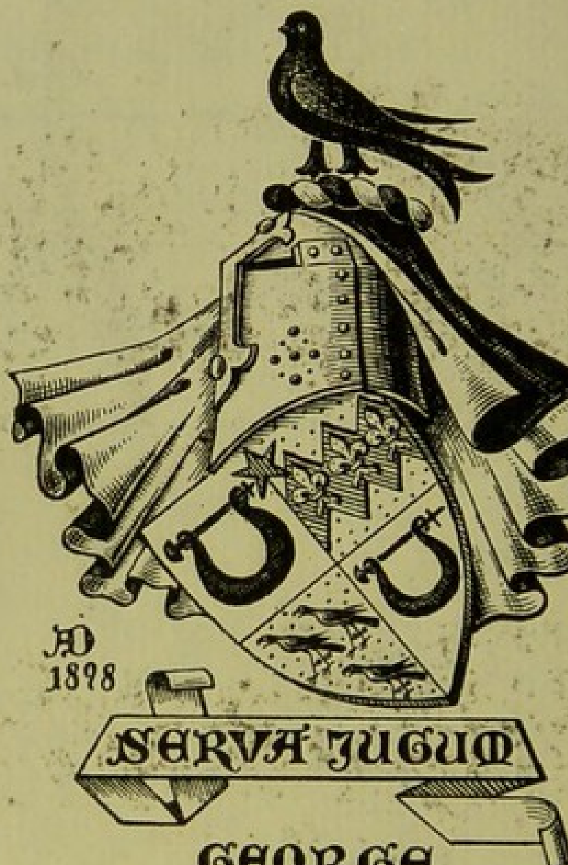
**The investigation of mine air : an account by several authors of the nature, significance, and practical methods of measurement of the impurities met with in the air of collieries and metalliferous mines / edited by Clement le Neve Foster and J.S. Haldane.**

# THE INVESTIGATION OF
# MINE AIR

C. LE NEVE FOSTER AND J. S. HALDANE



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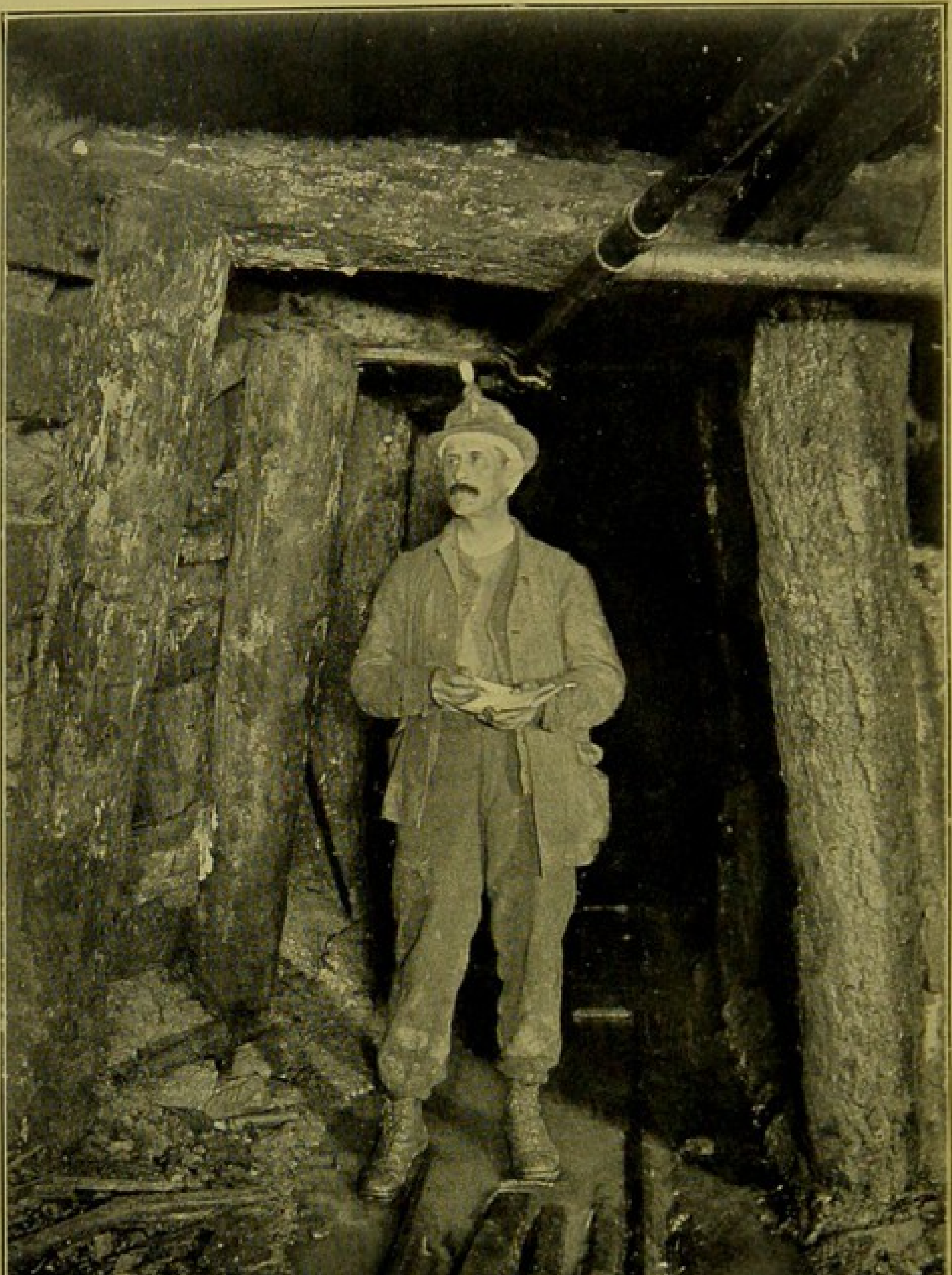

SIR CLEMENT LE NEVE FOSTER.

From a photograph taken in Foxdale Mine, Isle of Man, June 1897, by Mr G. J. Williams, H.M. Inspector of Mines.

# THE INVESTIGATION OF MINE AIR:

AN ACCOUNT BY SEVERAL AUTHORS OF THE NATURE,
SIGNIFICANCE, AND PRACTICAL METHODS OF
MEASUREMENT OF THE IMPURITIES MET
WITH IN THE AIR OF COLLIERIES
AND METALLIFEROUS MINES.

EDITED BY

SIR CLEMENT LE NEVE FOSTER, D.Sc., F.R.S.
LATE PROFESSOR OF MINING AT THE ROYAL SCHOOL OF MINES, LONDON;

AND

J. S. HALDANE, M.D., F.R.S.
FELLOW OF NEW COLLEGE AND LECTURER IN PHYSIOLOGY AND MINING HYGIENE,
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# PREFACE.

THE manuscript of the greater part of the present book was left in a nearly complete form by Sir Clement Le Neve Foster at the time of his unexpected death, and he had already made arrangements with Messrs Griffin for its publication as a companion book to his *Elements of Mining and Quarrying*, recently issued by them. As I was familiar with the object which he had in view, I willingly undertook such revision as was necessary.

No questions receive closer attention from mining engineers at the present time than those relating to the health and safety of the men under their charge; and among all the dangers which threaten the miner or impede his work, none are more real and urgent than those due to impure air. A knowledge of the impurities in mine air, the methods of identifying and measuring them, their sources, and their effects, has thus become almost a necessity to mining engineers. The aim of the book is to give English students of mining, and mining engineers, an account of this subject, with reference to both coal-mines and metalliferous mines.

It was characteristic of the broad outlook of Le Neve Foster that he wished to present to his students—for the book was originally intended for the special use of students at the Royal School of Mines—an account, not merely of English methods of mine air examination, but also (as far as possible) of methods in use in other countries. He therefore translated the two papers which form the first and second parts of the book, after obtaining the permission of the authors and publishers, whose courtesy I should like to take this opportunity of gratefully acknowledging.

The first part is a translation of the well-known short treatise on Mine Air Analysis, written for mining engineers by Prof. Brunck of the Freiberg Mining College. In this section will be found a general account of the normal and abnormal constituents of mine air, and a detailed description of the analysis of mine air by the very valuable technical methods of Winkler, Hempel, and other eminent German chemists.

The second part is an account by M. Léon Poussigue, Manager of the Ronchamp Collieries, of the méthods in use there under his direction for the systematic examination of the air and control of the ventilation. This description of the practice in a first-rate French colliery will be read with interest by English mining engineers, particularly as the method of fire-damp estimation employed (that of Le Châtelier) is as yet very little known in this country.

The third part, for which I am responsible, contains a description of rapid methods of analysis—for the most part not hitherto published—which I have devised in the course of investigations on mine air during the last few years. To this description there is added a section on the interpretation of mine air analyses, in which the origin, significance, and effects on men of the various impurities in mine air are discussed in the light of recent investigations. As the first two parts of the book refer more especially to the air of coal-mines, I have, in the course of revision, been careful to insert full references to the impurities met with in metalliferous mines, so that students of both metalliferous mining and coal mining may be able to find within the book the information which they require.

As an appendix, and as far as possible in Le Neve Foster's own words, I have added an account of the effects of carbonic oxide in the disaster at Snaefell Mine in 1897. Not only is this account of much scientific and practical interest, but it will be valued as a characteristic personal memorial of one who was respected even more for his devotion to the highest ideals of duty than for the benefits to the mining profession which resulted from his influence and teaching. His exposure to carbonic oxide during the exploration of the mine and recovery of the bodies was apparently the starting-point of the illness which ultimately proved fatal to him.

For the interesting photograph reproduced in the Frontispiece I am indebted to Mr G. J. Williams, H.M. Inspector of Mines. It was taken in a neighbouring mine shortly after the Snaefell accident, when Mr Williams had his camera underground for the purpose of photographing a life-saving apparatus which we were testing.

J. S. H.

## PART I.

### AN INTRODUCTION TO MINE AIR ANALYSIS BY SIMPLE METHODS.

By Dr OTTO BRUNCK,
PROFESSOR IN THE ROYAL SAXON MINING COLLEGE, FREIBERG.

*Pages* 1–62.

## PART II.

### THE MEASUREMENT OF AIR-CURRENTS AND FIRE-DAMP AT RONCHAMP COLLIERIES.

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## PART III.

### THE EXAMINATION OF MINE AIR.

By J. S. HALDANE, M.D., F.R.S.

*Pages* 95–156.

## APPENDIX.

### THE EFFECTS OF CARBONIC OXIDE IN CONNECTION WITH THE SNAEFELL MINE DISASTER IN 1897.

*From the Report to the Home Secretary,*
By Sir CLEMENT LE NEVE FOSTER.

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# I.—THE CHEMICAL INVESTIGATION OF MINE AIR:

*A Concise Introduction to the Analysis of Mine Air by simple methods, for the use of Mining Engineers.*

BY

DR OTTO BRUNCK,

EXTRAORDINARY PROFESSOR AT THE FREIBERG MINING COLLEGE.

# THE CHEMICAL INVESTIGATION OF MINE AIR.

## INTRODUCTION.

The dangers which threaten the miner in his calling, and especially the collier, are numerous. Water, fire, falls of rock, and a dangerous atmosphere—these are the enemies with which he constantly has to contend. But of all dangers those which he fears most are caused by gases underground, which may give rise to violent explosions or may endanger his health and life by impeding respiration. An enemy is more easily fought when he is visible; but mine gases, the invisible decomposition products of organic substances, entirely escape perception by our senses, and we only begin to recognise their presence by their noxious effects. The collier has therefore always endeavoured to discover ways and means of recognising these dangerous gases, and especially the dreaded fire-damp. Many appliances have been invented for the purpose; but not one of these so-called fire-damp indicators has made its way into ordinary practice. It is true that the miner's lamp is an appliance which will warn him when there is danger from fire-damp, or when the proportion of oxygen in the air is falling below the requirements for breathing. Unfortunately, the lamp does not begin to be an effective detector of dangerous mixtures of gases until the moment of danger has already arrived, the mine air already containing so much of these gases as to be dangerous. So-called indicator lamps affording more delicate tests for methane have been constructed; but the miner has not taken to them kindly, either because they are not easily managed, or because their indications are not trustworthy.

A plentiful supply of fresh air to all the workings of a mine has always been regarded as the best means of combating the dangers due to underground gases. The natural currents have long been strengthened by powerful fans, and to-day ventilation is one of the most important branches of colliery engineering. As the issue of gases from coal cannot be prevented, they must be rendered harmless by diluting them greatly with atmospheric air and then driving them out of the mine. The only means of deciding whether this object is properly attained is to determine the amount of methane and carbonic acid in the main and branch air-currents; for even with the best imaginable ventilation it is impossible to prevent the percentage of methane or carbonic acid from temporarily exceeding the desired standard in certain places. The main return current represents to a certain extent an average of all parts of the mine; and by determining the amount of methane and carbonic acid, and measuring the volume of air passing through the shaft in the unit of time, it is possible to ascertain the quantities of gas produced in a colliery, which are often very large.

Just as the smelter by analysing the smoke or furnace gases determines whether or no his firing is being carried on properly, so the miner is enabled, by regularly analysing the return air-current, to control the ventilation of his mine. Whether the quantity of air sent into a mine is insufficient or unnecessarily large—a danger in one case and a waste in the other—is a question which can only be answered by chemical analysis, unless the miner resorts to crude empiricism. And the case is one in which rules based simply on previous experience have little value, for the "chemical temperament" of mines is very varied.

The regular investigation of the return air-currents will reveal to the manager of a mine every disturbance in the ventilation; it will call his attention to any increase in the amount of gas given off, such as may be due to cutting into a new seam or any other cause. In determining whether the ventilating arrangements are acting properly the proportion of carbonic acid gives specially valuable information, as this gas is given off by the coal with far greater regularity than is methane. The amount of this latter gas often varies very considerably. In any case, the analysis will call the manager's attention to any increase in the amount of methane, and enable him to prevent a dangerous accumulation of gas by increasing the supply of fresh air.

The importance of regularly analysing samples of the air from the different mines has been recognised in various colliery districts; and central laboratories have been erected for making determinations of fire-damp. To these laboratories samples of mine air, either taken at regular intervals or as special circumstances may direct, are sent in by the managers of mines for determination of the percentages of methane and carbonic acid. Although analyses of this kind, repeated perhaps after considerable intervals of time, afford important information concerning the freedom of a mine from fire-damp, yet they cannot serve for controlling the ventilating arrangements. Analysis will not serve this purpose unless the mine manager has a determination made at any moment when it appears to him necessary, and receives the results with the least possible delay. This can only be ensured by having the analysis made at the mine itself.

The classical methods of exact gas analysis, which we owe to Robert Bunsen, have not been adopted in actual practice for the investigation of gaseous products formed in chemical and metallurgical processes, and in like manner the methods of analysing mine air which give satisfactory results in scientific laboratories and in the hands of practised chemists, will not be adopted at mines. Just as gas analysis first began to make its triumphal entry into chemical and metallurgical works after chemists had invented methods of analysis suited to the requirements of practice, so also mine air will not be regularly analysed at collieries until means are provided of enabling a person who is not an expert to obtain with the aid of simple apparatus results sufficiently accurate for practical purposes. Another condition which must be imposed in the case of technical analyses of mine air is that an analysis shall not take up too much time.

If we cast our eyes over the field of technical gas analysis for methods of analysing mine gas which will satisfy these requirements, it is easy to find all that is wanted in the case of all the important gases; the methods are suitable for the conditions of practical mining, they are simple, and they give results which in many instances, and especially with methane, the most important of all mine gases, are in no way less accurate than the most delicate methods of exact gas analysis.

As soon as the mining engineer has overcome his timidity with reference to this unaccustomed field of operations, he will quickly take to gas analysis, and learn to regard it as an important aid to the safety of the workings placed under his charge.

# I. THE CONSTITUENTS OF MINE AIR.

## 1. Oxygen.

The most important gas for the inhabitants of our planet is oxygen, without which animal life is impossible; it was consequently called "life-air" by the old chemists. In the free state it forms the most important constituent of our atmosphere, which contains 20·94 per cent. of it by volume, the remainder consisting chiefly of nitrogen. Although air is only a mechanical mixture of gases, and not, as was formerly believed, a chemical compound of oxygen and nitrogen, the percentage of oxygen which it contains is remarkably constant. In spite of the enormous daily consumption of oxygen upon the earth, no variations in the composition of our atmosphere can be proved. It is the vegetable world which balances the consumption by the giving off of oxygen, and if there are any small local differences of composition, the remarkable mutual diffusive power of the atmospheric gases soon brings back the atmosphere to its normal composition.

Where, however, masses of air are enclosed, so that the interchange of constituents with the outer atmosphere is not free and unimpeded, considerable variations in its composition are very easily possible, and the percentage of oxygen may fall considerably below the normal. On the other hand, no appreciable increase above the normal has ever been observed up to the present. Mine air is poorer in oxygen than atmospheric air, and the difference in the proportions of oxygen in the intake and return air in collieries may amount to several per cent. If the air is very poor in oxygen the miner speaks of it as "dead." The consumption of oxygen in the mine is due only in a very minor degree to the respiration of the workmen and the burning of lamps, and it must be ascribed in the main to the slow oxidation of the coal.

Oxygen is a perfectly colourless, inodorous, and tasteless gas, which by our senses we cannot distinguish from ordinary atmospheric air. It is slightly heavier than air; its specific gravity, reckoning air as unity, is 1·105 at 0° C. and 760 mm. of mercury in latitude 45°, and 1 litre of oxygen weighs 1·429 grammes. Below – 118° C., the critical temperature of this gas, oxygen may be compressed into a bluish liquid, which boils at – 184° C. At a temperature of – 200° C. it liquefies even at atmospheric pressure. It is only very slightly soluble in water: at 15° C. 100 volumes of water dissolve only 3·45 volumes of oxygen.

Oxygen has a great affinity for nearly all the elements. With some it combines even at the ordinary temperature; in most cases heat is necessary to start the process of combination, which then completes itself with great violence and evolution of heat. The slow and quiet combination of oxygen with other substances is called oxidation, whilst the violent combination accompanied by flame is known as combustion. When oxygen is added to combustible gases in certain proportions the mixture will explode if brought into contact with flame, an electric spark, or a glowing wire. As in the case of solids and liquids, so also in the case of gaseous mixtures, the temperature of ignition varies greatly.

In gas analysis we make use of the property possessed by oxygen of combining with certain substances at the ordinary temperature. The mixture containing oxygen is brought into contact with one of these bodies: the oxygen is absorbed; and the mixture undergoes a corresponding diminution of volume. An excellent absorbent of oxygen is yellow phosphorus, which, if wet, combines with oxygen at the ordinary temperature of dwelling-rooms, producing phosphorous and phosphoric acids, which easily dissolve in water. The reaction is accompanied by a peculiar evolution of light, which is very evident in a dark room. As soon as all the oxygen has disappeared, the glowing, which arises from the combustion of phosphorus vapour, ceases immediately. The commencement of the absorption is also recognisable by the appearance of white clouds of phosphorous acid, which only slowly clear away, but which, on account of their very small pressure, do not affect the volume of the remaining gas. At the ordinary temperature of dwelling-rooms, the absorption is complete in a few minutes; below 16° C. (61° F.) there is already a marked retardation, which increases as the temperature sinks, and the reaction ceases altogether at 8° C. (46° F.).

It is strange that the absorption takes place with greater difficulty as the proportion of oxygen in a gaseous mixture increases: a higher temperature becomes necessary to start the reaction, which, however, when once begun, proceeds very rapidly. In pure oxygen the absorption does not begin until the temperature is 23° C. (73° F.), and then the evolution of heat may be great enough to melt the phosphorus. Occasionally the combination takes place with explosion and flame. The reaction proceeds gently if the oxygen is rarefied by diminishing the pressure instead of by the admixture of an indifferent gas.

The employment of phosphorus in gas analysis is unfortunately somewhat limited by the fact that several gases and vapours, even when occurring in only very small proportions, completely stop the absorption of oxygen. Among them may be mentioned particularly phosphoretted hydrogen, sulphuretted hydrogen, chlorine, benzene vapour, petroleum vapour, and especially the unsaturated hydrocarbons contained in petroleum. On the other hand, methane, ethane, and the saturated hydrocarbons may be present in large quantity without exerting the slightest influence upon the reaction. It is remarkable that the absorption is not rendered slower or incomplete by the disturbing gases; it either goes on normally or is entirely prevented. If any cloudiness appears, it may be safely assumed that the oxygen will be completely absorbed. On the other hand, if a gaseous mixture of unknown composition is being analysed, the absence of cloudiness must never be regarded as proving the absence of oxygen.

Phosphorus is particularly well adapted for the analysis of mine air. It is only in the case of the gases given off by underground fires, or of the "after-damp" of coal dust explosions, that it is better to employ another material for absorbing the oxygen, because the air may then contain products distilled from the coal or the timber.

This other absorbent, which can be used in all cases, is pyrogallic acid, an organic substance. It is a white, very light crystalline powder which becomes brown when exposed to the light, and is extremely soluble in water. Whilst an aqueous solution of pyrogallic acid alone does not absorb oxygen rapidly, the addition of an alkali increases the absorptive power extraordinarily. If a solution of pyrogallic acid in an excess of potash solution is shaken up with a gaseous mixture containing oxygen, this gas disappears in the course of a few minutes, whilst the liquid turns brown, owing to the formation of complicated oxidation products. Though pyrogallic acid does not equal phosphorus in its absorptive capacity and in convenience of manipulation, it possesses the advantages that its action is not affected by the presence of other gases and that low temperatures do not appreciably lower its faculty of taking up oxygen.

The physiological importance of oxygen depends upon the fact that it oxidises the food material in the animal body with development of heat. It is consequently the most important factor in nutrition and the development of muscular energy. The oxygen inhaled in breathing is taken up by the blood in the lungs, and converts its hæmoglobin into a very unstable chemical compound, oxyhæmoglobin, which imparts a bright red colour to the blood. The oxygen in this state of combination is carried to all parts of the animal body, and on reaching the capillaries the oxyhæmoglobin is dissociated into hæmoglobin and oxygen. The latter oxidises the food material, whilst the hæmoglobin returns to the lungs in the dark venous blood, to receive a new charge of oxygen and once more become bright arterial blood. The saturation of the hæmoglobin with oxygen can only be accomplished in the lungs if the partial pressure of the oxygen in the air which is being inhaled is sufficiently great. Experiments have shown that this can be lowered to one-half of the normal without injury to health. It is not until the proportion of oxygen in the air has sunk below 12 per cent. that difficulties of breathing set in: with 10 per cent. the lips become bluish; with 6 per cent. there is violent palpitation of the heart and loss of consciousness, which is soon followed by death. The experiences of persons going up in balloons or ascending high mountains are in complete accord with the above facts, for it is found that difficulties of breathing commence at a height of about 5000 metres (16,000 feet), when the atmospheric pressure is reduced to about one-half of what it is normally, and when consequently the partial pressure of the oxygen in the inhaled air has likewise sunk to one-half. On the other hand, an increase in the air-pressure may partially compensate for the reduction in the percentage of oxygen. Consequently a diminution in the oxygen contents of the atmosphere is more easily borne at a great depth than at the surface. The partial pressure of the oxygen in the inhaled air may be increased threefold without injury to health; and pure oxygen may be inhaled into the lungs for a long time without danger. As blood in contact with pure oxygen saturates itself with this gas five times as quickly as it does when in contact with air, persons who have been suffocated from want of oxygen are made to breathe pure oxygen in the hopes of restoring them to life. Compressed oxygen contained in steel bottles is a regular article of commerce.

### 2. Nitrogen.

Of the various substances existing in the gaseous state upon the earth, nitrogen is the one which occurs in the largest quantity. Our atmosphere contains nearly four-fifths of its volume of nitrogen; more exactly, it contains 78·1 per cent. of nitrogen by volume. Although the percentage of oxygen in the air is very constant, the proportion of nitrogen is almost more so, as it scarcely has any share in the active chemical changes which are continually going on in our planet. It is only a few plants which, with the aid of bacteria, can extract the nitrogen from the air and build it up into molecules of albumen.

The percentage of nitrogen in the air increases where oxygen is consumed without a corresponding volume of carbonic acid taking its place. In mine air the proportion between oxygen and nitrogen is often decidedly different from what it is in the atmosphere; and the return air-currents usually show a percentage of nitrogen which is decidedly higher in proportion to the oxygen than that of the air on entering the mine. This is due partly to the partial absorption of the oxygen by the coal, and to its consumption by breathing and combustion; and, on the other hand, there is also a positive increase of nitrogen, due to the fact that the gases given off by the coal contain some free nitrogen, which does not come from the air, but which has been formed out of the albumen of the plants during the process of carbonisation. The "blowers" also often contain considerable quantities of nitrogen. The accumulations of gas known in England by the name of "black damp" consist solely of nitrogen and carbonic acid. An analysis of this mixture in one case gave 87 per cent. of nitrogen and 13 per cent. of carbonic acid. Here, however, the nitrogen probably came from the air, which, under suitable conditions, had had all its oxygen extracted from it by the coal, whilst its place was taken by the oxidation product of the coal, viz. carbonic acid.

