium | | | | Dy | 162.5 |
| Erbium . | | | | Er | 167.5 |
| Europium. | | | | Eu | 152 |
| Fluorine . | | | | F | 19 |
| Gadolinium | | | | Gd | 157 |
| Gallium . | | | | Ga | 70 |
| Germanium | | | | Ge | 72.5 |
| Glucinum . | | | | Gl | 9 |
| Gold . | | | | Au | 197 |
| Helium . | | | | He | 4 |
| Hydrogen . | | | | H | 1 |
| Indium . | | | | In | 115 |
| Iodine . | | | | I | 127 |
| Iridium . | | | | Ir | 193 |
| Iron. | | | | Fe | 56 |
| Krypton . | | | | Kr | 83 |
| Lanthanum | | | | La | 139 |
| Lead . | | | | Pb | 207 |
| Lithium . | | | | Li | 7 |
| Lutecium . | | | | Lu | 174 |
| Magnesium | • | | | Mg | 24 |
| Manganese | | | | Mn | 55 |
| Mercury . | | • | | Hg | 200 |
| Molybdenum | • | | | Mo | 96 |
| Neodymium | | | • | Nd | 144.5 |
| Neon | | | | Ne | 20 |
| Nickel . | | | | Ni | 58.7 |
| Nitrogen . | | | | N | 14 |
| Osmium . | | | | Os | 191 |
| Oxygen . | | | | 0 | 16 |
| Palladium . | | | • | Pd | 107 |
| | | | | | |

APPENDIX I

| | | | | Symbol. | Approximate Atomic Weights. |
|----------------|--------|------|----|---------------|--------------------------------|
| Phosphorus | | | | Р | 31. |
| Platinum . | | | | Pt | 195 |
| Potassium. | | | | K | 39 |
| Praseodymium | | | | Pr | 104.5 |
| Radium . | | | | Ra | 226.5 |
| Rhodium . | | | | Rh | 103 |
| Rubidium | | | | Rb | 85.5 |
| Ruthenium | | | | Ru | 101.5 |
| Samarium | | | | Sa | 150.5 |
| Scandium . | | | | Sc | 44 |
| Selenium . | | | | Se | 79 |
| Silicon . | | | | Si | 28 |
| Silver . | | | | Ag | 108 |
| Sodium . | | | | Na | 23 |
| Strontium. | | | | Sr | 87.5 |
| Sulphur . | | | | S | 32 |
| Tantalum . | | | | Ta | 181 |
| Tellurium . | | | | Te | 127.5 |
| Terbium . | | | | Tb | 159 |
| Thallium . | | | | Tl | 204 |
| Thorium . | | | | \mathbf{Th} | 232.5 |
| Thulium . | | | - | Tm | 168.5 |
| Tin | | | | Sn | 119 |
| Titanium . | | | | Ti | 48 |
| Tungsten . | | | | W | 184 |
| Uranium . | | | | U | 238.5 |
| Vanadium | | | | v | 51 |
| Xenon . | | | | Xe | 130 |
| Ytterbium (Neo | ovtter | bium |). | Yb | 172 |
| Yttrium . | | | | Y | 89 |
| Zinc. | | | | Zn | 65 |
| Zirconium. | | | | Zr | 90.5 |
| | | - | | | |

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APPENDIX II

THE METRIC SYSTEM OF WEIGHTS AND MEASURES

The standard length is 1 metre, which is 3.28 English feet; it is very nearly one ten-millionth of a quadrant of the globe.

| Milli- metres. m.m. | Centi- metres. c.m. | Deci- metres. d.m. | Metres. m. | Deca- metres. | Hecto- metres. | Kilo- metre. | English Equivalent. |
|---|--|-----------------------------------|-----------------------------|------------------------|---------------------|-----------------|--|
| 1 10 100 1,000 10,000 100,000 1,000,000 | 1 10 100 1,000 10,000 100,000 | 1 10 100 1,000 10,000 | 1 10 100 1,000 | 1 10 100 | 1 10 | 1* | 0.039371 in 0.39371 ,, 3.93708 ,, 3.2809 ft. 32.8089 ,, 328.0899 ,, 3280.8991 ,, |

Measures of Length

* 1 Kilometre = .62138 mile.