The physical properties of nitrogen differ but little from those of oxygen. Like the latter, it is a colourless, tasteless, and inodorous gas. Its specific gravity is somewhat lower, viz. 0·970. One litre of nitrogen under normal conditions weighs 1·251 grammes. Below its critical temperature, – 146° C., it may be liquefied by pressure. The colourless liquid boils at – 194° C. If liquid air is exposed to atmospheric pressure, nearly pure nitrogen evaporates first of all; and, finally, there remains behind a mixture in which the proportion between oxygen and nitrogen is almost the converse of what it is in air. The solubility of nitrogen in water is only about half that of oxygen.

Of all the gases nitrogen presents the greatest contrast to oxygen from a chemical point of view. In contradistinction to the latter, it shows very slight affinity for the other elements. At ordinary temperature it behaves with perfect indifference to all substances, and it is only at a red heat that it is able to combine with a few of the elements, such as the lighter metals, lithium, magnesium, and calcium.

For the purposes of technical gas analysis we therefore possess no practical absorbent for nitrogen, and are obliged, after the removal of all absorbable and combustible gases, to reckon the remainder as nitrogen.

In doing this we neglect a slight error, for recent investigations have shown that the atmosphere contains other elements extraordinarily similar to nitrogen, which, however, occur only in very small quantities. One of them, argon (from the Greek word ἀργός, inert), is found in air in the proportion of 0·94 per cent. by volume. Its specific gravity is 1·38, and it forms 1·19 per cent. of what is usually reckoned as nitrogen. In contact with chemical reagents it is still less active than nitrogen, for even at a red heat it refuses to combine with any one of the elements. As the nitrogen of the atmosphere in mines is derived almost entirely from atmospheric air, we should, strictly speaking, always deduct 1·19 per cent. by volume from the calculated nitrogen, and reckon it as argon. Practically this is quite unnecessary, as the two gases are so similar; consequently, both are always reckoned together as nitrogen.

Just as it cannot support combustion, nitrogen is unable to support respiration. Men and animals die very quickly in an atmosphere of pure nitrogen; but they perish simply from the want of oxygen, and not because nitrogen exerts any poisonous action upon the organism. That nitrogen is not a poison is evident from the fact of such large quantities continually passing through the lungs. The affinity of hæmoglobin for nitrogen is so small that, in spite of the inspired air containing four times as much of this gas as of oxygen, the gas extracted from the blood consists almost solely of oxygen, and the blood contains no more nitrogen than any other liquid which comes closely into contact with air.

### 3. Methane.

After the components of atmospheric air, methane or marsh gas is the most important gas for the miner; it is "mine gas" or "gas" κατ' ἐξοχήν. It is formed when organic substances are decomposed with absence of air and in presence of water, and it appears that vegetable fibre is specially liable to form this gas. It is formed in marshes, and escapes in bubbles when the mud is stirred with a stick. Methane appears in enormous quantities in coal seams, which are the products of processes of decomposition of this kind during the past ages of our globe. It is contained in cavities, especially in cracks and clefts in the enclosing rocks; and when one of these gas reservoirs is cut into, it issues forth with a hissing noise, and is called a "blower." These accumulations of gas are occasionally so enormous that the blower may be utilised as a source of gas for years continuously. The percentage of methane contained in the gas of blowers is very various: occasionally the blower gives off almost pure methane, though the gas is generally mixed with carbonic acid, hydrogen, and nitrogen. The greater proportion of the methane contained in coal seams fills up the pores of the coal and escapes from working faces with a peculiar crackling noise well known to the miner.

The gas pent up in the coal is often under a very considerable amount of pressure. Boreholes in coal have given off gas with a pressure of even 30 atmospheres. The amount of gas in coal varies very considerably. Some idea of the amount will be realised by looking at the quantities extracted from mines every day. Even with a coal poor in gas, the quantity is often 1000 cb.m. (35,000 cubic feet) daily and more; and with coal rich in gas the amount may be 25 times as great, and in a large colliery even 50 times as great. In order to arrive at a proper conception of such an enormous amount of combustible gas, it may be mentioned that the total amount of lighting gas produced daily for the town of Munich is about 45,000 cb.m. (1,600,000 cubic feet).

In the abandoned workings of many mines, the so-called "goaf," the air not infrequently contains a considerable percentage of methane, which in this case arises to a very small extent only from the coal, but is principally due to the decomposition of the old supporting timber.

Methane further appears in large quantities as a product of the decomposition of animal matter. Thus the gas springs of the petroleum districts, such as those which supply the holy fire of Baku, consist principally of methane; and the natural gas of Pennsylvania contains about 80 per cent. of it. In exceptional cases methane is found enclosed in rock-salt, and even in pyrites and zinc blende.

Methane is a completely colourless and inodorous gas. The peculiar smell of the methane prepared artificially, and occasionally of the natural methane, is due to other hydrocarbons mixed with it, or to traces of sulphuretted hydrogen. Methane is considerably lighter than oxygen and nitrogen; its specific gravity is 0·553, and 1 litre under normal conditions weighs 0·715 gramme. It is more easily liquefied than those gases; when cooled below $-82°$ C. and subjected to pressure it may be converted into a colourless liquid, which boils at $-164°$ C. It is only slightly soluble in water; 1 volume of water can dissolve at the ordinary temperature of dwelling-rooms only 0·035 volume of methane.

From a chemical point of view, methane is the simplest representative of the so-called saturated hydrocarbon group, which have the composition represented by the general formula $C_nH_{2n+2}$. It consists of only one atom of carbon, of which each of the four bonds is saturated by an atom of hydrogen. Like all the other members of this series, it has a very slight chemical affinity for other elements and compounds. From this fact all the hydrocarbons formed upon the type of methane are called the "paraffins" (from *parum*, little, and *affinis*, kindred), although the name is commonly applied only to the higher members of the series, which, at ordinary room temperatures, are solid. In consequence of this chemical indifference we possess no absorbent for methane.

Methane does not support combustion, but is itself combustible. In an excess of air it burns with a clear blue flame. If a jet of methane issuing from a pipe is ignited, the lower part of the flame is bluish, and the point yellow. The combustion takes place according to the formula—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

If we express the equation according to volume, we have 1 volume of methane combined with 2 volumes of oxygen forming 1 volume of carbonic acid and 2 volumes of aqueous vapour. 1 volume of methane requires, therefore, for complete combustion 2 volumes of oxygen or, roughly speaking, 10 volumes of air. If the gas has been previously mixed with oxygen or air and then is ignited, the mixture explodes, and the violence of the explosion increases as the proportion of the components in the mixture approaches that which is expressed in the equation. This fact has led to methane being called "fire-damp" by the miner. The explosive mixture of air and methane so dreaded by the miner is known in German as "Schlagende Wetter" or "Schlagwetter." Strictly speaking, these terms should be applied only to the explosive mixture; but, in practice, they mean any mixture of air and methane, and even methane or "fire-damp" itself. If the German miner speaks of so many per cent. of "Schlagwetter" in the air, he means so many per cent. of methane.

Like any other inflammable gas, a mixture of methane and air requires a certain temperature to bring about ignition. The temperature of ignition of methane is about 740° C. (1364° F.). If the flame is cooled below this temperature it goes out. It is upon this principle that the construction of the Davy safety lamp is based. In this lamp the flame of the burner is surrounded by a hood of closely woven wire gauze. When the lamp is brought into an explosive mixture of fire-damp, the gases pass through into the inside of the lamp and take fire at the flame. But the ignition cannot be propagated to the outside, because when the flame comes in contact with the metallic wires, which are good conductors of heat, it is so cooled down that it goes out. If the gases continue to burn inside the lamp, so much heat may be evolved that the wires get red hot, and no longer fulfil their office. The flame may then be driven through, especially in a strong draught, and cause an explosion.

A mixture of fire-damp and air has the maximum explosive force when the methane reaches the proportion of 9·38 per cent. The more the mixture is diluted by an excess of air, the more the explosive action is diminished; and when the proportion of methane drops below 6 per cent. the mixture will no longer explode. The space between two neighbouring molecules of methane has then become so great, owing to the interposition of the molecules of nitrogen and superfluous oxygen, that the heat generated by a burning molecule of methane is absorbed by them, and no longer suffices to ignite the next molecule of methane. Thus the combustion can no longer be propagated from one point through the whole mass. This effect can also be brought about by a diminution of pressure, the influence of which is exactly the same. A mixture of air with 7·5 per cent. of methane, which explodes with violence under atmospheric pressure, cannot be made to explode if the pressure is reduced to 200 mm. (8 inches) of mercury. On the other hand, by increasing the pressure, the lower explosive limit of a mixture of methane and air can be extended considerably. Consequently at a great depth air containing less than 6 per cent. of methane may become explosive.

An excess of methane acts like an excess of air. As the percentage of methane is increased above 9·38, the combustion becomes less and less perfect; and a mixture containing more than 15 per cent. of methane is no longer explosive.

Through continued application of heat from outside—for instance, by contact with red-hot metal or a flame—the methane in a mixture containing a small proportion of this gas is gradually consumed. The flame undergoes characteristic changes which serve as a means of recognising methane. If a flame is burning in air containing methane, there is a certain zone around the flame in which the methane burns, and the greater the percentage of methane and the hotter the flame, the broader this zone becomes. This zone of combustion appears to the eye as a bluish cone of light, the so-called "cap"; and this cap becomes more and more distinct as the illuminating power of the flame decreases. A cap also appears when other combustible gases are present, but as this is very rarely the case in mine air, and as the quantity of such gases, if they do exist in mine air, is extremely small in comparison with that of the methane, it is safe to conclude from the cap that methane is present; and after a little practice it is possible to infer, from the size and form of the cap, the approximate percentage of the methane. It is a lucky coincidence that the miner's inseparable companion, his lamp, calls his attention to his most dangerous enemy, viz. fire-damp.

The various lamps of different constructions do not all indicate the presence of fire-damp equally well. With Wolff's benzine lamp, when the flame is made as small as possible by drawing down the wick, 2 per cent. of methane may be recognised with certainty, and a practised observer will be able to notice a change in the flame with a still smaller percentage. However, below 2 per cent. the indications are not trustworthy. With 5 per cent. the point of the cap reaches the top of the gauze and makes it red hot. If the percentage of methane is increased to 7 per cent., the lamp goes out.

The endeavour to procure a lamp as sensitive to methane as possible, and especially one capable of indicating the presence of the gas even when its percentage is less than 2, has led to the construction of quite a number of so-called indicator lamps, of which the best known is Pieler's alcohol lamp. In the meantime no one of them has come into ordinary use.[1]

Still less success has attended the various fire-damp indicators intended to indicate automatically when the proportion of methane in the air exceeds a certain limit, their action depending either upon the greater speed with which methane diffuses compared with air, or upon its lower specific gravity.

For making quantitative determinations of methane, advantage is taken of its property of burning completely in air, with formation of carbonic acid and aqueous vapour. As the combination takes place according to well-defined volumetric proportions, and 1 volume of methane combines with 2 volumes of oxygen to make 1 volume of carbonic acid and 2 volumes of aqueous vapour, the quantity of methane may be determined either by the diminution in volume after combustion or from the quantity

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[1] This is not strictly correct, for Chesneau's modification of the Pieler lamp is in actual use at every fiery colliery in France. —TRANSLATOR.

of carbonic acid formed, which is equal to the original volume of methane.

In the first case, as the aqueous vapour condenses into water, 3 volumes of the mixture of methane and oxygen give 1 volume of carbonic acid; and the volume of methane originally present is consequently equal to half the diminution of volume which takes place. After the combustion the carbonic acid can be absorbed by means of caustic potash solution. Three volumes in all have then disappeared, and the methane is equal to one-third of the diminution of volume.

The amount of carbonic acid formed can be measured far more exactly than is possible from these differences of volume by a method to be described later on. This more exact method is consequently specially fitted for the determination of smaller quantities of methane.

From a physiological point of view methane is absolutely indifferent, like nitrogen, its action when present in the air being solely that of a diluent of the oxygen. So long as there is enough oxygen to support respiration, very considerable quantities of methane can be supported without difficulty.

Methane is obtained artificially by exposing organic bodies, and especially coal, to the action of strong heat with exclusion of air, or, as the chemist expresses it, by subjecting these substances to dry distillation. Consequently methane, together with hydrogen and carbonic oxide, forms a main constituent of lighting gas, the illuminating power of which depends upon the simultaneous presence of unsaturated hydrocarbons. It is upon this production of methane and other combustible gases that depends the dangerous co-operation of coal dust in fire-damp explosions. That coal dust takes part in fire-damp explosions and increases their force was already recognised in 1844 by Faraday and Lyell. Recent investigations have shown that the presence of coal dust in mixtures of air and fire-damp containing decidedly less than the explosive limit of 6 per cent. will render it explosive, so that even 2 per cent. of methane will become dangerous under these circumstances. It has even been proved that the dust of certain kinds of coal, especially the bituminous coals rich in gas, may be the cause of explosions when methane is completely absent.

An explosion of coal dust and air alone cannot be started by the flame of an open light, but it may be started by a blown-out shot fired with gunpowder, or by an explosion of fire-damp independent of the dust. In this manner it is possible for dust to propagate for long distances a fire-damp explosion which otherwise would remain strictly local, and to increase its violence tenfold.

The chemical action which takes place in these explosions, whether started by a purely dust explosion or a mixed explosion, is this: The heat evolved by a primary gas explosion, or by a blown-out shot, distils the fine particles of dust floating in the air and produces gases. With the adjacent air these form explosive mixtures which ignite at the flame, causing the evolution of more heat, which distils more gas out of the neighbouring particles of coal, and so the explosion is propagated further and further.

Whilst the possibility of a purely dust explosion is bound up with the presence of certain kinds of coal, and whilst, on the other hand, a comparatively high percentage of methane is necessary in order to form an explosive mixture with air, such as in most mines must be regarded as an exception, coal dust and methane co-operate; and it is therefore possible for explosive conditions to arise in almost any colliery, for no colliery is absolutely free from fire-damp, and there is everywhere the opportunity for coal dust to be formed. The recognition of the part played by coal dust in colliery catastrophes has had the effect of teaching that proper attention must be paid even to small percentages of fire-damp.

The chemical examination of the gases of various blowers has led to the supposition that mine gas contains, in addition to methane, higher hydrocarbons, such as ethane ($C_2H_6$), propane ($C_3H_8$), etc.; but up to the present time not one of them has been recognised with certainty. But even if small quantities of one or other of these gases are mixed with the methane, it is of no importance if they are determined as methane. The percentage of methane, in consequence of the higher percentage of carbon in these gases, would of course be a little too high, but this error would be counterbalanced by the fact that the maximum explosive force of mixtures of the higher hydrocarbons with air occurs with a much smaller percentage; for instance, in the case of ethane, with only 5·6 per cent. If, therefore, the percentage is in reality somewhat lower than indicated by the analysis, the error is compensated, as far as the practical inference is concerned, by the correspondingly easier inflammability.

## 4. Carbonic Acid.

Carbonic acid is the chief product of the oxidation of substances containing carbon, and is formed wherever such substances are burnt in an excess of air. But the regular combustion process is not the only source of the gas; it is also produced by imperceptible oxidation, by the process of respiration in animals, and by the decomposition of organic substances. The expired air of a man contains about 4 per cent. of carbonic acid; a grown man produces in twenty-four hours about 1 kilogramme (2·2 lbs.) of it. When we remember that the 1500 million inhabitants of the earth expire yearly about 500 million tons of carbonic acid, that the animal world takes perhaps an equal share in the production of the gas, and that finally the total amount of coal, amounting to 700 million tons yearly, is all burnt to carbonic acid, the weight of which amounts to about 2½ times that of the coal, it might be supposed that the percentage of this gas in our atmosphere must gradually be getting larger and larger. But in spite of the enormously increased consumption of coal in the last decade, no increase in the average percentage of carbonic acid in our atmosphere has been observed; indeed, the actual percentage, 0·03 per cent. by volume, remains extraordinarily constant. The cause of this phenomenon is the same as that which renders the percentage of oxygen constant, namely, the consumption of carbonic acid by plants, which extract the carbon which they require for their growth, and exhale oxygen. But even if this consumption of carbonic acid by the vegetable world did not take place, the yearly increase in the percentage of carbonic acid in the atmosphere would be so imperceptibly small, that it could not be determined by our most delicate analytical methods.

The conditions in a coal-mine are quite different: here there is no consumption of carbonic acid. On the contrary, it is being produced; and this production is so great in proportion to the quantity of air passing through the workings, that the percentage of carbonic acid in the return air is often ten times as much as that of the air entering the mine, and under unfavourable circumstances the proportion may even rise to several per cent. The increase in the percentage of carbonic acid in mine air is but very slightly due to the breathing of the workmen and the burning of the lamps. The greater part of the carbonic acid is given off by the coal, in the pores of which it has been locked up, just like the methane, as a product of the carbonisation of plants; and, as a rule, it is in greater quantity than the methane. In contradistinction to this carbonic acid already contained in the coal, fresh quantities of it are continually being formed by the oxidation of the coal in contact with atmospheric air. Whilst the percentage of methane in the air is very variable, in spite of the amount of work done underground remaining the same, the carbonic acid is given off far more regularly from the coal, and with the normal amount of ventilation its percentage in the air does not undergo great variations. Consequently, regular determinations of the percentage of carbonic acid in the return air form a useful means of checking the work of the ventilating appliances.

As a rule, the amount of carbonic acid in the gas of "blowers" is small; it is only in exceptional cases that they contain a fair percentage of it. Large quantities, however, of carbonic acid are formed by explosions of fire-damp and underground fires, so that after-damp and the gases from fires often contain a very high percentage. In the goaf it arises in considerable quantity from the rotting of mine timber. Accumulations of carbonic acid of this kind collect on the ground, on account of the high specific gravity of the gas, and are therefore sometimes called "heavy air" by the miner.

Carbonic acid is a colourless and inodorous gas, which produces a peculiar pricking sensation in the mucous membrane of the nose, and possesses a slightly acid taste, especially evident when it is dissolved in water. The gas is decidedly more soluble than oxygen, nitrogen, or methane, and especially so in water. At 0° C. water absorbs twice its volume of carbonic acid; at the ordinary temperature of rooms, about its own volume; and at blood temperature, half its volume. On being warmed, the gas dissolved in the water escapes; but it takes prolonged boiling to drive off the whole of it.

From a physical point of view carbonic acid is distinguished by its high specific gravity of 1·520. One litre of the gas at 0° C. and 760 mm. pressure weighs 1·965 grammes. It is liquefied with comparative ease, and at 0° C. a pressure of 36 atmospheres suffices to liquefy it. The critical temperature of carbonic acid is about $+31°$. If liquefied carbonic acid, which is supplied commercially in steel bottles, is allowed to escape freely, it is so much cooled down by the evaporation of a part of it that the remainder solidifies into a snow-like body, which passes directly from the solid into the gaseous state, as the boiling-point of carbonic acid is decidedly lower than the melting-point, viz. $-78°$ C., whilst the latter is $-57°$ C.

As carbonic acid is the final product of combustion, it is neither combustible nor capable of supporting combustion. When mixed in large quantities with air, its effect upon the human organism is not only that produced by lowering the percentage of oxygen, but it is also directly poisonous, and by its partial pressure in the lungs it hinders the giving off of carbonic acid by the blood.

When the percentage of the carbonic acid in air reaches from

3 to 4, a difficulty of breathing sets in: with 6 per cent., palpitation of the heart and headache: with 11 per cent., unconsciousness. Death, however, does not ensue until the person has remained some hours in an atmosphere of this kind. If taken out in time he can be restored to consciousness by breathing fresh air, or, better still, pure oxygen. Unconsciousness brought about by breathing carbonic acid is therefore far less dangerous than that due to deficiency of oxygen, which rapidly becomes fatal. As the carbonic acid, in consequence of its high specific gravity, collects on the ground,[1] a man standing upright may often go on quietly breathing the upper layers of air, which are poor in carbonic acid, whilst smaller animals such as dogs become unconscious, and a light goes out when carried low down.

The chemical properties of the gas are indicated by its character as an acid. Strictly speaking, the so-called carbonic acid is an anhydride, and would be more correctly designated as carbonic anhydride or carbon dioxide, from the unstable hydrate of which the salts called carbonates are formed. These are produced by the action of carbon dioxide upon bases, and especially upon their solutions in water. Carbonic acid combines most readily with the hydroxides of the alkalis and alkaline earths; for instance—

$$2KOH + CO_2 = K_2CO_3 + H_2O.$$
$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

We therefore possess in the aqueous solutions of potassium hydroxide (caustic potash solution) and barium hydroxide (baryta water) excellent absorbents for the gas. Whilst the potassium carbonate formed remains dissolved in the water, the barium carbonate separates out as a white, flocculent precipitate. Even a gas-mixture extremely poor in carbonic acid causes a white cloudiness when shaken up with baryta water. Baryta water is, therefore, not only a good absorbent, but also an excellent qualitative reagent for carbonic acid. Stronger acids decompose the carbonates with evolution of carbon dioxide.

### 5. Carbonic Oxide.

Whilst carbonic acid is the product of complete combustion of carbon, carbonic oxide (or carbon monoxide) is formed by its in-

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[1] It must not be supposed that when once diffused through the atmosphere the carbonic acid drops out; the falling to the floor occurs when the gas is produced, or issues out in a fairly concentrated state. The warm air laden with $CO_2$ from breathing or burning will keep at the *top* of a rise.—TRANSLATOR.

complete combustion. It is nowhere found in nature,[1] but it is produced wherever carbonaceous substances are burnt with an insufficient quantity of air, or when carbonic acid comes in contact with red-hot coal, which takes from it one part of its oxygen. These two processes of formation take place according to the following chemical equations:—

$$2C + O_2 = 2CO.$$

$$CO_2 + C = 2CO.$$

The formation of carbonic oxide in the second way may be observed in every fireplace. The tongues of blue flame on the surface of the red-hot coal are due to burning carbonic oxide; the carbonic acid produced in the excess of air in the lower part of the fireplace is reduced to carbonic oxide as it passes through the upper layer of red-hot coal. It is likewise formed by the dry distillation of coal, and is consequently an integral constituent of illuminating gas, which may contain as much as 10 per cent. of it.

It has never been proved with certainty that carbonic oxide is a normal constituent of mine gas. It is found, however, in the gases from underground fires, as indeed in all smoke, and its percentage increases in proportion as the amount of fresh air supplied to the fire decreases. It also forms a constituent of the after-damp produced by an explosion of fire-damp, when the percentage of methane exceeds 9·5, because then the proportion of air no longer suffices for the complete combustion of the methane. Such explosions are very rare, and in spite of this carbonic oxide is an almost invariable constituent of after-damp, because coal dust has taken part in the explosion. In a case of this kind the carbonic oxide may have arisen either from the dry distillation of particles of coal, in consequence of the heat evolved by the combustion of the gas, or by the incomplete combustion of the distillation products so generated.

Carbonic oxide is a colourless and inodorous gas with a specific gravity of 0·967; 1 litre of it under normal conditions weighs 1·251 grammes. It is much less easily liquefied than carbonic acid. Its critical temperature is about $-139·5°$ C., below which it is converted by pressure into a colourless liquid which boils at $-190°$. If the temperature is lowered to $-207°$, it solidifies into a transparent substance. Carbonic oxide will not support combustion, but itself burns with a pale blue flame to carbonic acid, and with great development of heat.

$$2CO + O_2 = 2CO_2.$$

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[1] *Cf.* pp. 132, 170.

It constitutes a main ingredient of the so-called producer gas, which is formed by the incomplete combustion of coal in a special furnace, the producer.

Two volumes of carbonic oxide require for complete combustion 1 volume of oxygen or 5 volumes of air. Mixed with oxygen or air, it forms explosive mixtures, which can be ignited even by a red-hot wire.

At the ordinary temperature carbonic oxide exhibits few active chemical properties. It combines neither with bases nor with acids, and has but little affinity for other substances. It is absorbed by the solutions of certain salts with formation of unstable compounds. The best absorbent is cuprous chloride, which is employed dissolved either in hydrochloric acid or ammonia. One molecule of cuprous chloride is capable of combining with one molecule of carbonic oxide, as shown by the following equation :—

$$Cu_2Cl_2 + CO = Cu_2Cl_2CO.$$

Carbonic oxide is extremely poisonous. It has an extraordinarily strong affinity for the hæmoglobin of the blood, with which it combines to form carbonic oxide hæmoglobin, which imparts to the blood a striking bright red colour. Blood containing carbonic oxide gives a spectrum with very characteristic absorption bands ; these may be employed as a means of detecting the carbonic oxide if diluted blood saturated with the gas under investigation is tested spectroscopically. As the affinity of carbonic oxide for hæmoglobin is 250 times as great as that of oxygen, the blood becomes saturated very quickly, even if the air contains only a small percentage of carbonic oxide. The blood is then no longer able to take up any more oxygen, and the person dies of suffocation. When an atmosphere contains only about 0·1 per cent., the carbonic oxide and oxygen enter into a state of equilibrium in the blood, and persons suffer from headache and loss of power in the limbs, but do not lose consciousness completely. Even after persons have been a long time in an atmosphere of this kind, they still may be rescued if they are made to breathe fresh air or, better still, pure oxygen, in order to enable the blood to free itself of the gas. If the atmosphere contains a high percentage of carbonic oxide, the blood becomes very quickly saturated with it, and death ensues. The highest allowable limit for carbonic oxide in the air is 0·05 per cent. Unfortunately, at the present time we possess no reliable, practical method of determining such small proportions of the gas, especially when other combustible hydrocarbons, such as methane, are present.[1]

Haldane proposes as a protection against possible poisoning by carbonic oxide, when penetrating into after-damp or gases from underground fires, that a live mouse should be carried in a cage, as it will show symptoms of poisoning much sooner than a man (see pp. 147, 174).

### 6. Hydrogen.

Hydrogen rarely occurs in nature in the free state. The gas is formed by the decomposition of organic matter without access of air; it is also to be found in fairly large quantities, mixed with methane and other hydrocarbons, in the natural gas of petroleum districts. It further occurs included in rock-salt and in the potassium salt carnallite. It is rarely found in coal, but has been identified as a constituent of many blowers.

Large quantities of hydrogen are formed by the dry distillation of coal—nearly one-half of illuminating gas is hydrogen—so the gas may occur in the after-damp of coal-dust explosions.

Hydrogen is specifically the lightest substance upon the earth. It is a colourless and inodorous gas with a specific gravity of 0·069; 1 litre of it under normal conditions weighs only 0·0895 gramme. When ignited in air it burns with a blue flame, producing steam, and develops an extraordinary amount of heat. Mixed with air or oxygen, hydrogen forms a very explosive mixture, the so-called detonating gas, which ignites at a temperature of 550° C., or considerably lower than does a mixture of methane and air. The combination of the hydrogen and oxygen takes place according to the equation—

$$2H_2 + O_2 = 2H_2O;$$

or, expressed in volumes: 2 volumes of hydrogen combine with 1 volume of oxygen and form 2 volumes of aqueous vapour.

As we do not possess any convenient absorbent for hydrogen, it is determined by the combustion method; we measure the contraction in volume which a mixture containing hydrogen undergoes when burnt in an excess of oxygen. As the aqueous vapour condenses into liquid, its volume practically disappears, and therefore, according to the above equation, the volume of the hydrogen will be equal to two-thirds of the contraction which takes place.

The combination of the two gases can be brought about by an electric spark; but as other combustible gases, such as methane,

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[1] See also pp. 115 and 147.

will combine with oxygen, advantage is taken, when determining hydrogen, of the property of certain metals in a finely divided state of bringing about the combination of oxygen and hydrogen at a temperature far below red heat. Palladium is usually employed.

From a physiological point of view hydrogen is completely indifferent, like nitrogen and methane.

### 7. Sulphuretted Hydrogen.

Sulphuretted hydrogen occurs in nature in the free state as a constituent of the gas emitted by many springs, and it is likewise found dissolved in mineral waters. It is formed by the decomposition of organic substances containing sulphur, especially animal and vegetable albumen, for which reason it is found among the gases occurring in coal. Occasionally it is noticed in very small quantity in gases given off by blowers, imparting to them a peculiar smell. It may also occur in coal as a secondary product from the action of carbonic acid upon easily decomposable metallic sulphides.

Sulphuretted hydrogen betrays itself even in very small quantities by its characteristic smell of rotten eggs. The colourless gas has a specific gravity of 1·18, and 1 litre weighs 1·52 grammes. It is unable to support combustion, but burns when ignited in air with a pale blue flame, producing sulphur dioxide and aqueous vapour.

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O.$$

If the supply of air is too small, or if the air is strongly diluted with indifferent gases, only the hydrogen burns, whilst the sulphur separates in a finely divided state.

$$2H_2S + O_2 = 2S + 2H_2O.$$

Sulphuretted hydrogen has a great affinity for the metals, and forms the so-called sulphides. Those of the light metals are easily decomposed, whilst those of the heavy metals are mostly stable in character. If a strip of paper is dipped in a solution of acetate of lead and allowed to dry, it forms an extremely delicate reagent for sulphuretted hydrogen, as the paper becomes brown if even traces of the gas are present, owing to the formation of lead sulphide. Potash solution absorbs sulphuretted hydrogen rapidly, with formation of soluble potassium sulphide.

Sulphuretted hydrogen is a very poisonous gas; if breathed in large quantity, it first of all deadens the sense of smell and then causes unconsciousness, which passes over into death unless the person is quickly brought into fresh air.

If fire-damp contains sulphuretted hydrogen, the after-damp will contain the product of its combustion, sulphur dioxide, easily recognisable by its characteristic pungent smell.

## 8. Aqueous Vapour.

Aqueous vapour is always present in atmospheric air; its quantity is very variable, and is influenced by several factors, especially by the temperature. For each degree of temperature air can take up a certain maximum amount of moisture, the quantity of which can easily be reckoned from the tension of aqueous vapour at the temperature in question.

Let $f$ be the tension of the aqueous vapour at the temperature $t^\circ$, B the height of the barometer, expressed in millimetres of mercury: then

$$\frac{100}{B} f = \text{percentage of aqueous vapour by volume.}$$

For instance, let $t = 8^\circ$ and $B = 760$ mm. In the case of complete saturation the quantity of aqueous vapour is

$$\frac{100 \times 8{\cdot}01}{760} = 1{\cdot}05 \text{ per cent. by volume.}$$

In reality this complete saturation is rarely reached.

The absolute amount of moisture in the air can be most correctly determined by passing a measured volume of air over a suitable absorbent for water, such as dry chloride of calcium contained in a tube which is weighed before and after. The increase in weight gives the amount of water. In practice, it is usual merely to determine by means of the hygrometer the relative amount of moisture, that is to say, the proportion between the amount actually present and the highest possible amount at the temperature in question. If the relative amount of moisture is $x$ per cent., then the actual amount of moisture W is deduced very simply from the equation—

$$W = \frac{xf}{B}.$$

The amount of moisture in the air underground is almost always greater than in the air above ground, and in many collieries very nearly reaches the point of saturation. If the temperature of the workings is high, the percentage of aqueous vapour is often very considerable. At a temperature of 30° C. (86° F.), and with the barometer at 770 mm. (30·3 in.), the moisture, supposing the air to be completely saturated, would amount to

$$\frac{100 \times 31 \cdot 6}{770} = 4 \cdot 10 \text{ per cent.}$$

A handy rule to remember is, that the tension of the aqueous vapour expressed in millimetres of mercury at a given temperature is almost identical with the number of grammes of aqueous vapour which 1 cubic metre of air will contain when completely saturated.

## II. TAKING THE SAMPLES.

The first operation in performing an air analysis is to take a sample. The place in the mine where the sample has to be taken depends, first of all, upon the object in view in the special case under consideration. It must here always be remembered that, in consequence of the very different specific gravities of the gases—methane is only about half as heavy as air and one-third as heavy as carbonic acid—there may be various layers of air at one and the same spot with very different percentages of some given gas, and that air-currents may run along the same air-way for considerable distances without mixing with one another completely. The sample must always be taken underground: taking a sample from pipes at the surface is untrustworthy, because it is scarcely possible to keep them absolutely tight and avoid some admixture of atmospheric air by diffusion. The value of an analysis of mine air will increase in proportion as the composition of the sample approaches the actual average of the air-current passing the place in question within a certain time. It may therefore under certain circumstances appear desirable to spread the taking of the sample over a considerable time, in order to attain this object as far as possible.

Taking the sample is usually a very simple operation. It is performed by filling the vessel intended for the sample with clean water, and then emptying it at the place whence a sample is required. The vessel becomes filled with air and is then carefully closed. It is best if the sample can be taken in the actual vessel intended for measuring it or absorbing it, for then there is no chance of the mixture being in any way altered by the transfer into another vessel. This plan is often adopted if the sample is taken for the purpose of determining the percentage of carbonic acid or methane. For this purpose a strong conical glass flask (fig. 1) is employed; a mark is made round the neck, and the contents up to this mark are determined exactly by weighing it very carefully when full of water. The number denoting the contents is then scratched upon the flask. A flask of this description is filled with water at the surface; it is best to use the condensed water of a steam engine, free from oil. The flask is then closed with a soft india-rubber cork with two holes, each of which is closed by a piece of thick glass rod.

FIG. 1.—Sampling Flask.

The flask prepared in this manner is carried to the place in the mine where the sample is required. The water is then allowed to run out, and the flask is at once closed with the cork, which is pushed in as far as the mark on the neck. It must fit tightly, for, if the sample is taken at a great depth, the pressure inside when the flask is brought to the surface will be considerably greater than the outside pressure, and may drive out the cork.

It is best to subject the sample to the chemical investigation immediately. If this is impossible, the flask should be placed in water with the neck downwards, so as to prevent any diffusion between the gas and the atmosphere in consequence of the cork becoming loose. If the cork is tight, bubbles of gas should escape when the flask is opened under water, in consequence of the excess of pressure inside.

For taking larger samples, if several constituents have to be determined or if the gas has to be sent a long distance, collecting vessels made of sheet zinc are employed, such as Winkler introduced specially for the investigation of mine air. They are used in collieries in Saxony. These receptacles are cylinders with conical ends, each of which terminates in a tube, which is closed either by a soft india-rubber cork, or by a lever and india-rubber washer, such as is common with bottles for beer and aerated waters. The collecting receptacle must be large enough to contain a quantity of gas sufficient to enable each constituent to be determined twice if necessary. Those employed in mines in Saxony contain 10 litres. However, in most cases half this amount of gas is sufficient.

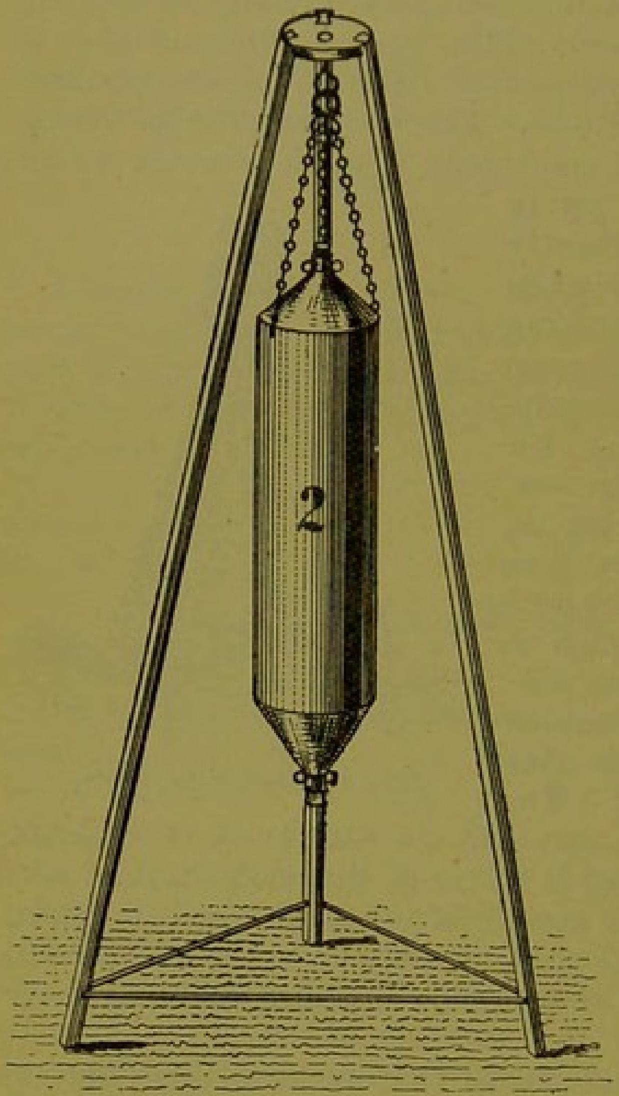

FIG. 2.—Sample Collecting Vessel.

If the operation of taking the sample has to be spread over a long period, the lower cork is removed at the place where the sample has to be taken, and is replaced by a cork with a hole through which is passed a piece of glass tube, which can be closed by a piece of india-rubber tube and a screw clamp. The vessel is then hung up at any suitable spot, the upper cork is removed, and the discharge of the water is regulated by the screw clamp. When all the water has run out, both the original corks are replaced, and are then tied down to the lugs on both sides of the tube to prevent their being blown out on reaching the surface in consequence of the excess of pressure inside.

## III. DETERMINATION OF THE MOST IMPORTANT GASES.

Although, as has been pointed out, the number of gases which may occur in mine air is very considerable, it is only with a few of them that a chemical determination is of practical importance for the working of mines. However interesting, for instance, it may be from a scientific point of view to ascertain whether or no any hydrogen is contained in a blower, this gas occurs so rarely and so sparsely in mine air, and is so difficult to determine quantitatively when occurring in small proportions if accompanied by çombustible gases, that it may be entirely disregarded in the technical analysis of mine air. It would, however, be wrong to consider that a gas may be ignored analytically unless it enters largely into the composition of mine air. A knowledge even of small proportions of certain gases in mine air may be of considerable technical interest, if these gases, for instance carbonic acid and methane, are contained in the air of all collieries.

In a general way the technical analysis of mine air has to be confined to the determination of oxygen, carbonic acid, and methane; under certain circumstances may be added the determination of carbonic oxide and of the floating coal dust. The amount of moisture in mine air is determined by calculation, after its relative humidity has been settled by aid of the hygrometer.

The separate gases are always determined volumetrically, and the quantities are always expressed in percentages by volume and not in percentages by weight, as is elsewhere customary in analytical chemistry. If, however, volumes of gases have to be compared with one another, they must be measured under similar physical conditions, *i.e.* at the same temperature and at the same pressure. Unless this is done, the observed volumes must be reduced by calculation to the same temperature and same pressure. From Gay-Lussac's and Mariotte's [Boyle's] laws, a calculation is made to ascertain the volumes of the gases at 0° C. and 760 mm. of mercury. To use the customary expression, the volumes are reduced to the normal conditions. Further, it is necessary to take care that the gases analysed are saturated with aqueous vapour.

Let B represent the recorded height of the barometer.
$t$ the temperature of the laboratory.
$f$ the tension of aqueous vapour at $t°$.
$v$ the volume of the gas measured at $t°$ and B millimetres of mercury.
$V_0$ the normal volume.
$a$ the coefficient of expansion of gas $= \frac{1}{273}$.

Then

$$V_0 = \frac{v}{1 + at} \times \frac{B - f}{760}.$$

Replacing $a$ by its value $\frac{1}{273}$ we get

$$V_0 = \frac{v \times 273(B-f)}{(273+t)760}.$$

Practically no great error is made if the mean value of B and $t$ are used, that is to say, if one takes for B the average height of the barometer in the place and for $t$ the average temperature of the laboratory, at all events so long as the departure from these average values is not exceptionally large. If these values are inserted in the equation above, and if $v=1$, the value of $V_0$ is the normal volume of 1 c.c. of gas at the average temperature and average pressure. Multiply the measured volume by this factor, and you reduce it to the normal conditions. In addition there are also various tables published for correcting volumes, which enable the calculations to be reduced to a minimum.

Small volumes of gas, up to 100 c.c., are measured in so-called *burettes*; these are graduated glass tubes provided at one end with a glass stop-cock or a pinch-cock, whilst at the other end the gas is shut off by a confining liquid. In technical gas analysis water is invariably used for the purpose. The error which arises in consequence of the solubility of many gases in water is too small, at all events in the case of the gases which come into consideration in mine air, to necessitate the use of mercury, which is much employed in exact gas analysis. Larger volumes of gas are measured in glass flasks of known volume.

The separate gases are determined either by measuring the diminution in volume which a mixture of gases undergoes in contact with a suitable absorbent or when the combustible constituents are burnt; or by employing a known quantity of absorbent and determining by titration what excess remains after the absorption.

Consequently we may distinguish :

A. Gas-volumetric determination.
B. Titration.

## A. Gas-Volumetric Determination.

The volumetric method of determining a single gas in a mixture of different gases consists in measuring off exactly a definite volume of the sample, bringing it into intimate contact with a suitable absorbent medium, and then measuring the volume remaining after the absorption is complete. The difference between the two measurements gives the quantity of gas absorbed. If, as is usual in volumetric analysis, exactly 100 c.c. of the sample are taken, the diminution in volume, expressed in cubic centimetres, gives the percentage by volume of the gas absorbed.

### 1. *Determination of Oxygen.*

The most convenient absorbent for oxygen is yellow phosphorus, which is employed in the form of thin sticks. There is no difficulty in making these out of the ordinary thick sticks of phosphorus, but it is better for the non-chemist to buy them ready made. Dr Th. Schuchardt of Gorlitz supplies them in tin boxes soldered up. These boxes should be opened under water; in fact, all manipulations with phosphorus should be so carried out, and in particular the filling of the absorption vessel, because phosphorus lying in the air, especially if it is rubbed, easily takes fire and causes very painful burns, which are not easily healed. If the necessary precautions are taken, phosphorus may be used in gas analysis without any danger whatever. When exposed to light, the phosphorus, which is originally of a pale yellow colour, becomes reddish yellow and finally red, for it passes over into the red variety, which is indifferent as regards oxygen. Consequently, when the apparatus is out of use the absorption vessel is kept protected from light, either in a cupboard or in a special case. When the temperature is above 16° C. (61° F.) the absorption is finished in at most three minutes, but below that temperature the absorption proceeds so slowly that in winter time it is necessary to keep the apparatus in a warm room, or at all events bring it there some time before it is used. As the acids formed by the absorption, viz. phosphorous and phosphoric acids, are soluble in water, the phosphorus will go on doing its work as long as any remains in the absorption vessel. One charge of phosphorus therefore lasts for many years, even if the apparatus is used frequently. It is only necessary to renew the confining water from time to time, as it gradually becomes saturated with the oxidation products.

As already explained in the first part (p. 7), phosphorus loses its power of absorbing oxygen when certain gases and vapours are present; but in testing mine air this difficulty will rarely arise. The presence of substances which will prevent the reaction may at once be recognised by the absence of any cloudiness when the sample is brought into contact with phosphorus, and by the absence of any glowing of the phosphorus, though this can only be seen in the dark. In a case of this kind pyrogallate of potassium must be used as an absorbent. Ten grammes of pyrogallic acid are dissolved in a minimum quantity of water, and the solution is placed in the absorption vessel, which is then filled with a 25 per cent. potash solution. One charge of this kind will absorb about 2·5 litres of oxygen, though a fresh charge must be put in before this amount has been taken up, because the absorption proceeds so slowly towards the end. As a rule, the absorption does not proceed so rapidly as with phosphorus; but if arrangements are made for bringing the gaseous mixture into close contact with the solution, it is over after the lapse of three minutes.

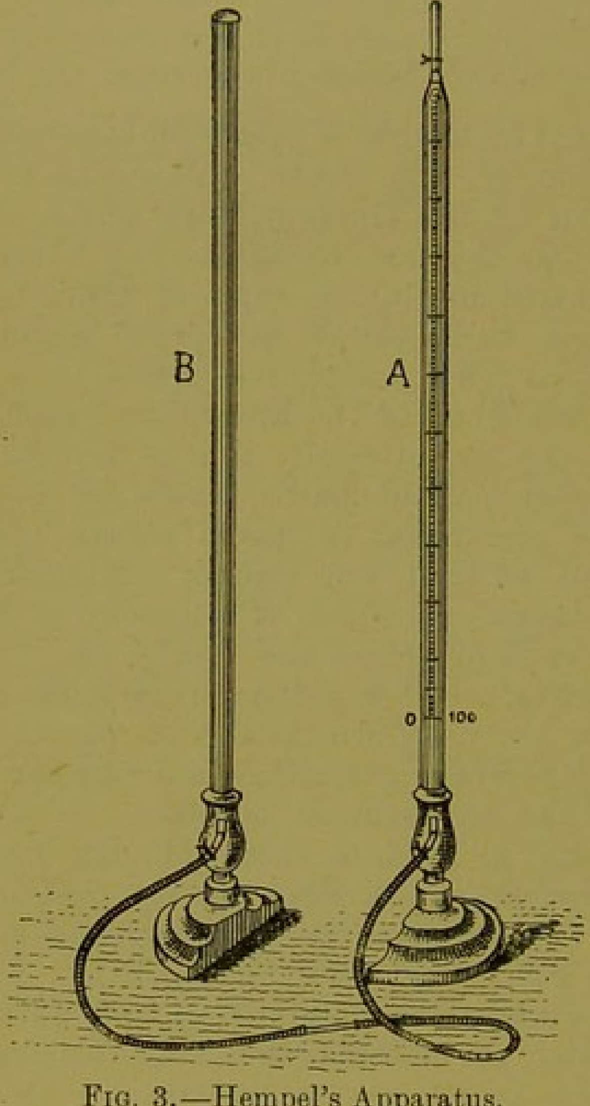

Fig. 3.—Hempel's Apparatus.

The presence of other gases does not affect the absorption; but as the alkali solution absorbs carbonic acid, this must be removed before testing for oxygen.

(*a*) *Determination with Hempel's Apparatus.*—Hempel's gas burette, with the necessary absorption vessels, the so-called gas pipettes, is found to be eminently suited for making volumetric determinations of oxygen. The burette (fig. 3) consists of two glass tubes about 1·5 cm. (·6 inch) in diameter and 65–70 cm. (26 to 28 inches) high; the bottom of each is drawn out small, and bent so that it projects sideways from the wooden or iron pedestal. A piece of india-rubber tube about 60 cm. (2 feet) long is attached to each projecting foot, and when in use the two pieces of india-rubber tube are connected by a piece of glass tube 10 cm. (4 inches) long. The measuring tube A of the burette (fig. 3) ends at the top in a capillary tube, which carries a piece of india-rubber tube about 4 cm. (1·6 inches) long, with a narrow bore. It is tied on by fine wire bound with silk, and is provided with a pinchcock. The tube contains rather more than 100 c.c. and is graduated, each division corresponding to ·2 cubic centimetre. The zero is marked near the pinchcock, and the division 100 about an inch above the pedestal. The measuring tubes are usually graduated also in the reverse direction. The other tube B, the so-called levelling tube, is somewhat taller than the measuring tube, and open at the top. It serves for fixing the volume of the gas and for causing the gas to shift from one vessel to another.

The shape of the absorption vessel, the gas pipette, varies according as it has to be used for a liquid or for a solid absorbent. The simple gas pipette for liquids (fig. 4) consists of two hollow glass bulbs communicating with each other by a tube; the first bulb *a* is rather larger than the other. A U-shaped capillary tube is joined on to the bulb *a*, and at its upper end it carries a piece of thick india-rubber tube with a narrow bore and about 4 cm. (1·6 inches) long; this tube is tied on firmly with wire. When the apparatus is in use it is closed with a pinchcock, and when out of use by a glass stopper. A piece of wide-bore glass tube is joined on to the bulb *b*, and serves for introducing the liquid absorbent. When out of use it is closed by a cork. The whole apparatus is mounted on a stand made of wood or iron, so that the end of the capillary tube projects above the upper edge. I prefer wooden stands, as they are less liable to breakage.

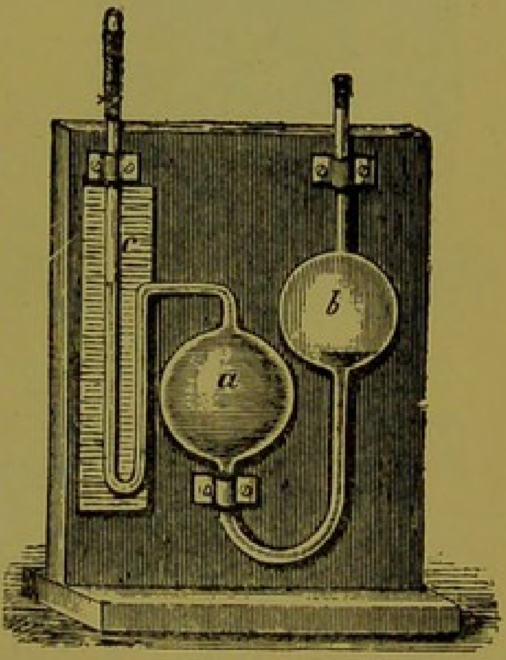

FIG. 4.—Gas Pipette.

The pipette is filled with the absorbent liquid by pouring it into the bulb *b* by the aid of a small glass funnel, and then sucking the india-rubber tube of the capillary tube until the bulb *a* is filled and the thread of liquid stands in the left-hand branch of the capillary tube above the horizontal part. The bulb *b* should then be empty.