Measures of Surface

| Square Millimetres. mm. ² | Square Centimetres. cm. ² | Square Decimetres. dm. ² | Square Metre. m. ² | English Equivalent. |
|---|--|---|-------------------------------------|------------------------------|
| I 100 | | | | 0.0015 sq. ins. 0.1554 ,, |
| 10,000 | 100 | 1 | | 10'04 ,, |
| 1.000,000 | 10,000 | 100 | 1 | 10.764 sq. feet |
| 100 Square Metres = 1 Are = | | | | 0.0247 acres |
| 10,000 ,, = 1 Hectare = | | | | 2.471 ,, |
APPENDIX II

| incusares of Oupacity | | | | | | | |
|--|-------------------------------|--|-------------------------------------|--|--|--|--|
| Cubic Millimetres. mm. ³ | Cubic Centimetres. c.c. | Cubic Decimetres or Litres dm. ³ or l. | Cubic Metres. m. ³ | English Eqnivalent. | | | |
| 1 1,000 1,000,000 1,000,000,000 | 1 1,000 1,000,000 | 1* 1,000 | 1 | 0.00006 c. ins. 0.06102 ,, 61.02 ,, 35.31 c. feet | | | |

Measures of Capacity

* 1 cubic decimetre is 1 litre.

Measures of Weight

The standard weight is 1 gramme, which is the weight at the latitude of Paris of 1 cubic centimetre of water at 4° C.; it is equal to 15.43235 grains.

| Milli- gramme. | Centi- gramme. | Deci- gramme. | Gram. | Deca- gram. | Hecto- gram. | Kilo- gram. | Englis Equivale | h ent. |
|-------------------|-------------------|------------------|-------|----------------|-----------------|----------------|--------------------|-----------|
| | | | | | | | | |
| 1 | | | | | | | 0.01543 | grs. |
| 10 | 1 | | | | | | 0.15432 | |
| 100 | 10 | 1 | | | | | 1.54323 | • • |
| 1,000 | 100 | 10 | 1 | | ••• | | 15.43235 | ,, |
| 10,000 | 1,000 | 100 | 10 | 1 | | | 0.3215 | ozs. |
| 100,000 | 10,000 | 1.000 | 100 | 10 | 1 | | 3.215 | |
| 10,000,000 | 1,000,00 | 10,000 | 1,000 | 100 | 10 | 1 | 2.20 | lbs. |
| | | | - | | | | | |

APPENDIX III

Density of Solids and Liquids

| | Weight in lbs. per c. ft. | Weight in Grammes per c.c. | | Weight in lbs. per c. ft. | Weight in Grams. per c.c. |
|--|---|--|--|---|--|
| Mercury Lead Brass Steel Iron, cast . Iron, wrought Tin Zinc Anthracite . Bituminous . Lignite | $\begin{array}{c} 850\\ 712\cdot7\\ 487\cdot5\\ 487\cdot5\\ 487\cdot5\\ 475\\ 456\cdot25\\ 425\\ 109\ {\rm to}\ 84\\ 81\ {\rm to}\ 83\\ 78\ {\rm to}\ 81\\ \end{array}$ | $13.6 \\ 11.4 \\ 7.8 \\ 7.8 \\ 7.4 \\ 7.6 \\ 7.3 \\ 6.8 \\ 1.34 \text{ to } 1.75 \\ 1.3 \text{ to } 1.36 \\ 1.25 \text{ to } 1.3 \\ 1.25 \text{ to } 1.3 \\ 1.25 \text{ to } 1.3 \\ 1.3 \ 1.$ | Water . Sea water . Fir, spruce Oak Alcohol Naphtha . Oil, linseed Oil, olive . Oil, whale . Turpentine | $\begin{array}{c} 62.5\\ 64.0\\ 30\ to\ 43.75\\ 43\ to\ 61.8\\ 49.5\\ 53.1\\ 58.75\\ 56.9\\ 57.5\\ 54.3\end{array}$ | $1 \\ 1.02 \\ 0.48 \\ 0.69 \\ 0.791 \\ 0.884 \\ 0.940 \\ 0.915 \\ 0.923 \\ 0.870 \\ \end{array}$ |

Gases

(At 0° C. and 760 mm. or 32° F. and 30 inches pressure.)

| Gas. | Weight in lbs. per c. ft. | Weight in Grams. per litre. | Gas. | Weight in lbs. per c. ft. | Weight in Grams. per litre. |
|---|--|--|--|---|--|
| Air Hydrogen Marsh gas Nitrogen Carbon monoxide | 0.0807 0.0056 0.0451 0.0783 0.0784 | 1·2932 0·0896 0·7168 1·2511 1·2544 | Oxygen Sulphuretted hydrogen Argon Carbon dioxide Sulphur dioxide | 0.0892 0.095 0.1117 0.1232 0.1813 | 1.4395 1.5232 1.7696 1.9712 2.8790 |