The phosphorus pipette (fig. 5) is constructed like the one just described, save that the vessel *a* is cylindrical and provided at the bottom with an aperture which can be closed with an india-rubber cork, and through which the sticks of phosphorus can be introduced. When the vessel has been filled with these under water, a cork is pushed in beyond the point where the connecting tube from *a* is attached. The cork is provided with lateral grooves which allow the passage of the confining water, but prevent any pieces of the phosphorus from passing over with it (in the figure this cork is covered by the metal clamp).

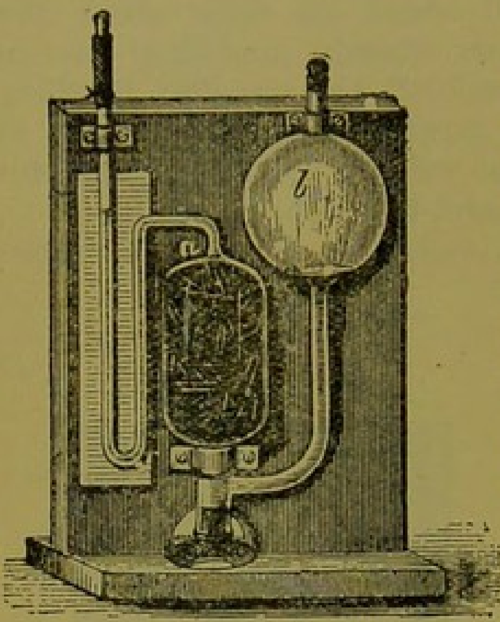

FIG. 5.—Phosphorus Pipette.

If the absorbent liquids used are affected by the oxygen of the atmosphere, as is the case with pyrogallic acid, for instance, the compound pipette (fig. 6) is employed; this is a simple pipette, such as *a*, fig 5, to which a second pair of bulbs *c* and *d* have been added; these serve to hold water as a confining liquid. For the purpose of filling the pipette a glass tube is fixed in at the lowest part of the piece connecting *a* and *b*, and this is closed by a piece of india-rubber tube and a stopper. When the apparatus has to be filled, the stopper is taken out, and into the india-rubber tube is slipped a bent glass tube ending in a funnel. The funnel is lifted high up and the liquid poured through it; from time to time the capillary tube is sucked until the bulb *a* is filled. Then, while squeezing the end of the india-rubber tube with the thumb and forefinger, the filling arrangement is removed and the glass stopper put back. The next thing is to blow down the capillary tube and drive the absorbent almost completely over into *b*; then pour the confining water into *d*, and bring back the absorbent into *a* by sucking as already explained.

*Manipulation of the Hempel Burette.*—The first thing to do is to measure off a definite volume of the sample which has to be tested. If, for instance, the amount of oxygen in our atmosphere has to be determined, the method of procedure is as follows:—

The two india-rubber tubes at the foot of the upright glass tubes (A and B, fig. 3) are connected, and water is poured into the levelling tube until it is more than half full. Then the levelling tube is lifted and the measuring tube is completely filled with water until it escapes from the india-rubber tube at the top;

this is at once closed by the pinchcock. The levelling tube is now placed upon the ground, and by opening the pinchcock rather more than 100 c.c. are sucked in; the pinchcock is then closed, and by raising the levelling tube the contents of the burette are compressed into rather less than 100 c.c., whereupon the connecting tube is squeezed by the thumb and fore-finger of the right hand immediately where it is fixed on. The levelling tube is now lowered, the eye is brought into line with the graduation mark 100, and by carefully slackening the thumb pressure the level of the liquid is brought exactly to the graduation. It is now only necessary to relieve the excess of pressure existing in the tube, which is effected by opening the pinchcock for a moment. Exactly 100 c.c. at atmospheric pressure are now shut in; this may be proved by bringing the level of the liquid in the two tubes to the same point. The level of the liquid in the measuring tube should now stand exactly at the graduation mark 100. Before setting the burette and reading off, a couple of minutes should always be allowed to elapse, in order to give the water time to run down properly. For reading off the volume of a gas or of a liquid, the lower concave line of demarcation of the spherical section forming the surface of the liquid in the measuring tube, the so-called meniscus, should be chosen, and not the upper horizontal line. If, for instance, the level of the liquid has to be brought to the graduation mark 0, the line must be a tangent to the spherical section (fig. 7).

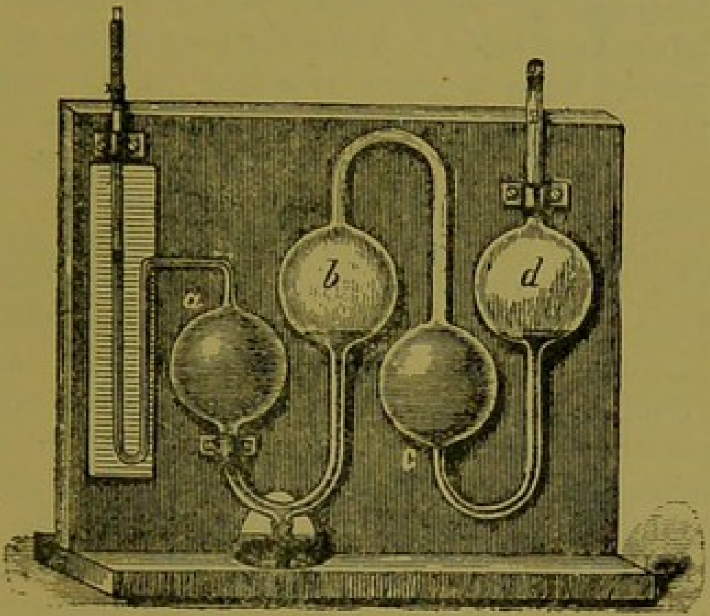

Fig. 6.—Compound Pipette.

If the burette has to be filled with a gas from a sample in a collecting cylinder, the latter must first be prepared for the purpose. The plain corks are exchanged under water for india-rubber corks each bored and provided with a piece of glass tube bent at a right angle and carrying a piece of india-rubber tubing and a screw pinchcock. On first opening the cylinder under water, gas escapes in consequence of its excess of pressure. If there is an excess of pressure, this is a proof that the cylinder was tightly closed. If no gas escapes, the sample should be discarded as untrustworthy. After having been thus prepared, the collecting cylinder is hung on to the stand, fig. 8, and the pipe of the lower neck is connected by a long piece of india-rubber tube to a reservoir of water, fixed about 1 metre above the laboratory table. A similar long piece of thin india-rubber tube is then attached to the upper neck of the cylinder. The lower pinchcock is now opened completely, the pressure water runs in, and if the pinchcock is open the sample escapes. A little gas is allowed to escape, in order to drive the air out of the tube, and this is now connected by a piece of bent tube with the capillary tube of the measuring burette, which is full of water. The levelling tube is now placed on the ground, and on opening the pinchcock the gas flows into the burette. It is measured off in the manner already explained.

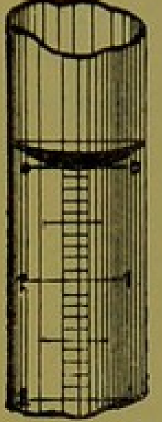

FIG. 7.
Meniscus.

In order to determine the amount of oxygen in the sample, the gas pipette is placed upon a little wooden stand just high enough to bring the end of the capillary tube of the burette on a level with that of the pipette, the pinchcock is put upon the india-rubber tube, and then the glass stopper which closes it is removed, and likewise the cork. The operator first satisfies himself that the thread of liquid in the pipette has been properly set, and then connects the measuring tube and the absorption vessel by a piece of ⊓-shaped glass capillary tube. The pinchcock of the burette is then placed upon the glass connecting tube, the levelling tube is lifted high with the left hand, and with the right the pinchcock of the pipette is opened, allowing the gas to pass over into it (fig. 9). When the measuring tube is filled with water right up to the capillary, both pinchcocks are closed, the connecting capillary tube is removed, and by gentle shaking the gas is brought into close contact with the absorbent.[1] As soon as the absorption is complete, which is usually the case after two

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[1] When phosphorus is used as the absorbent, this is not necessary; the burette and the pipette can be left connected with each other.

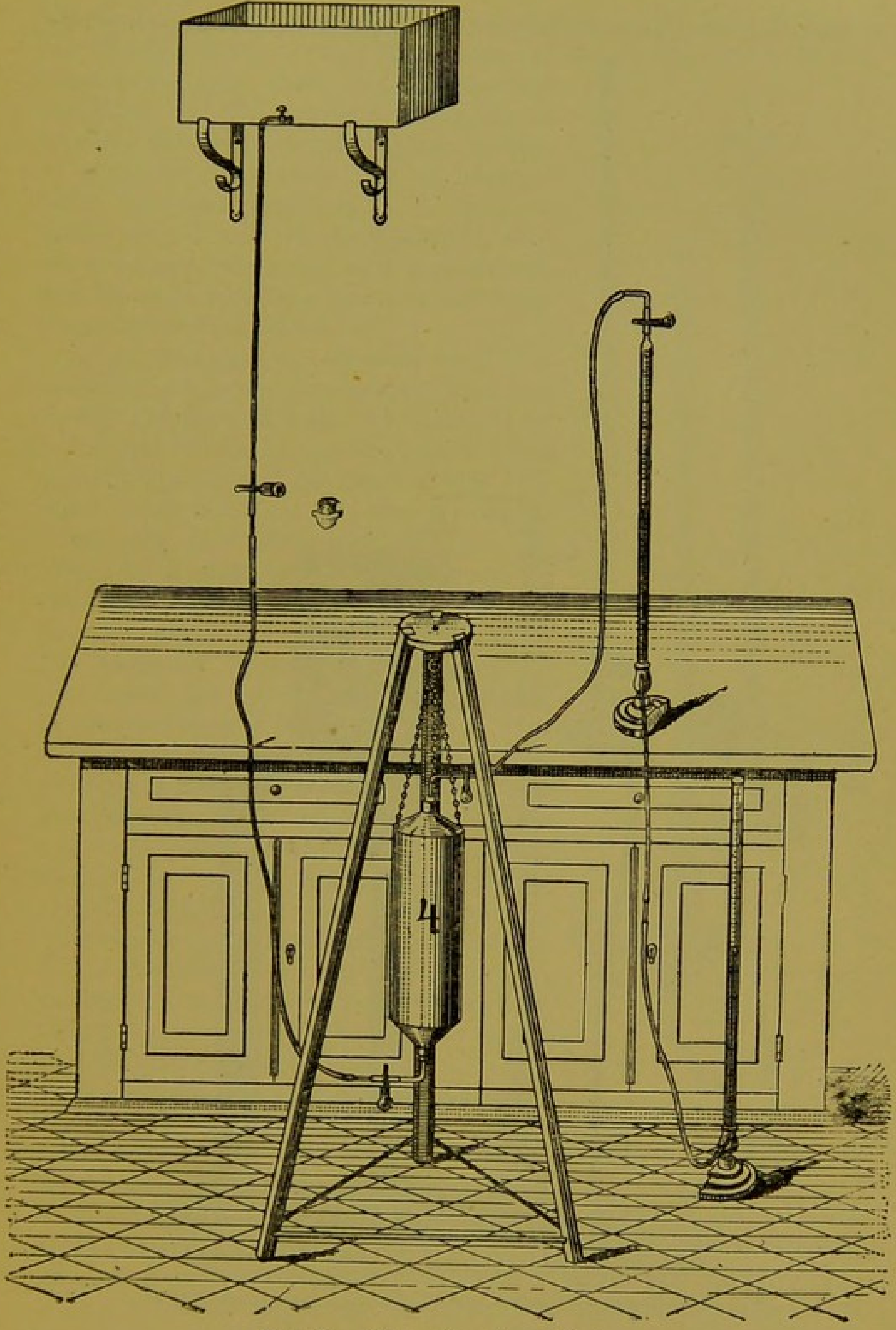

FIG. 8.—Filling Burette with Gas.

or three minutes, the two parts of the apparatus are re-connected by

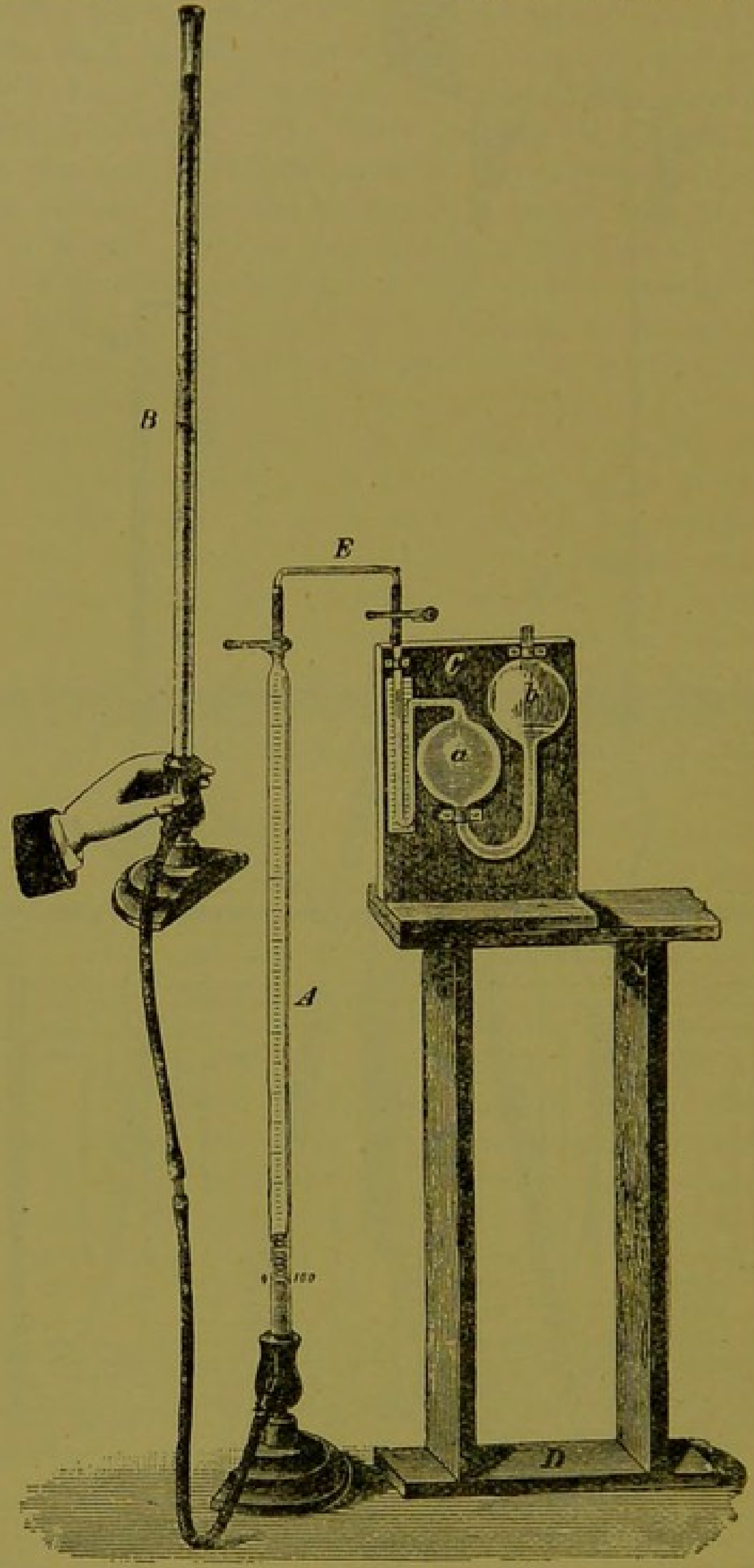

Fig. 9.—Method of transferring Gas to Absorption Pipette.

the capillary tube, the levelling tube is placed on the ground, and by opening both pinchcocks the unabsorbed gas is brought back into the measuring tube. Care must be taken that none of the absorbent gets into the connecting capillary. If this happens with alkaline liquids, the ends of the tubes become so slippery that they will no longer hold the glass capillary. A drop of dilute acetic acid or hydrochloric acid must be put into them with a glass rod, and the capillary tube must be carefully washed out with water.

After waiting two minutes until the confining water in the burette has run down, the tops of both the columns of liquid are brought to the same level and the quantity of gas read off (fig. 10). After use, one end of the pipette is closed by the glass stopper and the other by a cork, and the pinchcock is removed. If things are done in the reverse order, the thread of liquid in the capillary becomes shifted out of place, and the next time the apparatus is used this has to be put right.

(*b*) *Determination with the Lindemann-Winkler Apparatus.*—When nothing but the percentage of oxygen in mine air has to be determined, without troubling about the other ingredients, Lindemann's apparatus as improved by Winkler may be used with advantage. The apparatus is shown in fig. 11; it enables the analysis to be performed on the spot, and therefore no sample has to be taken and carried about.

The principal parts of the apparatus are the measuring tube A, the absorption vessel B, and the levelling bottle C. The measuring tube has a spherical bulb at the top, and from the tap to the zero mark contains 100 c.c. The lower cylindrical part is divided into ·1 c.c., but the graduation does not go any further than 25 c.c. The lower part of the measuring tube is connected with the levelling bottle C by a piece of india-rubber tube, whilst the

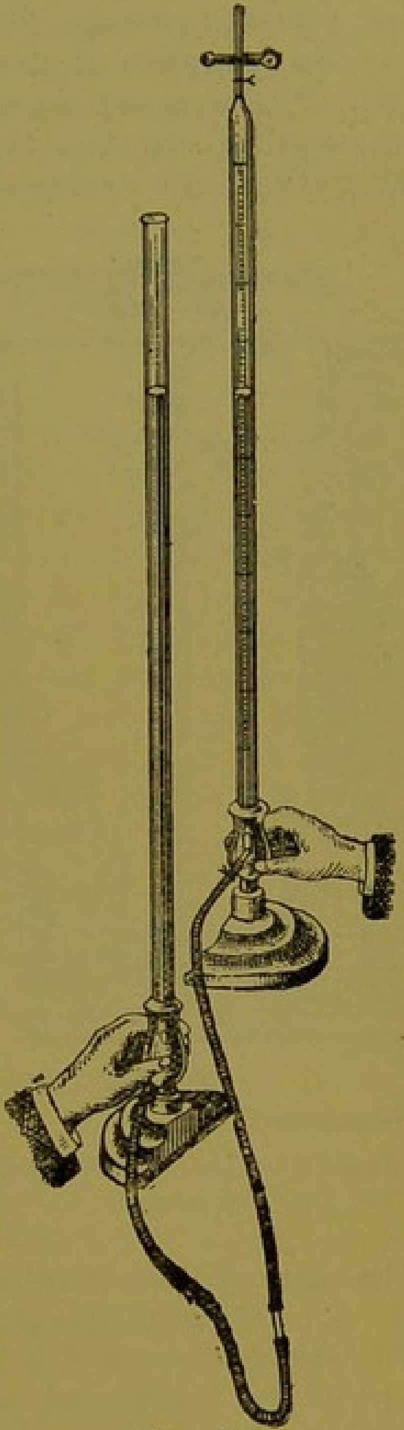

FIG. 10.

upper end is shut off by a three-way tap from the ⊓-shaped piece of capillary tube which leads to the absorption vessel. This tap, in addition to the ordinary straight hole through it, has a curved passage which leads from the end of the barrel of the tap to a piece of glass tube fused on to it. In the position A (fig. 12) the measuring tube and the capillary tube are connected; on turning the tap through 90° (fig. 13) the interior of the measuring tube communicates with the surrounding atmosphere.

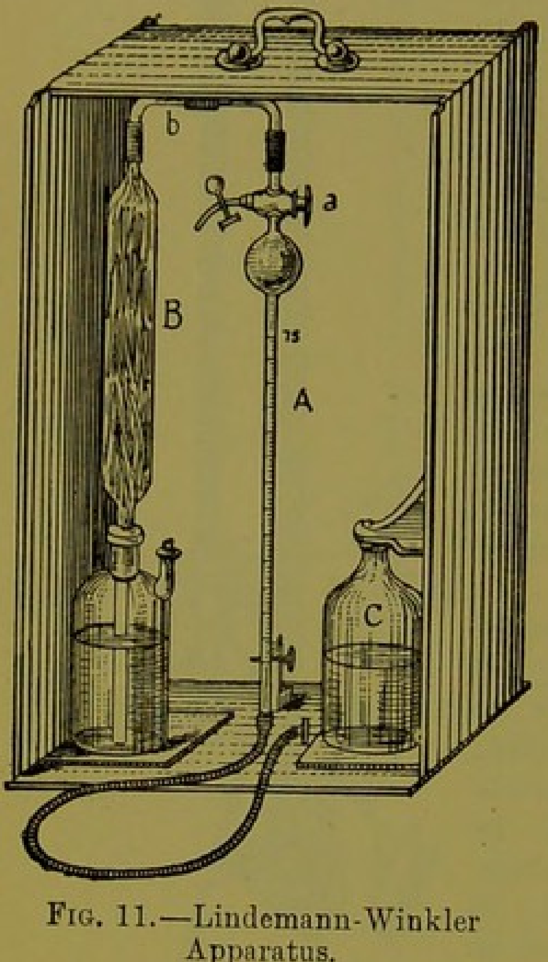

FIG. 11.—Lindemann-Winkler Apparatus.

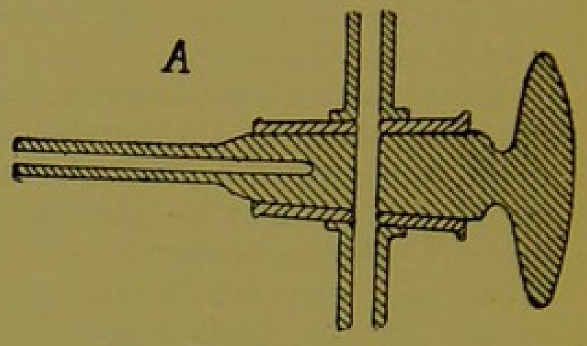

FIG. 12.—Tap.

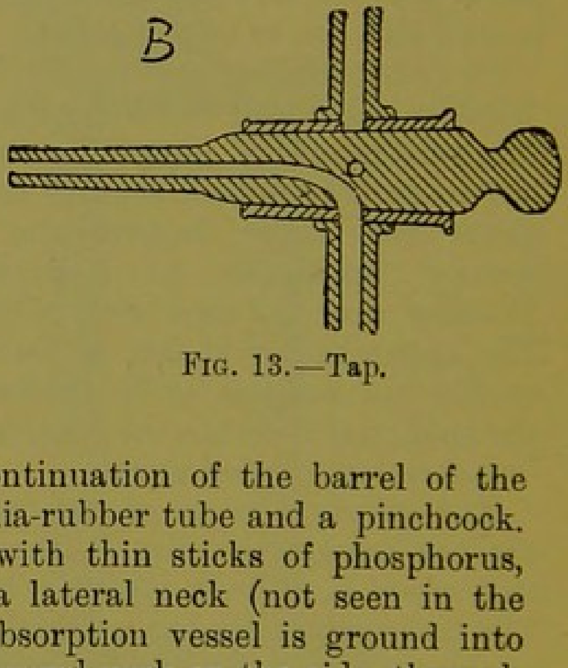

FIG. 13.—Tap.

The piece of tube forming the continuation of the barrel of the tap is provided with a piece of india-rubber tube and a pinchcock. The absorption vessel B is filled with thin sticks of phosphorus, which are introduced through a lateral neck (not seen in the figure). The lower end of the absorption vessel is ground into the neck of a bottle which has a second neck on the side, through which the confining water is introduced. The whole apparatus is contained in a light portable case; when not in use, or when being carried about, the case is closed with two wooden sliding doors. A small wooden flap with a hinge and spring keeps the levelling bottle in position when the apparatus is being moved about.

In order to prepare the apparatus for use, the measuring tube is first filled with water by raising the levelling bottle, the tap being in the position B and the pinchcock open. The tap is then turned round 90°, and by lowering the levelling bottle the water in the absorption vessel rises up to a mark made in the capillary connecting piece. The tap is then turned into the position B, and the measuring tube is filled with water until it runs out at the india-rubber tube; this is then closed with the pinchcock.

The apparatus so prepared is taken to the place in the mine where the oxygen has to be determined. By opening the pinchcock and lowering the levelling bottle, a sample of the air is drawn in. A little more than 100 c.c. is allowed to enter; the sample is then compressed into rather less than 100 by raising the levelling bottle. While the india-rubber tube immediately below the measuring tube is firmly held between the thumb and forefinger, the levelling bottle is lowered, and by carefully relaxing the pressure the level of the liquid is brought to the zero. A momentary opening of the pinchcock suffices to release the excess of pressure, and now exactly 100 c.c. of gas are shut off in the measuring tube. As a check, the level of the water in the levelling bottle may be compared with that in the measuring tube; the level of both should agree exactly with the zero mark.

In order to absorb the oxygen, the three-way cock is turned into the position A, the levelling bottle is raised, and the gas passes over into the absorption vessel, where it should be left for three minutes. It is then sucked back into the measuring tube by lowering the levelling bottle, care being taken that the confining water of the absorption vessel shall rise exactly to the mark on the capillary; the tap is then turned 90°, and the levelling bottle is held so that the water in it and in the measuring tube is at the same level, and the quantity of gas is read off. When the analysis is finished in this manner, the pinchcock is opened and the levelling bottle raised; the gas is driven out, and the apparatus is ready for the next determination.

### 2. *Determination of Carbonic Acid.*

The absorbent employed for carbonic acid in volumetric analysis is potash solution. A solution of suitable strength is obtained by dissolving in 1 litre of water 250 grammes of pure caustic potash. 1 c.c. of this solution will absorb about 40 c.c. of carbonic acid. If the solution becomes cloudy from the formation of a precipitate, it is allowed to clarify by leaving it for some time in a covered stoneware pot and then pouring it off carefully. It is kept in a bottle closed with an ordinary or india-rubber cork ; glass stoppers, if moistened with potash solution, are apt to stick very tightly, especially if the bottle is rarely opened, and are then difficult to get out.

(*a*) *Determination with Hempel's Apparatus.*—As the limit of exactness with Hempel's apparatus is only 0·2 per cent., this apparatus is not suitable for determining carbonic acid in mine air, unless comparatively large proportions of this gas are present.

The determination is made exactly in the same manner as an oxygen test. The absorption vessel employed is a simple gas pipette (fig. 4), which is charged with potash solution of the strength just mentioned. If the intimate contact of the gas with the liquid is brought about by gentle (not violent) shaking, the absorption is complete in less than one minute. However, it is advisable, in the case of unpractised observers, to send over the gas into the pipette a second time, in order to make sure that the absorption has been complete.

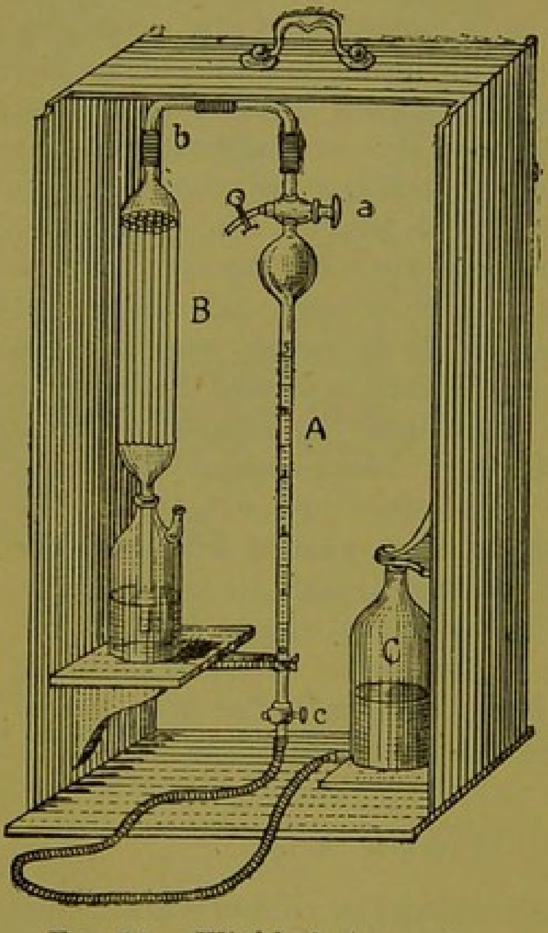

Fig. 14.—Winkler's Apparatus.

If oxygen and carbonic acid have to be determined from the same sample, the carbonic acid is first absorbed by potash solution, and then the oxygen by phosphorus or pyrogallic acid.

(*b*) *Determination with Winkler's Apparatus.* — The construction of the apparatus (fig. 14) is exactly like that of the Lindemann-Winkler instrument, and, *mutatis mutandis*, what has been said about using the latter applies in the case of the former. It is suitable for determining carbonic acid in mine air poor in fire-damp, but rich in carbonic acid, where no fire-damp determination need be carried out in addition to the carbonic acid determination. It may. therefore be used with advantage where brown coal is mined. The limit of exactness which may be attained is about 0·1 per cent.

The measuring tube A is enlarged at the top into a bulb, and the lower cylindrical part is so narrow that it contains only about 5 c.c. It is graduated into ·1 c.c. The upper end is closed with a three-way cock, and the lower end with an ordinary cock, so as to ensure more accurate setting, and it contains rather over 100 c.c. The absorption vessel B receives a charge of potash solution, which is poured in through the lateral neck of the bottle. In order to increase the amount of surface wetted by the absorbent, B is filled with glass tubes.

The apparatus is arranged and the sample drawn as described on p. 41. The setting at zero, however, is effected, not by squeezing the india-rubber tube, but by carefully opening and shutting the glass cock *c*. When the excess of pressure has been relieved by opening the pinchcock, the cock *c* is opened, and the three-way cock *a* is turned so that the measuring tube communicates with the absorption vessel; the levelling bottle is then lifted and the gas driven over. The absorption may be hastened by lifting the levelling bottle up and down, and so making the gas travel forwards and backwards, without altering the position of *a*. When this has been done several times, the gas is brought back into the measuring tube, *a* is turned through 90°, and *c* is closed, after the liquid has been brought to the same level in A and C. The reading is now made.

### 3. *Determination of Carbonic Oxide.*

Simple methods of determining small percentages of carbonic oxide have, unfortunately, yet to be discovered, and it is rarely that largish proportions of this gas have to be determined in mine air. However, the case arises in testing after-damp, or the gases produced by underground fires.

The absorbent employed is an ammoniacal solution of cuprous chloride, which Winkler prepares as follows: 250 grammes of ammonium chloride are dissolved in 750 c.c. of water; the solution is put into a bottle; 200 grammes of cuprous chloride are added, and the bottle closed with an india-rubber stopper. By frequent shaking, this dissolves almost completely, giving a brownish solution which keeps good for any length of time in a closed vessel, provided a piece of copper wire twisted into a spiral is placed in the bottle and made to reach from the bottom to the top. Before use, a third of its volume of concentrated ammonia solution must be added to the liquid. In determining carbonic oxide Hempel's apparatus is employed. As the ammoniacal solution becomes oxidised by the oxygen of the atmosphere, it is placed in a compound pipette (fig. 6). In charging the pipette, 50 c.c. of concentrated ammonia solution are first introduced into the bulb by the aid of a funnel and india-rubber tube, and then 150 c.c. of the cuprous chloride solution are added. 1 c.c. of this ammoniacal solution is capable of absorbing 16 c.c. of carbonic oxide. As the solution after frequent use absorbs very slowly, it is advisable to recharge the pipette pretty often; this is possible without any great waste of material, as determinations of carbonic oxide at mines will rarely have to be made.

As the ammoniacal cuprous chloride solution also absorbs oxygen and carbonic acid, these two gases must be removed before testing for carbonic oxide. If there is a suspicion that a sample of mine air contains carbonic oxide, the carbonic acid is first determined by potash solution, then the oxygen by absorption with phosphorus or pyrogallic acid, and finally the carbonic oxide by ammoniacal cuprous chloride.

## B. Titration.

Chemical reactions invariably take place according to definite unalterable proportions by weight. A definite quantity of a gas, on being absorbed by a suitable substance with formation of a chemical compound, requires therefore during the absorption a certain definite quantity of the absorbent, which can be calculated from the combining proportions. And, *vice versâ*, a given quantity of the absorbent is capable of absorbing a definite quantity of the gas under consideration. If, therefore, a known quantity of the absorbent is brought into contact with a gaseous mixture containing the absorbable gas, and if, after the absorption is complete, the quantity of absorbent remaining unaltered is ascertained, it is possible to calculate from the amount consumed how much gas has been absorbed. Upon this principle are based some of our most exact methods of gas analysis.

With the object of substituting an easy measuring operation for that of weighing out the absorbent, which takes time and trouble, solutions of definite strength are employed for absorptive purposes, and these are usually so made that 1 c.c. is capable of absorbing exactly 1 c.c. of the gas in question under normal conditions, *i.e.* at 760 mm. of mercury and 0° C., and dry. Solutions of this kind are designated as gas-normal solutions. The quantity of substance to be dissolved in 1 litre of water is determined from the weight of a litre of the gas and the combining proportions. The excess of the absorbent is also determined volumetrically by titration, that is to say, by adding from a measuring vessel a solution of some other substance, which will enter into chemical combination with the absorbent, until a change of colour of the solution, due to the addition of a so-called indicator, denotes the end of the reaction. This solution is also made of such a strength that 1 c.c. of it corresponds to 1 c.c. of the normal absorbent solution, and consequently to 1 c.c. of the gas. It is then only necessary to subtract from the volume of the normal absorbent solution the volume used in titrating back in order to ascertain the number of cubic centimetres which were required for the absorption, and consequently the number of cubic centimetres of the gas present in the sample under investigation.

In the analysis of mine air the titration method is especially employed for determining the carbonic acid. This method possesses the advantage over the gas-volumetric method that far larger volumes can be employed for testing, and that the carbonic acid can be determined with far greater exactness. It is especially employed when very exact determinations of carbonic acid are required.

As methane when burnt with an excess of oxygen produces an equal volume of carbonic acid, the titration of the carbonic acid renders it possible to determine in the same way methane, the most important of all mine gases.

### 1. *Determination of Carbonic Acid.*

The absorbent employed is a gas-normal solution of barium hydroxide, the so-called baryta water, which absorbs carbonic acid very greedily, with formation of an insoluble, white, flocculent precipitate of barium carbonate. The quantity of barium hydroxide required for making a gas-normal solution may be calculated from the chemical equation

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

Replacing the chemical symbols by their molecular weights, we have—

$$\begin{aligned}171 \text{ parts } Ba(OH)_2 + 44 \text{ parts } CO_2 \\ = 197 \text{ parts } BaCO_3 + 18 \text{ parts } H_2O.\end{aligned}$$

1 litre of carbonic acid under normal conditions weighs 1·965

grms. The quantity of barium hydroxide is calculated from the equation

$$44 : 171 = 1{\cdot}965 : x.$$
$$x = 7{\cdot}637 \text{ grms. } Ba(OH)_2.$$

Commercial crystallised barium hydroxide contains 8 molecules of water in addition, consequently

$$7{\cdot}637 \text{ grms. } Ba(OH)_2 = 14{\cdot}009 \text{ grms. } Ba(OH)_2 + 8H_2O.$$

If crystallised barium hydroxide were obtainable in the pure state, and remained constant in quality, it would only be necessary to weigh out this quantity with the greatest accuracy and dissolve it in a litre of water in order to obtain a gas normal solution. But as barium hydroxide always contains considerable quantities of insoluble barium carbonate, and as it will not keep unaltered when in solution, we content ourselves with a solution of approximately gas-normal strength, and each time before using it determine its standard, *i.e.* its strength as regards carbonic acid. 15 grammes of commercial barium hydroxide (the excess corresponds approximately to the average degree of impurity of the substance) are weighed out, put into a stoppered bottle, and 1 litre of distilled water is added. By frequent shaking the crystals gradually dissolve, and a fine flocculent precipitate of barium carbonate is left. The solution is allowed to stand, and as soon as the precipitate has completely settled the clear solution is carefully decanted into the stock bottle.

If a definite volume of baryta water were taken out of this bottle for each analysis by the aid of a suction pipette, the solution would speedily become turbid by attracting carbonic acid from the atmosphere, and gradually lose its strength. We therefore employ an arrangement which enables any desired quantity of baryta water to be drawn from the stock bottle, and to be measured off without the contents being affected by the carbonic acid of the atmosphere. It consists (fig. 15) of a measuring burette A containing 50 c.c., divided into ·1 c.c., and drawn out to a point at the bottom. This end is connected by a piece of india-rubber tube with a ⊣ shaped tube, and this with a piece of tube 10 cm. long drawn out to a fine point. Between it and the ⊣ piece is the pinchcock *a*. Placed on a bracket against the wall is a stock bottle B, closed by a cork with three holes in it. Through one of the holes is put a piece of glass tube bent into siphon shape and passing down to the bottom of the bottle, whilst the other end is connected by a piece of india-rubber tube with the ⊣ piece of the burette, in front of which is a second pinchcock *b*. Through the second hole is likewise passed a bent tube, one limb of which is cut off close to the bend, whilst the other is connected by a piece of india-rubber tube with the top of the burette. The third hole carries an absorption tube *e* charged with soda-lime.

The siphon *c* is filled with the solution by blowing into *e* with the pinchcocks open. If *b* is opened whilst *a* is shut, the burette becomes filled with the solution. If *b* is now shut and *a* opened, the solution flows out of the discharge nozzle as a fine stream, and the air flowing in through *e* is freed from carbonic acid by the soda-lime. Before use, care must be taken to get rid of any air-bubbles in the discharge nozzle and the india-rubber tube. This is easily done by opening and shutting *a* for a moment, or by pressing upon the india-rubber tube. When a definite volume of solution has to be measured off, the level of the top must be first set at the zero near the top of the burette. The setting and reading off are done precisely as with the gas burette (fig. 7). The reading can be made still more sharply by employing a so-called float, that is to say, a hollow glass cylinder weighted with mercury, which floats in the solution and has a line marked round it. In setting the burette at any particular point, this is made to coincide with the corresponding graduation.

When the burette is out of use the discharge nozzle is covered

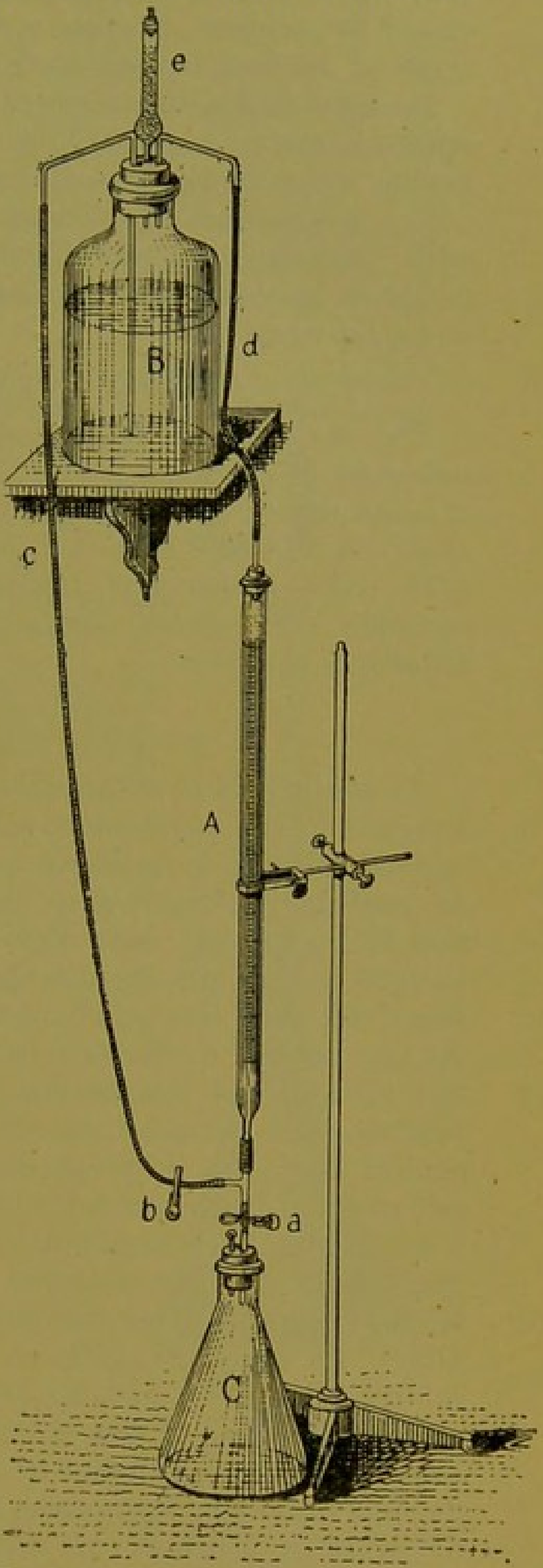

FIG. 15.—Apparatus for Determination of Carbonic Acid.

over by a piece of india-rubber tube, the open end of which is closed by a piece of glass rod. If this precaution is omitted, a crust of barium carbonate forms on the end.

In order to fix the standard of the baryta water, which is only approximately gas-normal, as well as for measuring the excess of baryta water remaining after absorption of the carbonic acid, we use a gas-normal solution of oxalic acid. This acid combines with barium hydroxide in the same way as carbonic acid, and forms an insoluble salt, barium oxalate, according to the following chemical equation:—

$$Ba(OH)_2 + C_2O_4H_2 = C_2O_4Ba + 2H_2O.$$

One molecule of oxalic acid is therefore equivalent to one molecule of carbonic acid. As crystallised oxalic acid contains 2 molecules of water, 44 parts by weight of carbonic acid correspond to $90 + (2 \times 18) = 126$ parts by weight of crystallised oxalic acid. The quantity of oxalic acid corresponding to 1 litre of carbonic acid under normal conditions is calculated from the following equation:—

$$44 : 126 = 1{\cdot}965 : n.$$
$$n = 5{\cdot}628 \text{ grms. } C_2O_4H_2 + 2H_2O.$$

As oxalic acid is obtainable chemically pure, and as it can be weighed in the atmosphere without suffering any change, the gas-normal solution is made by weighing out 5·628 grms. as carefully as possible, putting it into a measuring flask containing 1 litre, and filling this up with distilled water to the mark. The glass stopper is then put in, the whole shaken up until the crystals are dissolved, and the solution then put into a stoppered bottle. As the normal oxalic acid solution is employed for determining the standard of the baryta water, and so forms as it were the fundamental measure for the carbonic acid, the greatest care should be taken in preparing it. If crystals of oxalic acid are left exposed to the air for some time they lose a little water by "weathering." They must therefore be kept in a well-closed glass bottle. The solution also undergoes gradually a very slight decomposition, especially under the action of light, and alters its standard. It is therefore advisable to make only 1 litre at a time, and to keep it in the dark.

The standard of the baryta water is determined by allowing exactly 10 c.c. to run out of the burette (fig. 15) into a conical flask, a so-called Erlenmayer flask, and then adding two or three drops of a solution of phenolphthalein, which serves as an indicator. This is an organic substance which has the property of colouring caustic alkalis violet red, whilst acid solutions are colourless. To the reddish solution oxalic acid is added gradually from a burette with a glass tap, as shown in fig. 16, whilst the flask is continually but gently agitated until the red colour disappears. In order to show the change of colour with the greatest sharpness, a sheet of white paper is placed under the flask. The number of cubic centimetres of normal oxalic acid solution are now read off, and the standard is obtained by dividing by 10. If, for instance, 10 c.c. of baryta water required 9·6 c.c. of normal oxalic acid, 1 c.c. of baryta water = 0·96 c.c. of oxalic acid = 0·96 c.c. of carbonic acid.

Although the baryta water in the stock bottle is protected against the entrance of atmospheric carbonic acid, it is necessary, unless carbonic acid determinations follow each other immediately, to check the standard each time, which after all requires only a few minutes.

The titration of carbonic acid is performed with Hesse's apparatus (fig. 16). It consists of a strong conical flask, the contents of which, up to a ring-like mark round the neck, are determined once for all by weighing the flask full of water. The number of cubic centimetres the flask contains is scratched upon the glass. The flask is at the same time the measuring and the absorption vessel. It is filled with water and corked with an india-rubber cork with two holes in it, each of which is closed by a glass stopper (see fig. 1). The sample of air is taken in the manner already explained. The absorbent is introduced by pulling out one of the glass stoppers and introducing the nozzle of the burette until it projects through the cork (fig. 15). A definite volume of baryta water is now allowed to run into the flask, care being taken that it does not run down the sides.

The quantity of baryta water run in, which in every case must be considerably in excess, depends upon the volume of gas being tested, that is to say, upon the size of the flask, and the percentage of carbonic acid expected. If the flask contains less than 1 litre, and if the probable percentage is under 1 per cent. by volume, 20 c.c. are amply sufficient. Opening the other glass stopper while the baryta water is being run in is, as a rule, unnecessary. The burette is removed and the hole re-closed with

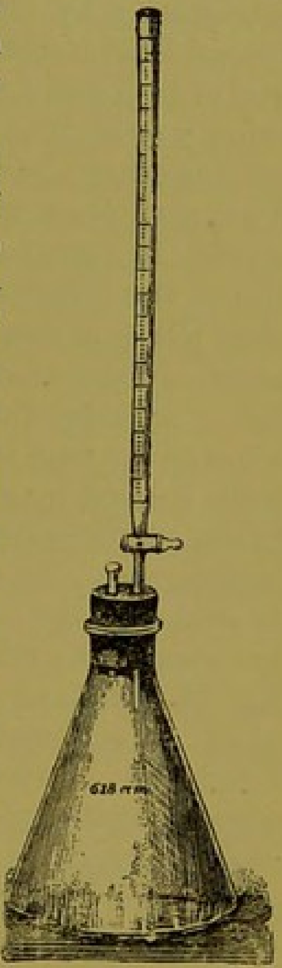

FIG. 16.—Hesse's Apparatus.

a glass stopper. A quantity of gas equal in volume to the baryta water employed escapes from the flask, and this must be deducted from the quantity of the sample. The flask is gently but frequently shaken, so as to bring the gas into contact with the baryta water, until it is certain that all the carbonic acid has been absorbed. The interval is utilised for determining or checking the standard of the baryta water in the manner described. After about ten minutes' interval the amount of baryta water remaining unused is determined with gas-normal oxalic acid. The burette with the glass tap is filled with oxalic acid, and the top of the liquid brought to zero. One of the stoppers of the absorption flask is drawn out, and two or three drops of phenolphthalein are introduced by the aid of a small glass tube, so as to tinge the turbid liquid distinctly red. If it were to remain colourless, this would be a proof that all the baryta water had been used up, or in other words, that too little had been employed originally. In this case another charge of baryta water would be added equal to the first, and then after complete absorption the unused remainder would be measured. For this purpose the nozzle of the glass tap of the burette is passed through one of holes in the cork, so that the acid can run in freely (fig. 15), and by turning the tap carefully the oxalic acid is allowed to drop in whilst the flask is being gently, but constantly, agitated. If the oxalic acid is allowed to run in too quickly, the barium carbonate which has been formed may be attacked by the oxalic acid as well as the barium hydroxide, and the determination will therefore be rendered inaccurate. As soon as the red colour has disappeared, the tap is shut and the amount of acid employed read off. The difference between this and the volume of baryta water employed multiplied by its standard gives the volume of carbonic acid. As this is always reckoned as in the normal state, the quantity of gas employed, minus the baryta water added, must be reduced to the normal state from a knowledge of the barometric pressure and the temperature at the time (see p. 29). The percentage is then calculated by comparing the corrected volume with the number of cubic centimetres of carbonic acid ascertained by the experiment.

*Example.*

Barometer =722 mm.
Temperature =19° C.
Standard of the oxalic acid : normal 1 c.c. =1 c.c. carbonic acid.
Standard of the baryta water, 1 c.c. =0·94 c.c. carbonic acid.
Contents of the absorption flask =1022 c.c.
Baryta water employed =10 c.c.

Actual volume of sample employed, 1012 c.c., corrected 878 c.c.

10 c.c. of baryta water require . 9·4 c.c. oxalic acid = 9·4 c.c. carbonic acid.
In titrating back used . . 5·2 c.c. oxalic acid = 5·2 c.c. carbonic acid.
Difference . . . . . 4·2 c.c. oxalic acid = 4·2 c.c. carbonic acid.

Consequently . 878 c.c. of the sample contained 4·2 c.c. carbonic acid.

$$878 : 4{\cdot}2 = 100 : n.$$

$n = 0{\cdot}48$ per cent. by volume of carbonic acid.

## 2. *Determination of Methane.*

The methane may be determined by a purely gas volumetric method by measuring the reduction in volume which the sample undergoes when this hydrocarbon is burnt. However simple and convenient this method may be for the determination of large percentages of the gas, for instance, in analysing lighting gas, it is nevertheless difficult to ascertain by its means the presence of tenths or hundredths of a per cent. The quantity of air which can be employed for the analysis is comparatively small; hence the difference in volume after combustion is so minute that it is necessary to prevent all disturbing influences, such as fluctuations of temperature and pressure, to avoid the error which arises in consequence of the solubility of the gas in water by employing mercury as the confining liquid, and to use the very finest measuring instruments, if the analysis is to have any pretension to exactness and trustworthiness: consequently, the whole apparatus becomes so complicated and requires so much practice for its manipulation that it appears little fitted for practical use at mines, where the analysis has generally to be made by a foreman. The same objection applies to the apparatus whose action is based upon measuring the difference of pressure with the volume remaining constant.