APPENDIX IV

Specific Gravity and Vapour Density of Gases

| | Specific Gravit | y. Vapour Density. |
|--|--|--|
| Hydrogen Marsh gas Ammonia Nitrogen Carbon monoxide . Air | . 0.06926 . 0.559 . 0.589 . 0.9713 . 0.9720 . 1.0 . 1.1056 | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ |
| Sulphuretted hydrogen Argon Carbon dioxide . Sulphur dioxide . | $ \begin{array}{c} 1 & 1030 \\ 1 & 1\cdot1781 \\ 1 & 1\cdot3843 \\ 1 & 1\cdot5291 \\ 2 & 2\cdot2471 \\ \end{array} $ | $ \begin{array}{r} 10 \\ 17 \\ 0 \\ 19 \\ 75 \\ 22 \\ 0 \\ 32 \\ 0 \end{array} $ |

Specific Gravity of Solids and Liquids

| | | | 1 | |
|-------------------|--------------|--------------|---|----------|
| Mercury | 13.596 | Water . | | 1.0 |
| Lead | 11.4 | Sea water | | $1\ 026$ |
| Brass | 78 | Oak . | | 0.69 |
| Steel | 7.8 | Fir, spruce | | 0.48 |
| Iron, cast | 7.4 | Alcohol . | | 0.791 |
| Iron, wrought . | 7.6 | Naphtha . | | 0.848 |
| Tin | 7.3 | Oil, linseed | | 0.940 |
| Zinc | 6.8 | Oil, olive | | 0.915 |
| Anthracite | 1.34 to 1.75 | Oil, whale | | 0.923 |
| Bituminous coal . | 1.3 to 1.36 | Turpentine | | 0.870 |
| Lignite | 1.25 to 1.3 | - | | |
| - | 1 | | | |

APPENDIX V

HYGROMETRIC TABLES

THE following Hygrometric Tables are copied by kind permission of Mr. Henry Davis of Derby.

INSTRUCTIONS FOR READING THE TABLES

Read the dry- and wet-bulb temperatures carefully, and deduct one reading from the other.

Look in the column on the left or right for the nearest degree to the dry-bulb reading, and carry the eye horizontally along until the column is reached corresponding to the difference between the dry- and wet-bulb thermometers, when the relative humidity will be found. Intermediate readings can be interpolated in the usual way.

Example.—Dry bulb, 62.5; wet bulb, 55.7; the difference is 6.8. Having found 62 in the column on the left or right, run the eye along the column until 6.8 is reached, when the relative humidity will be found, namely, 63 per cent.