To answer the requirements of practical mining, the method of determining methane should be capable of ascertaining the percentage of this gas exactly within hundredths of a per cent., and, in spite of being very simple in construction, should give satisfactory results even in less practised hands. Winkler's method satisfies these conditions; it depends upon the volumetric determination of the carbonic acid formed by the combustion of methane. It has also this pre-eminent advantage, that the quantity tested in each experiment may be as large as one likes.

A further advantage of this method is that all the operations, viz. measuring the sample, burning the methane, absorbing the carbonic acid, and measuring back the excess of baryta water, are performed in one and the same vessel, so that the sample has not to be shifted about.

As the combustion of the methane takes place according to the following volumetric proportions:—

1 vol. $CH_4 + 2$ vols. $O = 1$ vol. $CO_2 + 2$ vols. aqueous vapour,

the volume of carbonic acid formed is equal to the volume of the original methane.

When the gaseous mixture is brought into contact with platinum made red hot by the passage of an electric current the combination of the methane and the oxygen takes place quietly so long as the percentage of methane is below 6, so that the mixture is not explosive.

The apparatus in the main consists of an absorption flask similar to those used in the volumetric determinations of carbonic acid (fig. 17). The size of the flask employed depends upon the percentage of methane expected. For determining small proportions in the return air-currents flasks containing 2 litres are usually chosen. For analysing samples which are richer in methane, and contain about 1 per cent. by volume or more, flasks holding 1 litre each are large enough. A mark is made around the neck and the cork is pressed in as far as this mark. The contents of the flask up to the mark are determined exactly by filling with water and weighing; the number of cubic centimetres is then scratched on the glass. In addition to a cork with two holes provided with glass stoppers, each flask has a second cork with three holes which carries the combustion apparatus, consisting of two brass rods which project into the middle of the flask. Their ends are connected by a piece of platinum wire twisted into a spiral and fastened on by small binding screws. The wire is 0·35 mm. thick, and when drawn out straight 7 inches long, exclusive of the pieces held by the binding screws. The outer ends of the rods are provided with binding screws for fastening on the wires bringing the electric current. The third hole contains a glass stopper. In order to cool the flask during the combustion, a cylindrical metal vessel is

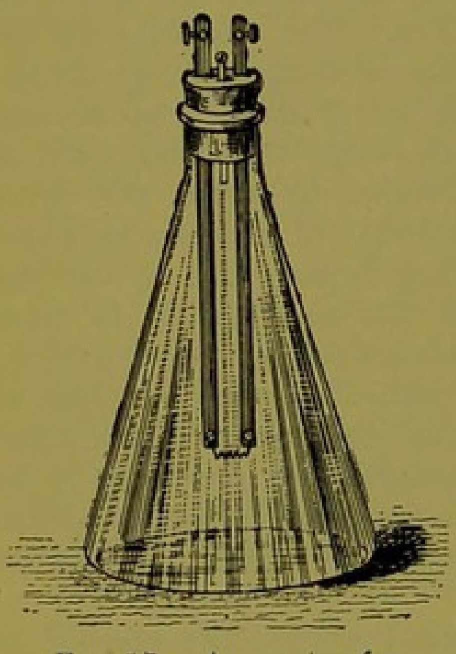

Fig. 17.—Apparatus for Determination of Methane.

employed, 45 cm. high and 30 cm. in diameter; attached to it is an iron rod, with a movable holder which is intended to keep the flask down under water. The wires for conveying the electric current must be at least 1 mm. thick, and, as they are immersed in water, they must be insulated with gutta percha.

The best plan is to take the sample of the air by filling the flask with water and then emptying it at the place where the sample has to be taken. The flask must then be closed with the cork and its two stoppers; the cork should be pressed down as far as the mark. When brought to the surface, this cork is exchanged under water for the one carrying the electrodes, care being taken not to bend the platinum wire. If the sample was taken in a collecting cylinder, the flask is filled in the manner explained by fig. 18. The first thing is to exchange under water the corks of the collecting cylinder for others closed by glass tubes and pinchcocks. The lower tube of the cylinder, hung from a frame, is connected to the water reservoir, and the gas is driven through an india-rubber tube into the flask filled with water, and held upside down under water. The cork with the electrodes is then inserted.

It has been shown by experience that the presence of organic substances affects the correctness of the results. In order to protect the gas from contact with the india-rubber cork during the combustion, the glass stopper is taken out and 10 c.c. of water are inserted from a measuring pipette, the stopper being then replaced. On reversing the flask the layer of water covers the cork. Naturally the volume of this water added, as well as the known volume of the electrodes, must be subtracted from the contents of the flask. The electrodes are then connected to the wires and the flask is immersed upside down in the cooling vessel, so that its bottom is completely covered with water, and the current is now turned on (fig. 19). The platinum wire must be brought to bright red heat, which will be effected with a wire of the given dimensions by a current of 7—8 amperes. If the current is weaker than this, the wire does not glow actively, and the combustion remains imperfect; if the current is too strong the platinum wire melts. The wire should be allowed to remain red hot for half an hour, in order to be on the safe side, although the combustion is usually complete in a far shorter time.

After disconnecting the current the flask is taken out of the cooler, and, after removing the third stopper, 25 c.c. of baryta water are allowed to flow in from the burette, taking care that the electrodes are not splashed by it. By frequent agitation the carbonic acid formed by the combustion is gradually absorbed.

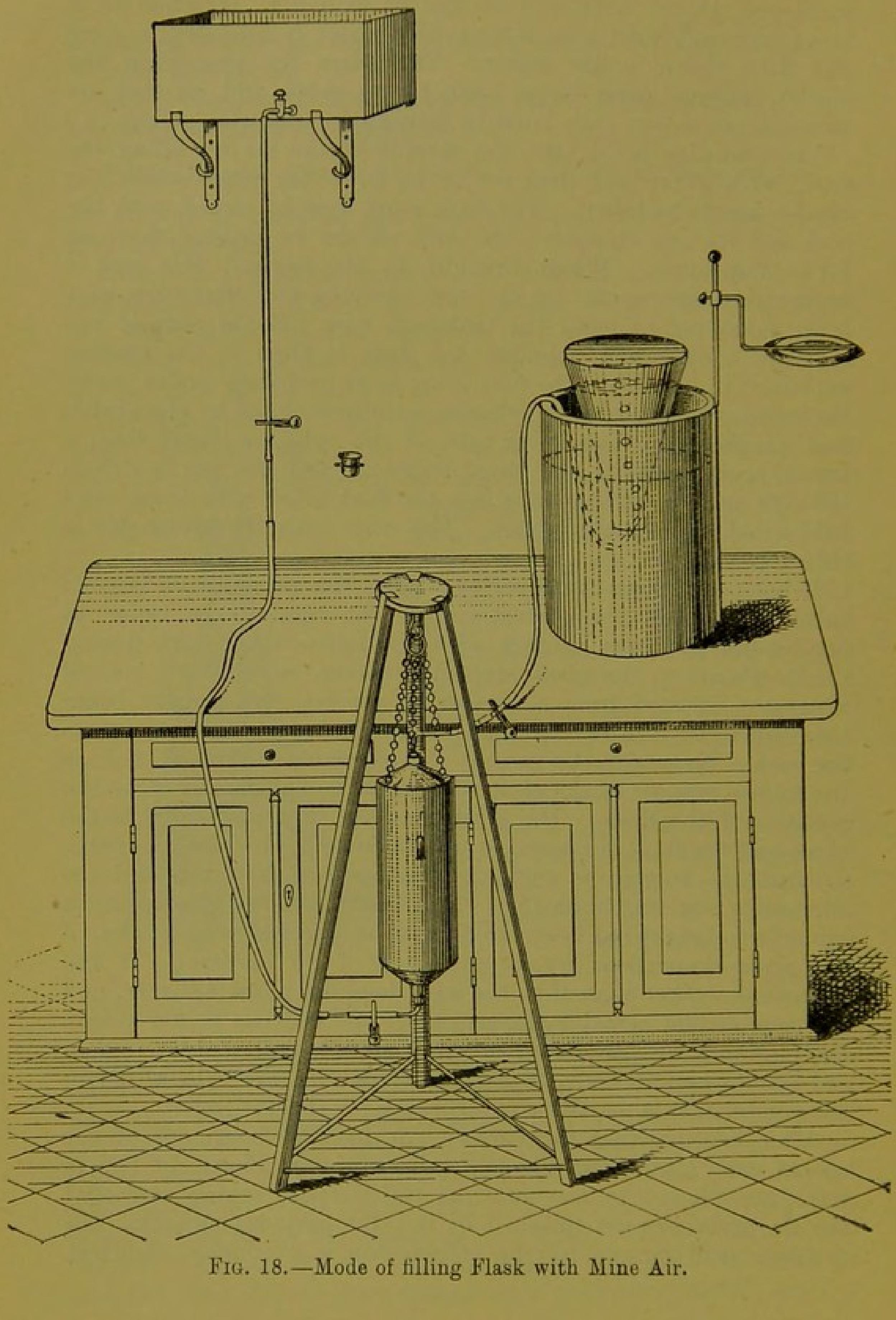

Fig. 18.—Mode of filling Flask with Mine Air.

While the absorption is proceeding the standard of the baryta water should be checked. Then after exchanging the cork with the electrodes for the former one, the excess of baryta water is determined as explained on p. 50. The difference between the total amount of baryta water used, multiplied by its standard, and the number of cubic centimetres of normal oxalic acid used, gives the quantity of carbonic acid in the sample after the combustion.

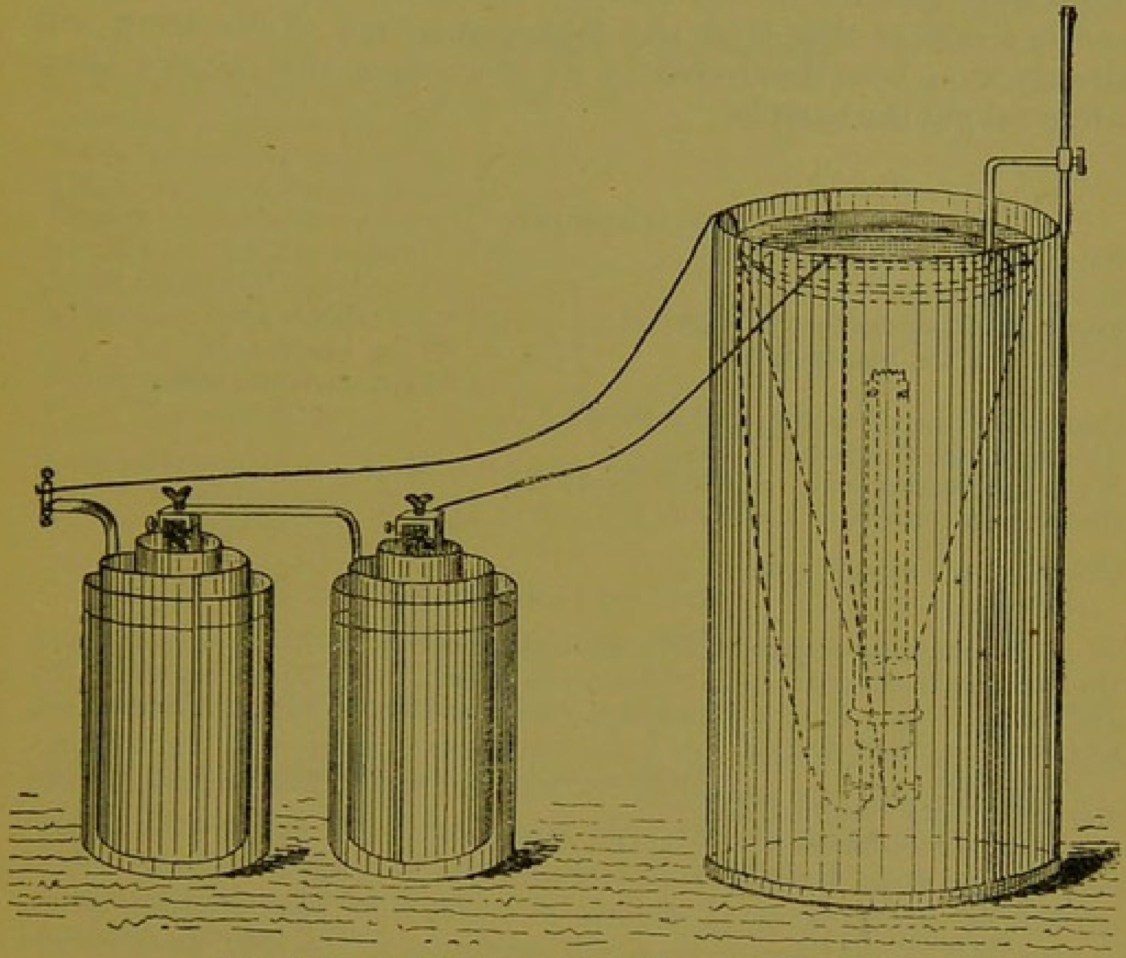

FIG. 19.—Combustion of Fire-damp in Mine Air.

As mine air is never free from carbonic acid, the result so obtained includes the amount of this gas which was originally present. This must be ascertained by a separate determination by Hesse's method, and deducted from the total amount of carbonic acid. The difference is then the amount of carbonic acid formed by combustion, and its volume is equal to that of the methane originally present in the sample. It is convenient to make the carbonic acid determination during the combustion of the methane.

In analysing mine air comparatively rich in methane, it may happen when the electric contact is made that an explosion takes place, driving the cork and the electrodes out of the flask. However, no such explosion will happen unless the proportion of methane has reached the lower limit, *i.e.* 6 per cent., and unless the temperature of the glowing platinum wire is very high. Winkler's method is not suitable for analysing such mixtures, and in a case of this kind the high percentage of fire-damp will already have been discovered by its effect upon the miner's lamp while taking the sample.

### *Example.*

Barometer = 740 mm.
Temperature = 19°.
Standard of the oxalic acid : normal 1 c.c. = 1 c.c. carbonic acid.
Standard of the baryta water . . 1 c.c. = 1·03 c.c. oxalic acid.
= 1·03 c.c. carbonic acid.
Contents of the absorption flask = 2000 c.c.

$$\left.\begin{array}{ll}\text{Volume of the electrodes} & = 8 \text{ c.c.}\\ \text{Water, protecting cork} & = 10 \text{ c.c.}\\ \text{Baryta water used} & = 25 \text{ c.c.}\end{array}\right\} = 43 \text{ c.c.}$$

| | | |
|---|---|---|
| Quantity of sample employed . . . . | 1957 c.c.; corrected 1743 c.c. | |
| 25 c.c. baryta water require | 25·75 c.c. oxalic acid | = 25·75 c.c. carbonic acid. |
| On titrating back used . | 10·20 c.c. oxalic acid | = 10·20 c.c. carbonic acid. |
| Difference . . . | 15·55 c.c. oxalic acid | = 15·55 c.c. carbonic acid. |
| Obtained in 1743 c.c. of the sample . . . | 15·55 c.c. carbonic acid = 0·89 per cent. by volume. | |
| Carbonic acid originally present (determined by separate test, Hesse's method) . . . | | = 0·31 per cent. by volume. |
| Therefore found . | | = 0·58 per cent. methane. |

### *Entry of an Analysis in the Laboratory Journal.*

| | |
|---|---|
| Place where sample was taken . | Winding shaft, 380 m. below the surface. |
| Time when sample was taken . | 1st March 1900, 4.30 p.m. |
| Temperature of the laboratory . | 19°. |
| Height of barometer on the surface | 720 mm. |
| Standard of the baryta water . . | 1 c.c. = 0·96 c.c. oxalic acid.<br>= 0·96 c.c. carbonic acid. |

#### *A. Determination of the Oxygen.*

| | |
|---|---|
| Volume of gas employed . . | 100 c.c. |
| After absorption with phosphorus | 81·1 c.c. |
| Diminution in volume . . . | 18·9 c.c. = 18·9 per cent. of oxygen by volume. |

### *B. Determination of the Carbonic Acid.*

| | |
|---|---|
| Contents of the absorption flask | 1022 c.c. |
| Baryta water employed | 20 c.c. |
| Employed for analysis | 1002 c.c. = 867 c.c. corrected. |
| 20 c.c. baryta water require | 19·2 c.c. oxalic acid. |
| By titrating back employed | 15·9 c.c. ,, |
| Difference | 3·3 c.c. = 0·38 per cent. carbonic acid. |

### *C. Determination of the Methane.*

| | |
|---|---|
| Contents of the absorption flask | 1960 c.c. |
| Volume of the electrodes, 8 c.c.<br>Water, protecting cork, 10 c.c.<br>Baryta water employed, 25 c.c. | 43 c.c. |
| Volume employed for analysis | 1917 c.c. = 1660 c.c. corrected. |
| 25 c.c. baryta water require | 24·0 c.c. oxalic acid. |
| By titrating back employed | 10·2 c.c. |
| Difference | 13·8 c.c. = 0·83 per cent. of carbonic acid by volume. |
| Found under B | 0·38 ,, ,, |
| Consequently | 0·45 per cent. of methane by volume. |

| | |
|---|---|
| Found : Oxygen | 18·9 per cent. by volume. |
| Carbonic acid | 0·38 ,, ,, |
| Methane | 0·45 ,, ,, |

## Determination of Dust.

Ever since the important part played by coal dust in colliery explosions has been recognised, the determination of the dust floating in the air has become of interest for ascertaining the safety of a mine, apart from any hygienic considerations.

The determination of the amount of coal dust in air is a very simple operation. All that is necessary is to draw a definite volume of the air in question through a tube provided with a suitable filtering material, and ascertain the increase in weight that the tube has undergone. The amount of dust per cubic metre is then ascertained by calculation. A suitable form of the small apparatus is shown in fig. 20. It consists of a piece of tube A, about 15 mm. (·6 inch) in diameter, drawn out below to a narrow piece 3 cm. long, and widened out somewhat above; it can be closed by two glass caps, B and C, which are ground on. The best filtering material is cotton-wool, and the tube should be filled with it until it reaches half-way up the wide part. In this manner a filtering stratum is obtained 10 cm. (4 inches) long. The tubes prepared in this manner are kept in twos or threes in a box lined with sheet cork, and made just long enough for the tubes to fit in exactly, and to prevent the caps from falling off when the box is carried about. The tubes are always weighed in the closed state.

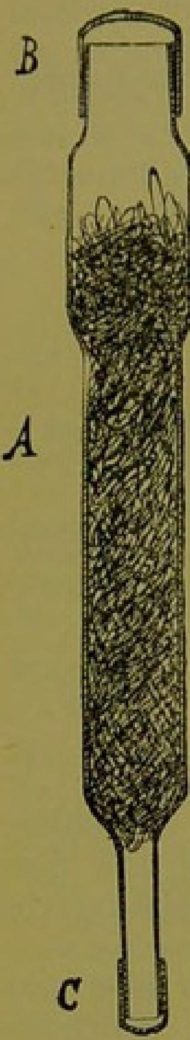

Fig. 20.—Dust Measurer.

The simplest plan is to combine the dust determination with the taking of a sample, using a collecting cylinder containing 10 litres (fig. 2) as an aspirator. At the place where the sample is to be taken, the cylinder full of water is placed upside down, and the cork of the lower neck exchanged for an india-rubber cork bored through, and having a glass tube and a screw pinchcock. The vessel is then hung up in its ordinary position at a suitable place, the two caps are taken off the filter tube, and the small end is thrust into the hole of an india-rubber cork, so that its end comes flush with the face of the cork, which is then placed in the upper neck of the metal cylinder, care being taken that the end of the tube is not wetted by the water. The screw pinchcock is loosened, the water runs out, and the air is sucked in. If the conditions of the place make it desirable, the filter tube is not placed directly upon the cylinder, but is connected with it by a piece of india-rubber tube with a piece of glass tube inserted through the cork; this enables the sample to be taken at any height. When the water has all run out, the filter tube is closed by its two caps and brought up to the surface to be weighed exactly. The increase in weight gives the amount of coal dust in the moist state contained in 10 litres of air. It is easy to dry the coal dust before weighing it, by drawing through it for some time a current of air which has been freed from moisture by concentrated sulphuric acid; but this does not appear to be necessary, as the determinations made in practice deal only with largish quantities of dust, in which a small difference of a few per cent. is not worth consideration.

If the stratum of cotton-wool is blackened completely from one end to the other, it is to be feared that a portion of the coal dust has been carried right through the filter. By stuffing in the cotton-wool more tightly, and by letting the water run out less rapidly, this evil may be corrected. The filling of cotton-wool must be renewed for every determination.

## IV. ARRANGEMENT OF THE LABORATORY.

It is only in exceptional cases that the amount of certain gases in mine air can be determined at the very spot in the mine where the sample is taken; as a rule, it is necessary to perform the analysis of the sample above ground. It then becomes desirable to do the work in a suitably arranged laboratory.

In choosing a place for the laboratory, special care must be taken that it shall possess as even a temperature as possible. Consequently a room facing north, which is not exposed to the direct action of the sun's rays, is to be preferred. It is especially necessary that the temperature of the sample should be kept constant while it is being analysed. It is best to work in a room which is not heated artificially; if this is out of the question, however, care should be taken to heat the laboratory uniformly, and, if possible, by indirect means. All liquids which have to be brought into contact with gases, such as confining water, absorptive solutions, etc., must have the same temperature as the laboratory, and are therefore kept in it. In order to have water at the temperature of the laboratory constantly at hand, a reservoir made of zinc or galvanised iron is fixed about 1 metre above the laboratory bench. At the bottom it is provided with a nozzle with stopcock, or with a neck into which a bored cork carrying a piece of glass tube is placed; the tube is bent downwards, and receives an india-rubber tube which can be closed by a pinchcock, and which ends in a glass nozzle (fig. 18). When out of use the nozzle is placed in a little glass dish fixed against the wall. The reservoir is filled from time to time with distilled water; this is ready at hand at nearly every mine in the form of condensed water from the steam engine. Care must be taken that it is not contaminated with lubricating oil.

A bench for performing all measurements, titrations, etc., is placed against the window, whilst other operations, such as the combustion of methane, can be carried out upon a table in a less favourable light.

A barometer and a thermometer are part of the outfit indispensable for the simplest mining laboratory. Ordinary barometers cannot be used for exact measurements. The best plan is to have one of Bunsen's siphon barometers with the scale engraved upon the barometer tube itself, or a good aneroid duly checked by comparison with a mercurial barometer. The thermometer must be graduated at least into half-degrees, and may conveniently be hung up upon the barometer itself. It is self-evident that this piece of apparatus must not be placed near the fireplace, whilst the measurements are being made at the window.

As a source of electricity for heating the platinum wire in making methane determinations, accumulators are to be preferred to any other, especially on account of the regularity of the current they furnish and the ease with which they are handled. They may be employed either where there are means of charging them from a dynamo at the mine or where they can be charged somewhere else in the neighbourhood. In the latter case portable accumulators are used. In order to heat a platinum wire ·35 mm. thick and 7 cm. long red-hot, a current of 7 to 8 amperes is necessary, and this is afforded with a potential of 4 volts. Two cells arranged in series will suffice, and it is advisable not to choose them too small. An analysis requires about 4 ampere-hours from each cell. From this, and from the number of fire-damp analyses to be performed in a given time, it is easy to calculate the necessary capacity. It must be remembered that the accumulators should never be completely exhausted, and that after standing unused for some time their strength is diminished.

If circumstances prevent the use of accumulators, the best plan is to employ large Bunsen cells. Two of these coupled in series afford the necessary potential, but as this begins to diminish after a time, it is advisable to have a reserve cell, which can be introduced when the platinum begins to glow less vividly. If Bunsen cells are used for a long time, the acid vapours given off become troublesome, on which account it is preferable to place the battery outside the laboratory and bring in the current by thick copper wires to a couple of binding screws on the laboratory bench. The acid should be poured in just before use and emptied immediately afterwards; in this manner it can be used over and over again. If the amalgamation of the zinc cylinder has become defective, a few drops of mercury should be put into the liquid. Otherwise both the zinc and the acid would soon be used up.

For weighing the reagents and barium hydroxide a good ordinary balance of small size suffices. In weighing the necessary quantity of oxalic acid for preparing the gas-normal solution, a delicate balance is, however, required, which will turn with at least 1 mg. with a load of 50 grms. A regular analytical balance in a glass case is not imperatively necessary. In case of necessity a pair of good apothecary's hand-scales may be made to do the work. In any case, it is advisable to keep the balance in a different room from that in which the acid vapours are given off by the battery, and to protect it from dust by a cover.

If volumetric determinations of carbonic acid or methane are not performed often enough to make it worth while procuring a good balance, the ready-made normal solution of oxalic acid may be purchased.

No rules applicable to every case can be laid down as regards the inventory of apparatus required for a mining laboratory: it must depend upon the nature of the proposed investigations. If only methane and carbonic acid are to be determined, a Hesse and a Winkler apparatus will suffice, and they require nearly the same subsidiary outfit. If complete analyses of mine air have to be carried out, Hempel's apparatus must likewise be procured. In certain circumstances, that is to say, in so-called non-fiery mines, which have a great deal of carbonic acid, such as mines in brown coal, Winkler's carbonic acid apparatus alone may satisfy all the requirements.

From the following list of the apparatus and accessories employed in testing mine air, the mining engineer will easily be able to select what he requires for his purposes.

### *List of the Apparatus and Accessories required for the Chemical Investigation of Mine Air.*[1]

*For taking Samples.*—Several collecting cylinders made of sheet zinc, with india-rubber corks, or closed by lever and washer arrangement, containing 5 litres or 10 litres.

A stand for supporting the cylinders.

A pair of india-rubber corks bored through with bent glass tubes and two screw pinchcocks.

*For Volumetric Analysis.*—One Hempel's burette with connecting tube and glass tube 10 cm. long.

A simple Hempel's pipette for caustic potash.

A phosphorus pipette.

Two compound pipettes for pyrogallic acid and cuprous chloride.

A small wooden bench.

Several connecting capillary tubes.

A few small pinchcocks.

Several glass rods and small corks for closing the gas pipettes.

One metre of thick india-rubber tubing about 2 mm. in diameter inside and 6 mm. outside.[2]

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[1] All the apparatus, accessories, and reagents are supplied by Franz Hugershoff, 13 Carolinenstrasse, Leipsic.

[2] India-rubber tubing becomes hard and stiff when kept in cold rooms; it becomes soft again if it is brought into a warm place or if put into warm water.

Thin covered copper wire for wiring the india-rubber tubes.

Reagents : Potassium hydroxide, pure.
Phosphorus in thin sticks.
Pyrogallic acid.
Cuprous chloride.
Sal ammoniac.
Concentrated ammonia.

Or : A Lindemann-Winkler apparatus for determining oxygen and a Winkler apparatus for determining carbonic acid.

*For Titration.*—Two absorption flasks of about 1000 and two of about 2000 c.c., with india-rubber corks and glass rod stoppers (for carbonic acid determinations according to Hesse, and methane determinations according to Winkler).

Two pairs of electrodes with india-rubber corks having three holes, and one glass rod stopper. A few pieces of platinum wire 0·35 mm. thick and 8 cm. long.

One cooling vessel of sheet zinc, with holder.

One burette fitted as in fig. 15, and graduated into ·1 c.c., with nozzle 10 cm. long and float.

A store bottle for normal baryta water with siphon discharge and soda-lime tube.

One burette with glass tap holding 30 c.c., graduated into ·1 c.c., with outlet nozzle 10 cm. long, and one measuring pipette holding 10 c.c.

One small funnel.

Several conical flasks.

As source of electricity : Either two accumulator cells or three large Bunsen elements with binding screws.

Several metres of copper wire 1 mm. thick insulated by gutta percha.

A measuring flask holding 1 litre, with glass stopper.

A balance, with set of weights.

Reagents : Crystallised barium hydroxide.
Chemically pure crystallised oxalic acid.
Phenolphthalein solution, 1 : 1000.

*For determining Coal Dust.*—One box with two filter tubes.

*For General Purposes.*—A good barometer.

A thermometer, 0 to 30° C., graduated to ·5 degree.

Several stoppered glass flasks holding 1 litre.

A few metres of ordinary india-rubber tubing of 4–5 mm. diameter internally.

# II.—THE MEASUREMENT OF AIR-CURRENTS AND FIRE-DAMP AT RONCHAMP COLLIERIES.

BY

LÉON POUSSIGUE

MANAGER OF RONCHAMP COLLIERIES.

# MEASUREMENT OF AIR-CURRENTS AND FIRE-DAMP AT THE RONCHAMP COLLIERIES.

## INTRODUCTION.

The Ronchamp Collieries are decidedly fiery. Fire-damp is not harmless unless it is diluted in all parts of the mine with a large quantity of air. Consequently, for fighting it successfully it is necessary to know at the outset :—

(1) The quantity of air sent into the workings, and the manner in which this air is distributed.

(2) The quantity of fire-damp given off.

Hence it is necessary to make two kinds of tests :—

(1) Measurements of the quantity of the air.

(2) Analyses of the air.

These measurements and analyses have been carried on systematically for a long time at Ronchamp, and constitute one of the subjects requiring greatest attention from the officials at the mine.

A knowledge of the quantities of air circulating in a district and of the quantity of fire-damp given off from the workings enables the maximum output of the district to be fixed, if a rule is made, as is done at Ronchamp, that a certain maximum percentage of fire-damp shall not be exceeded.

The observations carried on continuously for a number of years in our mines tell us that in a certain district a certain seam gives off so many cubic metres of fire-damp per ton of coal. When we are arranging to work a new district, we know that, for a given number of tons to be extracted, a definite volume of fire-damp has to be got rid of. We stipulate, for instance, that our return air-currents shall not contain more than 0·5 per cent. of fire-damp; and we can calculate therefore at once how much air must be sent into the workings. If our means of ventilation are not sufficient to furnish the necessary amount of air, we reduce the output, in order to remain within the limits laid down beforehand.

After work in a district has been started, it may happen that changes in the ventilation take place, or that unexpected outbursts of fire-damp occur, and these are matters which must be remedied at once. It is consequently imperative that the manager should be posted up, at every moment almost, upon the travel of the air-currents and the amount of inflammable gas they contain.

If, in the first place, the ventilation is carefully watched, and, secondly, if the air is frequently analysed, the manager will be able to keep himself thoroughly informed upon both these points.

We will now describe briefly how we carry on these two kinds of checks at Ronchamp.

## SUPERINTENDENCE OF THE VENTILATION.

**Routine Observations.**—The ventilation has been tested regularly at Ronchamp ever since the year 1876.

The tests are carried out by means of a Casartelli anemometer in all the principal intake and return air-ways, with the object of determining:—

(1) The mean speed of the fans.

(2) The depression of water-gauge produced by them.

(3) The depression produced by other causes besides the fans (owing to the depths of the pits, this depression is far from being negligible).

(4) The quantity of air circulating in the workings in consequence of the artificial and the natural ventilation.

(5) The "equivalent orifice" of the mine and of its subdivisions.

(6) The "splitting" of the air-currents in the mine.

(7) The depression of water-gauge in each district.

(8) The temperatures of the different splits of air, particularly at the farthest points.

Each pit has its own special ventilating appliances, and these are in duplicate, so that one set is always idle and ready to start in case an accident should happen to the one in use.

The ventilating appliances are under the direct orders of the under-manager, and their speed must not be altered, nor must any change be made in them without his orders. If some unexpected accident makes it necessary to change from one ventilating appliance to the other, the foreman miner and the under-manager must be informed immediately, and the men must be withdrawn from the mine if the interruption of the ventilation has to last more than ten minutes.

An order posted in the fan-room indicates the number of revolutions to be made by the fan, and this speed must be strictly observed until it is altered by a new order signed by the under-manager.

The machinery is stopped for oiling, and for examining the moving parts, twice a day, at hours strictly laid down by the under-manager, and when there is no one in the mine. These stoppages must not exceed ten minutes as the maximum. Should any defect be discovered during the stoppage, which would prevent the machinery from being re-started immediately, the under-manager and foreman miner are informed without delay, and it is their business to take all necessary measures.

The under-manager knows whether his ventilating appliances are working properly by the self-registering water-gauges. The sheet of paper upon which the diagram has been traced is taken off every day at noon by the foreman miner, who then inserts a fresh sheet. He makes a note of the irregularities in the running, and reports them if necessary. The sheet is then sent to the official in charge of the ventilation, who files it, after having drawn the line of average depression of water-gauge. In addition to changing the water-gauge sheet, the foreman miner notes down daily the number of revolutions of the engine as indicated by a counter.

Besides the self-registering water-gauge, an ordinary water-gauge consisting of a U-tube containing water is placed in the fan-room. One of the limbs is open to the external atmosphere, and to the other is attached a copper tube of the same diameter, which is carried into the fan-drift near the fan. It opens exactly at right angles to the direction of the current, at a point where the latter is weak.

As already stated, the ventilation tests are made by an official and an assistant by means of a Casartelli anemometer, suitably standardised beforehand for determining the small velocities for which the usual formula $V = a + bn$ is not applicable.

The ordinary observations for ventilation are always made at the same part of the day, between noon and 5 p.m. As the volumes are observed during the warmest mean period of the day, they are the smallest possible, because the depression of water-gauge from natural causes is then smallest. The proportion of fire-damp in the air is at the same time greatest, because it is then that the largest quantities of coal are being handled in the mine. And, further, as the fan is stopped at 5 p.m. for oiling, this stoppage is utilised to gauge the natural draught and the corresponding compression in the fan-drift.

In making the ventilation tests, the following operations and calculations are carried out:—

First of all the observer writes down in his note-book (*before beginning his tests*) the number on the engine counter; and he again notes the number at the end of his tests. The difference gives the number of revolutions of the fan during the time which has elapsed, and consequently the average speed of the fan.

Places are chosen for the observations underground in roadways which are timbered or walled, and which present an easily measured cross section, and are as far as possible in solid ground so as to avoid leakages of air; as a rule the place for the test is a roadway lined with steel frames well lagged with planks. Any openings around the frames are carefully filled up so as to make all the air pass through the visible part of the roadway.

The observer first fixes the thermometer on the side of the roadway, and leaves it there till the end of the experiment; he thus obtains the temperature of the air. A lamp is hung up a little in front of the frame where the test will be made; it gives the observer light, while leaving his hands free.

The anemometer is fixed on the end of a rod or stick 1·20 m. (4 ft.) long, and the observer without altering his position in the least holds the instrument at arm's length so that it faces square to the current, and moves it slowly but methodically over the whole of the section of the roadway. The observer should keep his body rigid and move nothing but his arm.

On starting his anemometer, the observer makes a signal, and his assistant, starting a stop-watch, calls out every tenth second loudly. At the fiftieth second the operator disengages his instrument. By this time he ought to have passed over the whole of the section of the roadway, which is easily accomplished with a little practice. The test is invariably repeated a second time. The operation is concluded by reading the thermometer and the barometer and by taking the principal dimensions of the section of the roadway. The area is then determined at the surface by the planimeter or by calculation. Finally the observer notes the time at which the experiment was made.

When there are doors in a roadway for the purpose of causing the air to take some definite course, the observer notes the barometric pressure on both sides of the door.

The number of observations needed is naturally more or less great according to the importance of the district.

On going back to the surface the observer, as already said, notes the number of revolutions marked by the counter of the fan, and calculates the mean velocity during the making of the observations. He then goes into the fan-drift and measures the air-current which is passing, at the same time counting the number of revolutions made by the fan, which is easily done by listening to the sound. He also notes the temperature and the pressure.

Returning to the fan-room, he notes the water-gauge and the velocity at that precise moment.

He repeats these observations twice after altering the speed of the engine. Lastly, he has the fan completely stopped, and at the end of seven or eight minutes he reads off from the water-gauge the compression, and measures the quantity of air. With these three speeds, giving three depressions and one compression, the curves of the depressions can be drawn. (See curve of the calculated depressions, fig. 22.)

From this curve it is possible to determine, with a sufficient degree of approximation, what was the depression of water-gauge at the precise moment when the observer was measuring the air current in the fan-drift, when he was only able to note the number of revolutions.[1]

The observer will also be able to calculate what water-gauge corresponds to the average speed of the day. He arrives at this from the number of revolutions indicated by the counter at the beginning and at the end of the observations. These various depressions are depicted upon the curve of which we speak. If we examine this curve, we shall see that when the fan is stopped a compression is produced in consequence of the resistance which the air encounters in escaping from the fan-drift. When the fan is started this compression diminishes, and ends by disappearing when a certain speed is reached.

---

[1] This depression may be calculated by the formula—

$$\frac{h' + h_0}{h + h_0} = \frac{N_1^2}{N^2}.$$

$h'$=calculated mechanical depression corresponding to $N_1$ revolutions per minute,

$h$=observed mechanical depression corresponding to N revolutions per minute.

$h_0$=observed compression during stoppage of fan.

On the other hand, the volume of air passing through the drift when the fan is stopped is the consequence of the natural depression minus the compression.

If we recollect that the volume of air passing is proportional to the square root of the depression which causes the current, it is evident that we have all the data for calculating this natural depression. A simple rule of three sum will tell the difference between the natural depression and the compression, and, consequently, the exact value of the former. When this is known, it is easy to ascertain the volume of air which would be due to it with openings unimpeded.

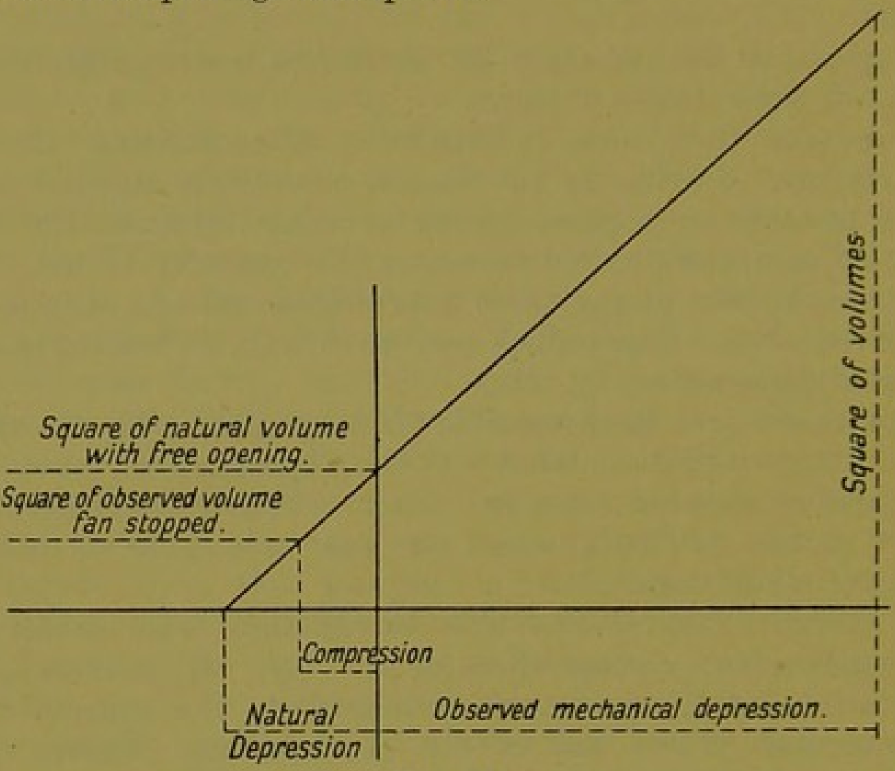

FIG. 21.

It is also possible to calculate the volume corresponding to any depression which has been observed, and especially the volume corresponding to the mean depression calculated in the manner pointed out above.

In order to determine all these volumes easily, a diagram (figs. 21 and 23) is constructed from the data obtained by the experiments, in which the abscissæ are proportional to the depressions and the ordinates to the squares of the corresponding volumes.

The diagram of the depressions and the diagram of the volumes are constructed every month for each fan and kept in the office.

These data furnish the means of calculating the equivalent orifice of the mine, that is to say, the area of an orifice in a thin plate which with the depression at the observed time of measur-

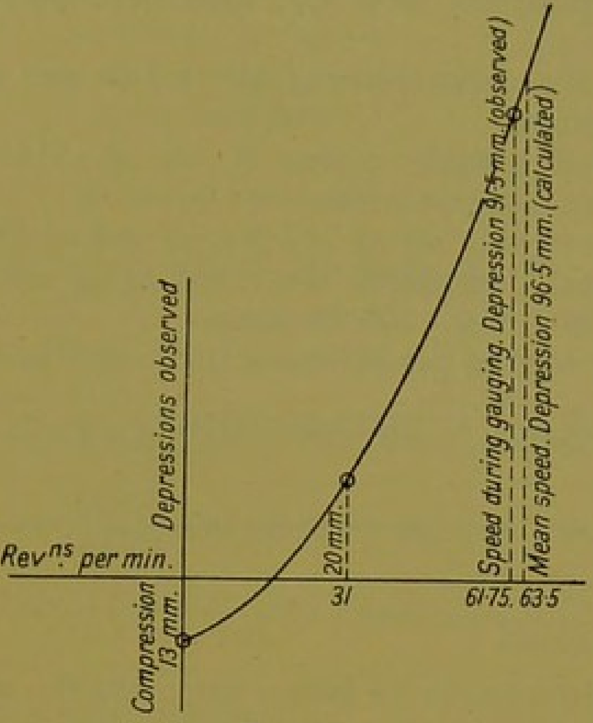

FIG. 22.

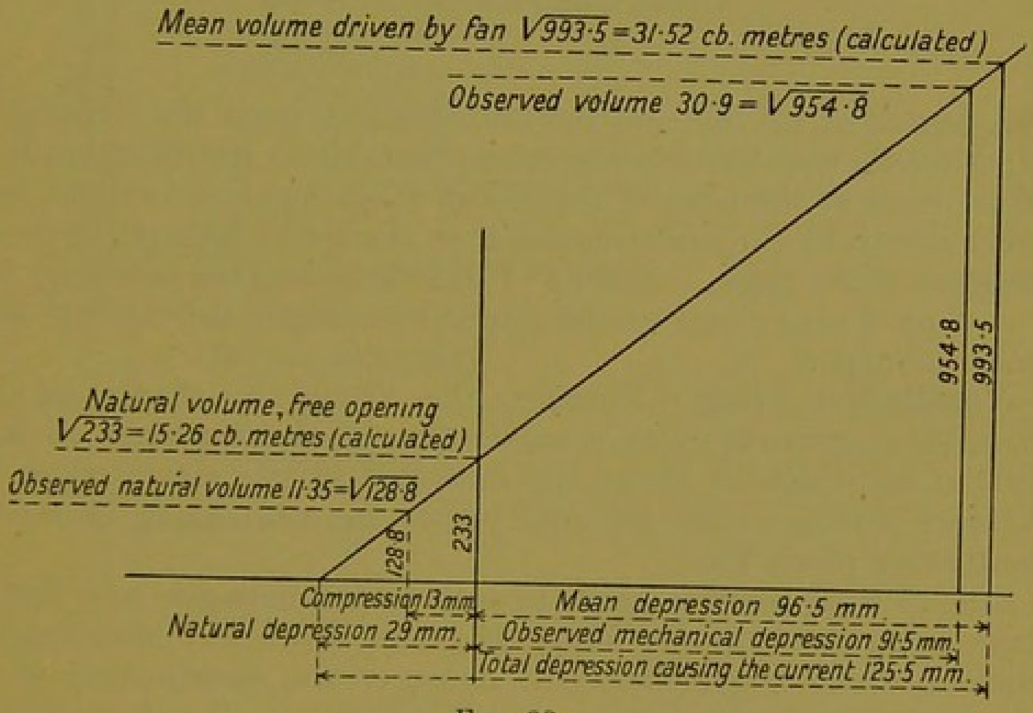

FIG. 23.

ing would give a volume of air equal to that measured during the experiment.

*Example.*—Quantity of air circulating through the workings, 35·2 cubic metres per second, at a pressure of 716·5 mm. of mercury; temperature, 18·4° C.; total depression, 120·5 mm. of water-gauge.

The weight of a cubic metre of air at 760 mm. and at 0° C. is 1·293 kilogrammes.

The weight of a cubic metre of air at 716·5 mm. and at 18·4° C. is 1·144 kilogrammes.

The density of this air at 716·5 mm. and at 18·4° C. is $\frac{1}{874}$ of water; the total depression, measured as a column of air, is therefore $0·1205 \times 874 = 105·32$ metres.

The velocity of flow per second is given by the formula—

$$V = \sqrt{2gh} = \sqrt{2 \times 9·8088 \times 105·32} = 45·45 \text{ metres.}$$

The theoretical section is therefore $\frac{35·20}{45·45}$, and the practical section $\frac{35·20}{0·65 \times 45·45} = 1·19$.

Following Murgue, we no longer calculate the equivalent orifice in this manner, but simply apply the formula—

$$O = 0·38 \frac{\text{Gross volume}}{\sqrt{h}} = 0·38 \frac{35·20}{\sqrt{120·5}} = 1·21.$$

A *résumé* of all the information obtained from the ventilation experiments is entered in the form of a table in the official journal of the mine at the head of the report which has to be written in it every month by the under-manager in charge of each pit upon the progress of the work. A copy of this table is given below (p. 73).

A copy is also given to the general manager, and to the chief under-manager.

**Ventilation Plans.**—Further, the official in charge of the ventilation prepares every month a plan of the workings in each district, on which he shows the direction of the air-currents, the volumes passing at the principal points, the ventilating doors, the ventilating pipes, etc.

One of these plans is given to each under-manager, and day by day during the following month he notes down any modifications made in the arrangement of the doors or the distribution of the air-current, and the driving or the filling up of any roadways. The manner in which the ventilation is arranged is thus always known.

All these ventilation plans are kept; they are easily prepared,

VENTILATION DURING MARCH 1897.

| Fan. | Date. | Barometric Pressure at the Offices in mm. of Mercury. | External Temperature. | Currents circulating without the Aid of the Fans. | | | | Mean Speed of the Fans. | Forced Current delivered by the Fans. | | Proportion of Fire-damp in the Forced Current (in thousandths). | Temperature of the Current leaving the Mine. | Current circulating in the Mine in Cubic Metres per second. | Depression in mm. of Water. | | | Equivalent Orifice—$S=0{\cdot}38\frac{V}{\sqrt{h}}$ (Murgue's Formula). V = gross volume. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Passing through the Fans at rest. | | | | | | | | | | | | | |
| | | | | Compression of Passage. | Volume reduced to Normal Cubic Metres per second. | Approximate Orifice of Passage in Square Metres. O. | Theoretical, with Shaft Open. | | Volume Observed. Cubic Metres per second. | Volume Reduced to 0° and 760 mm. | | | | Mechanical (Observed). | Other (Calculated). | Total causing the Current. | S |
| Ser fan, Magny pit . . . . | 29 | 722·2 | 10° | 13 mm. | 11·35 | 1·35 | .. | 190·5 | 35·70 | 31·52 | 2·1 | 18·4° | 31·52 | 96·5 | 29 | 125·5 | 1·21 |
| Mortier fan, Chanois pit . . . . | 11 | 735 | 12·3° | 1 mm. | 4·23 | .. | .. | 325 | 53·65 | 49·08 | 8·8 | 15° | 41·71 | 149 | 2·4 | 151·4 | 1·40 |
| Sainte Marie pit . | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | 6·6 | .. | .. | .. | .. | .. | .. |

as they are made upon tracing-paper, and, consequently, there is no trouble in making fresh ones every month.

**Ventilation Register.**—Lastly, a special ventilation register is kept by the official entrusted with the monthly experiments. This register is simply the *résumé* for each month of the statements and plans which we have just mentioned.

The following is a copy of a page of this register for the month of March 1897 :—

| Pit. | Name of the Current. | Inflow. | Outflow. | Total Outflow. |
|---|---|---|---|---|
| Magny pit | Loss at the hooking-on places | 0·90 | 0·90 | |
| | Third Level: Southern district, 1st seam | 7·20 | 7·20 | |
| | Third Level: Southern district, 2nd seam | 9·20 | 9·20 | |
| | Third Level: Eastern district, 2nd seam | 6·14 | 6·14 | |
| | Western district, 8·23, of which 0·15 goes to the Chanois | 8·23 | 8·08 | 31·52 |
| Chanois pit | Losses at tbe hooking-on places at the first levels | 1·50 | 1·50 | |
| | Third Level: 1st seam South | 6·0 | 6·0 | |
| | Third Level: 2nd seam South, Pope sinking | 5·21 | 5·21 | |
| | Third Level: 1st seam North | 5·54 | 5·54 | |
| | Third Level: 2nd seam North, roof | 11·26 | 11·26 | |
| | Third Level: 2nd seam North, floor | 12·05 | 12·05 | |
| | From Magny to Chanois | | 0·15 | 41·71 |

## ANALYSES OF MINE AIR.

Ever since the month of November 1891, a special service has existed at the Ronchamp Collieries for the purpose of determining the quantity of fire-damp in the workings.

We have been led to organise this service in consequence of the experiments of M. Le Châtelier upon the limit of inflammability of gaseous mixtures.

**Object of the Control Service.**—Our object is :—

(1) To know each day the exact proportion of fire-damp in all the return air-ways and in the workings.

(2) To determine periodically the nature of the gases enclosed in, or given off from, the goaf.

(3) To analyse the air of cavities in the roof, or gas from fissures, faults, etc.

These experiments enable the amount of the outflows of fire-damp and their variations to be followed day by day, and they are of great use in studying the ventilation of the mine.