| Julb. | Read Dry-I | 28 25 25 20° | 888 88 89 88 88 88 88 88 88 88 | 4 4 44 46 48 48 48 48 48 48 48 48 48 48 48 48 48 | 52 54 58 58 58 58 58 58 58 58 58 58 58 58 58 | 6644 20 6644 20 6644 20 | 720 100 100 100 100 100 100 100 100 100 1 |
|--------------|---------------|--|---|--|--|--|---|
| | 0.9 | 110 114 118 118 25 | 32 41 53 56 | 58 59 61 62 62 | 62 63 65 65 66 | 89 88 89 89 | 69 72 73 74 |
| - | 00° 01° | 11 112 115 119 26 26 | 33 54 54 57 | 59 60 62 63 63 | 63 64 65 66 66 67 | 68 69 69 69 | 720 772 755 |
| | 9.9 | 8 13 16 20 27 | 35 55 58 58 | 60 62 63 64 | 64 65 67 68 68 | 89 69 60 20 20 | 73 73 73 73 |
| | 5.4 | 9 14 17 21 29 29 | 36 57 57 60 | 61 62 63 65 65 | 65 68 68 69 69 | 69 02 11 12 | 722 778 76 |
| | 5.5 | 9 15 18 23 23 30 | 37 47 53 58 61 | 62 64 65 66 65 66 | 89 89 99 | 222222 | 73 77 77 77 |
| | 0.g | 10 15 17 19 25 32 | 39 55 59 62 | 63 64 65 66 67 | 68 69 70 71 | 72 722 733 738 | 74 74 77 77 78 |
| ters. | °.00 | 11 16 18 21 26 33 | 40 56 60 63 63 | 64 67 68 68 | 69 71 72 72 | 722 733 744 74 | 74 775 776 778 |
| nome | 4.6 | 12 17 19 23 23 23 23 23 23 23 23 23 23 23 23 23 | 42 51 51 61 64 | 65 68 69 69 69 69 69 69 69 69 69 69 69 69 69 | 72 72 73 73 | 73 74 75 75 | 775 776 778 |
| hern | 4.4 | 14 18 21 25 29 36 | 44 53 63 66 66 | 67 70 71 71 | 72 722 738 74 | 74 75 75 76 76 | 77 779 80 80 |
| Ub T. | 4.2 | 16 19 23 23 27 31 33 | 45 54 60 64 67 | 68 71 72 72 | 72 73 73 74 | 75 77 77 | 77 77 80 81 |
| -Bu | 4°0 | 18 21 25 29 33 33 40 | 47 56 62 66 69 | 70 72 72 73 | 73 74 75 75 76 | 76 77 78 78 78 | 78 79 81 82 82 |
| Wet | 00 63 | 20 23 23 35 35 42 | 49 58 63 68 68 70 | 71 722 733 74 | 74 75 76 776 | 77 78 79 79 | 79 80 81 82 82 |
| put | 3.6 | 23 25 29 37 37 44 | 51 66 69 69 71 | 72 74 74 75 | 75 77 77 78 | 78 79 80 80 80 | 80 82 82 83 83 83 |
| ulb e | 3.4 | 25 27 31 34 39 39 46 | 53 61 71 73 73 | 74 75 76 77 77 | 77 78 79 80 | 80 80 81 81 81 81 | $\frac{81}{82}$ |
| y-B | 3.2 | 27 29 33 36 41 48 | 55 63 72 74 | 75 77 77 78 | 78 79 80 81 | 81 81 82 82 82 82 82 82 | 82 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 |
| Dr | 3.0 | 30 32 33 39 39 43 43 43 | 58 65 71 74 76 | 76 77 78 78 79 | 79 80 81 82 82 | $\begin{smallmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $ | 855 855 855 855 855 855 855 855 855 855 |
| f the | 5°° | 32 34 38 38 45 45 45 52 | 60 67 72 77 77 77 77 | 78 79 79 80 | 81 81 82 83 83 83 83 | $\begin{array}{c} 83\\ 84\\ 84\\ 84\\ 82\\ 83\\ 82\\ 82\\ 83\\ 82\\ 82\\ 83\\ 82\\ 82\\ 83\\ 82\\ 82\\ 82\\ 82\\ 82\\ 82\\ 82\\ 82\\ 82\\ 82$ | 86 86 86 86 86 86 86 |
| 98 0 | 2.6 | 35 37 41 48 48 54 | 62 69 74 77 78 | 79 80 81 81 81 81 81 | 82 82 83 84 83 | 84 84 85 85 85 | 85 87 87 87 87 87 87 |
| adin | 2.4 | 38 44 51 57 | 64 76 70 80 | 81 82 82 82 82 82 82 82 82 82 82 82 82 82 | ${}^{8}_{8}{}^{$ | 855 85 86 85 85 85 85 85 | 86 88 88 88 88 88 88 88 88 88 |
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USEFUL INFORMATION

| 1 inch | = | 2.54 centimetres. | 1 cub. inch | | 16.386 c. cent. |
|-----------|---|--------------------|-------------|----|------------------|
| 1 foot | = | 0.3048 metre. | 1 cub. foot | _ | 0.0283 c. metre. |
| 1 yard | = | 0.9144 metre. | 1 cub. foot | = | 28.3153 litres. |
| 1 mile | = | 1.6093 kilometres. | 1 gallon | == | 4.5434 litres. |
| 1 litre | = | 1.76 pints. | 1 pint | == | 0.568 litre. |
| 1 grain | = | 0.0648 gramme. | 1 oz. av. | = | 28.35 grammes. |
| 1 lb. av. | _ | 453.6 grammes. | | | |

1 litre of water at 4° C. weighs 1000 grammes.

1 gallon of water at 60° F. weighs 10 lbs.

1 cubic foot of water at 60° F. weighs 62.5 lbs. = 1000 ounces.

The number of ounces in 1 cubic foot of water equals the number of grammes in 1 litre.

1 cubic foot of air at 32° F. and 30 inches pressure weighs 0.0807 lb. 1 litre of air at 0° C. and 760 mm. pressure weighs 1.293 grammes.

- 1 litre of hydrogen at 0° C. and 760 mm. pressure weighs 0.0896 gramme.
- 1 gramme hydrogen at 0° C. and 760 mm. pressure occupies 11.16 litres.
- 1 lb. hydrogen at 32° F. and 30 inches pressure occupies 178.44 cubic feet.

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