**Taking the Samples.**—The samples of air are taken :—

(1) On leaving the last working face of each district of the mine.
(2) Before arriving at the upcast shaft.
(3) At points which it is desired to supervise more specially.
(4) In the goaf or in the stowing, by means of special arrangements.

The samples are taken by the subordinate officials in the following manner :—

(1) Where samples are regularly taken at the same place (tops of working places, main return air-ways, etc.), bottles are placed on a support at half the height of the roadway, at a point where they will not interfere with the current.

The bottles hold 1½ litres, and have the form shown in fig. 24. They are placed so that the lower aperture faces the air-current. Twenty-four hours afterwards, the appointed official closes the upper and lower apertures with india-rubber stoppers, and carries away the bottle, leaving another in its place for the next sample.

Each bottle has a label affixed showing the place where the sample was taken and the date.

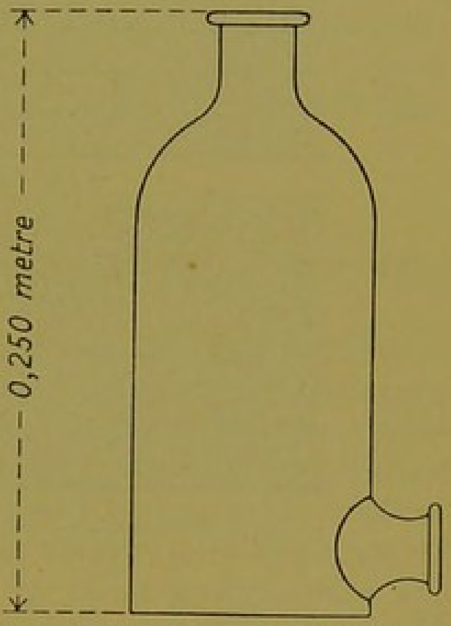

FIG. 24.—Sampling Bottle.

(2) Where samples are taken only occasionally, and where it might be inconvenient to leave a bottle, the official contents himself with emptying the bottle previously filled with water; he then corks it up and carries it away.

(3) When it is necessary to take a sample from some special point in a roadway, such as a cavity in the roof, or fissure, etc., the bottle is filled with water, and a stopper provided with a cork is inserted into the upper neck, and a piece of india-rubber tube is attached to the stopper. The end of this tube is put into the cavity or fissure, and the bottle is placed as close as possible to the place whence the sample is required. The lower cork is taken out (or if a tap has been fitted on, it is opened), the water

runs out, and the bottle becomes filled with the gas from the cavity. Another simple plan is to empty an ordinary bottle previously filled with water.

(4) In order to take samples of the gases in the goaf, small chambers about 2 m. by 2 m. are left in the middle of the stowing, and a pipe is taken from the chamber into the roadway above (fig. 25).

As the stowing proceeds the chamber is soon completely isolated, and samples may begin to be taken. Air is drawn out of the chamber by means of a small pump and forced into the sample bottle. The bottles are arranged in boxes, each holding six, and they are easily carried about: they are brought to the shaft and sent up to the analyst.

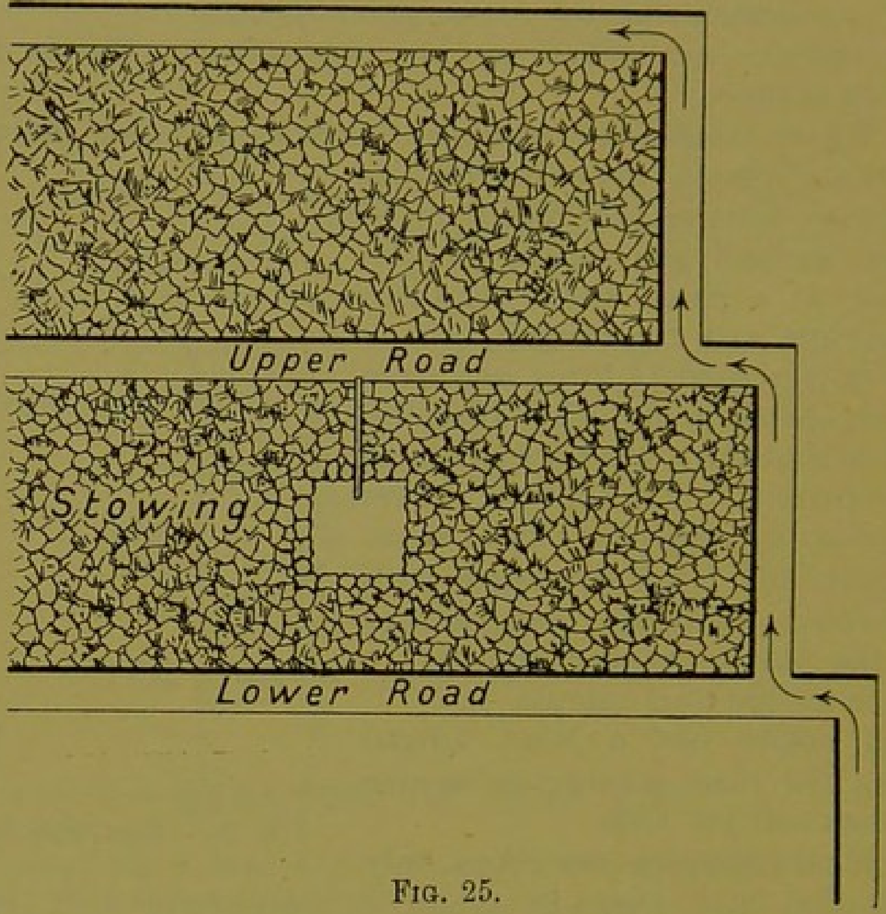

FIG. 25.

**Principles of the Method of Analysis.**—The method which we employ in our air tests is based upon the fact that the limit of inflammability of a gas (that is to say, the amount of this gas which must be added to air to obtain a combustible mixture) is a definite quantity, measurable with exactness.

M. Le Châtelier has determined this limit of inflammability for ordinary combustible gases, and he has also verified the correctness of the principle enunciated above.

The limit of inflammability of methane has been found to be 6·1 per cent.; this means that, supposing a mixture of air and methane in the proportion of 93·9 per cent. of the former and 6·1 per cent. of the latter to be placed in a test tube and a lighted match to be applied to the mouth of it, combustion will take place around the flame, but will not propagate itself much beyond. If the mixture contains 6·2 per cent. of methane the combustion is complete. If there is only 6·0 per cent. there is no sign of ignition.

Now suppose that we have a mixture of air and methane which is not inflammable, and want to determine the percentage of combustible gas. Mix some pure methane with some of the sample, and let the total volume represent 100. Try with a match whether the mixture is inflammable, and go on repeating the experiment with varying quantities of methane until the exact limit is reached. Let $x$ be the quantity added in this last case. Then

$$6{\cdot}1 - x$$

will represent the percentage of fire-damp contained in the sample. Such is the principle of the method of analysis.

The combustible part of fire-damp is composed principally of methane; sometimes there is a very small quantity of hydrogen (never more than 1 per cent., as has been proved by direct analyses), and never any ethane. Therefore, fire-damp, or rather the inflammable part of the fire-damp, may be regarded without any sensible error as pure methane when determining the limit of inflammability in practice. Therefore, in order to determine the amount of fire-damp in mine air, all that is necessary is to add methane until the limit of inflammability is reached; and although it cannot be said, strictly speaking, that the sample analysed contains such and such a percentage of fire-damp, we shall always be within the truth in saying that it behaves like a mixture with so many per cent. of methane. This will suffice, because the object of the test is not so much to make an exact analysis of the sample as to measure its approach to explosiveness. I have said that in practice it is impossible to say with certainty from the analysis by this method that the air contains so many per cent. of fire-damp, and one reason of this is that experiments have shown beyond a doubt that the composition of the air affects the limit of inflammability.

If 6·1 per cent. of methane are required with normal air to reach the limit, more than 6·1 per cent. will be required to reach this limit with air containing less oxygen or more carbonic acid than normal air. This is precisely what happens in the goaf, where an increase in the percentage of carbonic acid is accompanied by a decrease in the percentage of oxygen.

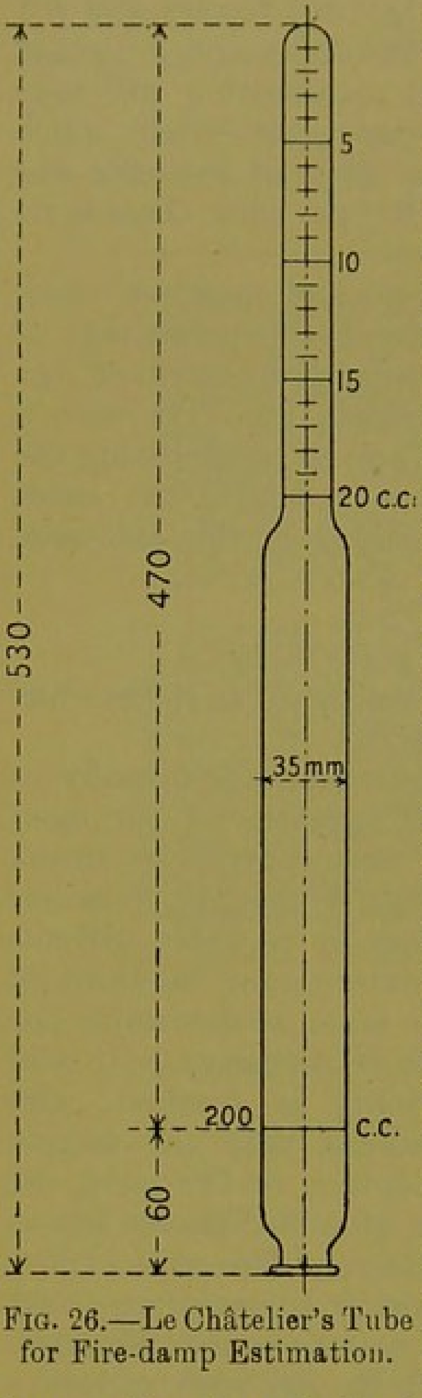

Fig. 26.—Le Châtelier's Tube for Fire-damp Estimation.

From the point of view of inflammability, the atmosphere of the goaf is in the same condition as a certain mixture of air and pure methane, which the system of analysis we are about to explain will enable us to determine, but in reality there may be much more fire-damp present than appears by this method. If it is considered desirable to ascertain exactly what this quantity is, another method of analysis must be employed. One per cent. of carbonic acid modifies the limit of inflammability by one per thousand; it is easy, therefore, to make the correction in the case of there being small quantities of $CO_2$ in the air to be analysed.

In studying the atmosphere of the goaf in order to ascertain the nature of the inflammable gases which would be introduced into the roadways in consequence of a drop in the barometer or a heavy fall of roof, it is necessary to take the exact percentage of fire-damp into account, and in this case the determination by limit of inflammability should be replaced by a second method which I will describe later on.

**Process of Analysis.**—The method depends upon the mixture of the sample with a certain quantity of methane; it is therefore necessary to have a supply of this gas for the purpose. But there is no advantage in having it pure; all that is necessary in the case of its not being pure is to determine its limit of inflammability. The best gas to use is fire-damp itself coming from a blower in the mine or collected bubble by bubble over water in a trench, as we do at Ronchamp. However, the fire-damp taken should be as pure as possible: generally speaking, the fire-damp employed by us contains from 80 to 90 per cent. of methane.

An analysis comprises two operations :—

(1) Determination of the standard or limit of inflammability of the fire-damp used as a reagent. This is the standardising.

(2) The analysis properly so called.

For these two operations we make use of the test tube which M. Le Châtelier employed in his experiments upon the limits of inflammability. It is a glass tube (fig. 26) 35 mm. (1·4 inches) in diameter, contracted at the lower end so that it may be closed with the thumb. The upper part is a cylinder of small diameter divided into tenths of a cubic centimetre, and holding 20 c.c. The total capacity of the test tube up to the circular mark 6 cm. (2·4 inches) from the opening in the base is 200 c.c.

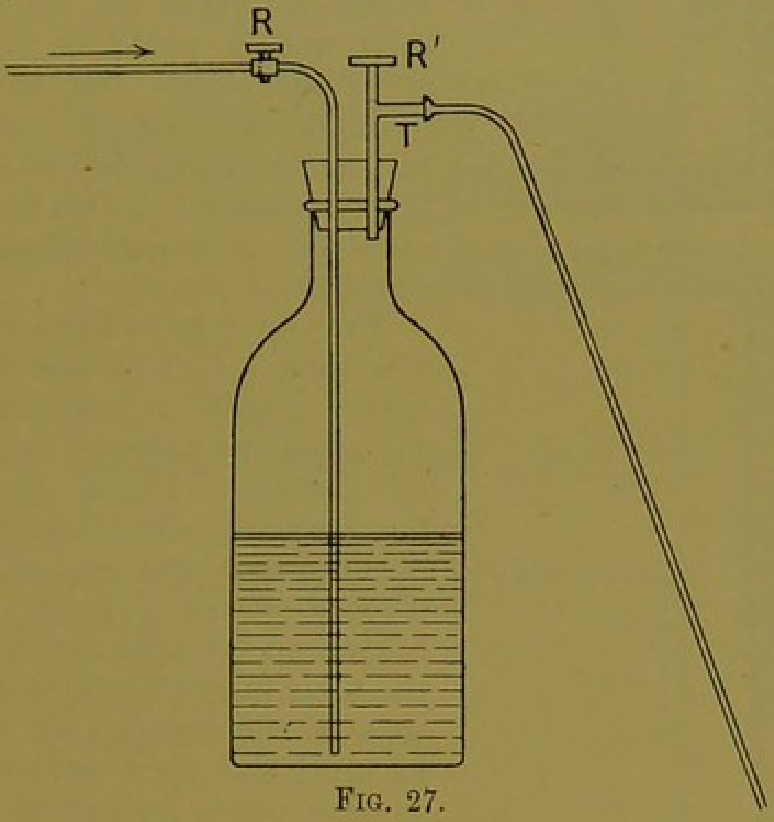

FIG. 27.

*Standardising.*—The fire-damp or methane used as a reagent is kept in a large bottle closed by an india-rubber cork with two perforations (fig. 27). Into one of the holes a tube with a tap R is inserted, and it reaches down to the bottom of the bottle; the other hole takes a screw cock R′ (fig. 28), which serves to regulate the outflow of the gas. To the nozzle of the tap is soldered a piece of capillary copper tube which reaches down to a pneumatic trough.

The tap R is placed in communication with a reservoir of water placed above it. If R and R′ are both open, the water flows in gradually, fills the bottle, and drives out the gas, which escapes from the end of the capillary tube in the pneumatic trough. The object of the capillary tube is to regulate the outflow of the gas and enable it to be stopped at the precise moment that R[1] is shut.

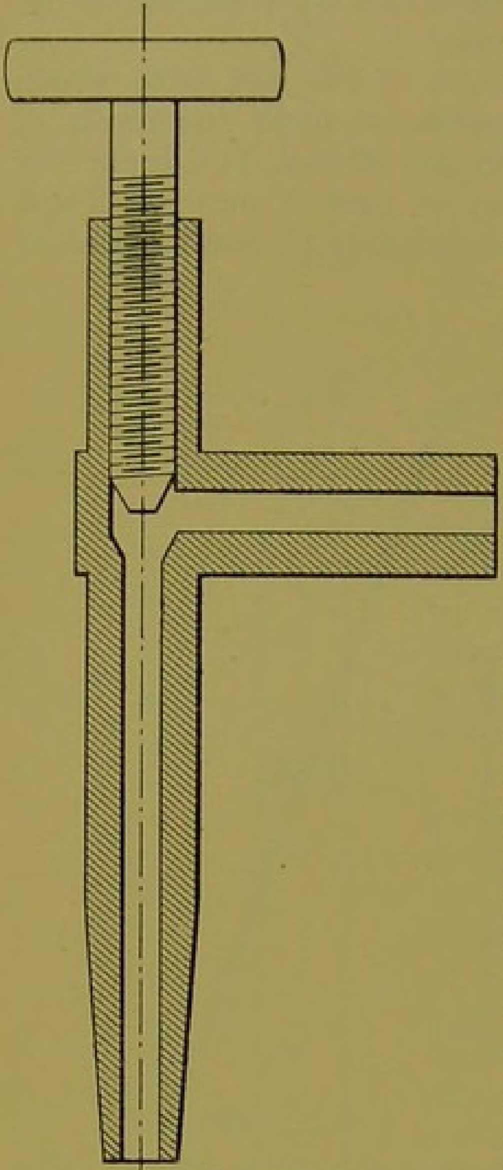

FIG. 28.

If the diameter of this tube were too large, a bubble or two of gas would be given off after R[1] was shut, and it would be impossible, or at all events very difficult, to limit the amount let out exactly to the quantity desired. Things being arranged in this fashion, the operation of standardising is performed as follows :—

The test tube is filled with water and then reversed over the pneumatic trough immediately above the capillary tube, which is bent up slightly. 14 c.c. of methane, for instance, are allowed to pass into the test tube, and then, before reading off the quantity, the tube is lowered into the water to make the level inside the tube agree with that of the trough; air is now let in until the water stands exactly at the mark indicating 200 c.c. The test tube is then taken in the right hand; closing the orifice with the thumb, it is removed from the trough, held vertically with the graduated part below, and shaken. The small quantity of water left in the tube assists in mixing. After two or three shakes, the tube being kept thoroughly closed all the time, it is held once more upright, the orifice above. The thumb is removed sharply, and a lighted match is plunged a few centimetres into the gaseous mixture, the tube being kept quite still.

One of the three following things will happen :—

(1) Combustion of the mixture for a few centimetres only.

(2) Complete combustion, the flame descending gradually to the very bottom of the test tube.

(3) No combustion.

In the first case it may be assumed that the exact limit of inflammability has been hit.

In the second case the limit has been passed, and the experiment is repeated with a smaller quantity of methane, and so on until little by little the limit is hit.

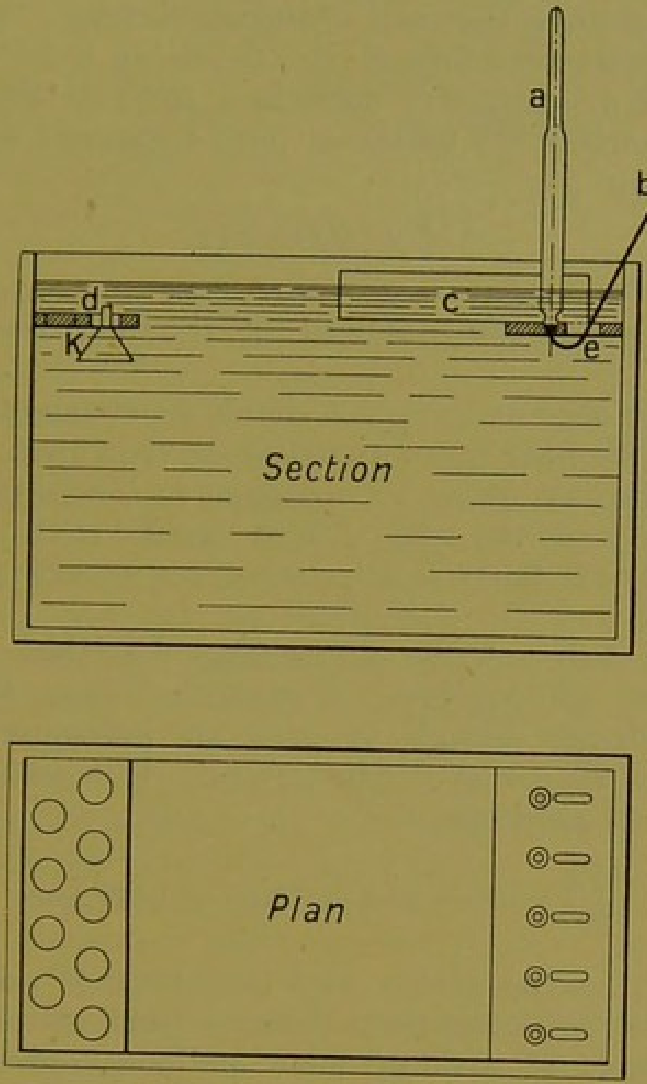

FIG. 29.—Water-bath used in Fire-damp Estimations.

In the third case, the operation is repeated as in the second, but with this difference, that the quantity of methane added is increased gradually.

The pneumatic trough which we employ is made of wood lined with lead. On two of the sides a strip of glass is let in, which enables the operator to look along the surface of the water; this renders it easier to read off the amount of gas and to bring the water in the tube to the same level as that in the trough.

The shelf, which supports the test tube while gas is being let in, is arranged so that, when the test tube is standing up vertically upon it, the level of the water in the trough corresponds exactly to the 200 c.c. mark on the tube.

Suppose 145 tenths of a cubic centimetre to be the volume necessary for reaching the limit of inflammability. We see that, as the limit of inflammability of pure fire-damp is 6·1 per cent., or 122 tenths of a centimetre cube in a total of 200 c.c., these 145 divisions contain 122 tenths of pure methane; consequently, 1000 will contain

$$\frac{122}{145} \times 1000 = 841.$$

145 is what we call the standard of the methane used as a reagent.

The fire-damp used as a reagent should be standardised at least twice a day, as we have found that the standard may alter during the course of the day, owing to variations in the temperature and in the solubility of the gas. These variations in one and the same laboratory are fairly small, and never exceed two to three thousandths.

With a test tube of the dimensions described above, it is evident that no standardising is possible unless the fire-damp employed is strong enough to give an inflammable mixture when less than 20 c.c. of it are put in. This amount, 20 c.c., corresponds to a percentage of

$$\frac{122}{20} \times 100 = 61 \text{ per cent. of pure gas.}$$

If the mine has no blower and no source of gas capable of supplying a few bottlefuls from time to time, or it is wished to avoid the trouble of making some methane, ordinary lighting gas may be employed. Its limit of inflammability is 8·1 per cent. The use of lighting gas may lead to errors, as its composition is not uniform, and, consequently, its limit of inflammability is not constant. Furthermore, it contains inflammable constituents which are condensable; and, as the gas is brought in by a capillary tube (that is to say, in the form of very fine bubbles, which remain in contact with the water and present a very large surface compared with their volume), a considerable amount of condensation may take place and modify the limit. The same thing happens to a slight extent with methane. This gas is slightly soluble in water. The small bubbles passing through the water of the test tube lose some of their combustible matter. It is therefore necessary to be careful always to do the work in the same manner, so that the amount dissolved may always be about the same. It is a good plan to have a large pneumatic trough.

It is also necessary that the laboratory in which the analyses are performed should not be liable to very considerable variations of temperature.

These are the reasons which have led us to do the standardising two or three times a day, so that the work may be done under the conditions most likely to ensure exactness.

The operation of shaking the test tube so as to mix the gases must be performed with a certain amount of method. In the first place, the test tube must be held vertically, the orifice upwards, until the gas of the narrow part has been driven up by the small quantity of water remaining. Then the tube must be shaken horizontally, and if the operator is not ready to apply the light, the tube is held vertically with the orifice downwards. As soon as he is ready for lighting he turns the tube up, but does not introduce the match until all the gas has come out of the narrow part and the water has become quiet. The tube must not be shaken too much, for the warmth of the hand will in time heat the gas, and on removing the thumb there will be a puff which may prevent the mixture from taking fire.

In order to obtain proper comparative results, it is necessary invariably to use a flame of the same size for igniting the gas, to plunge the match precisely the same distance into the tube, and always to hold the tube at the same angle.

It is well to allow an appreciable but excessively short delay between the removal of the thumb and the introduction of the match. This delay gives time enough for the pressures to become equal, but is too short to allow any mixture of the gases with the outer atmosphere. In a word, the important point is always to carry out the operation in precisely the same manner. An assistant who has to make two hundred determinations a day, as at Ronchamp, very soon manages this.

*Analysis.*—When the stock of fire-damp or methane has been standardised, we proceed to analyse the mine gas as follows:—

Two cases may present themselves—

(1) The sample is not inflammable.
(2) The sample is inflammable.

A preliminary test is therefore required in order to decide to which category the sample in question belongs. In actual practice this test is rarely made, because it is almost always known what to expect concerning the inflammability of the gas which is being tested.

Let us take the first case.

### 1. *The sample is not inflammable.*

Suppose the standard of the stock of fire-damp to be 130; a quantity of this fire-damp less than 130 divisions, say 120, for instance, is introduced into the test tube, and it is then filled up to the 200 mark with the gas to be analysed. In order to do this a cork with a metal screw-cock and a piece of india-rubber tube is fitted to the upper neck of the sample bottle, and a cork with a tap and a piece of india-rubber tube is inserted into the lower neck; this tube is put into communication with the water-supply (see fig. 30). The india-rubber tube from the top of the sample bottle is brought into the pneumatic trough and is placed under the test tube when this has to be filled. When the tube is full it is taken away and the orifice closed with the thumb. It is now shaken in the manner already explained, and the inflammability of the mixture is tested.

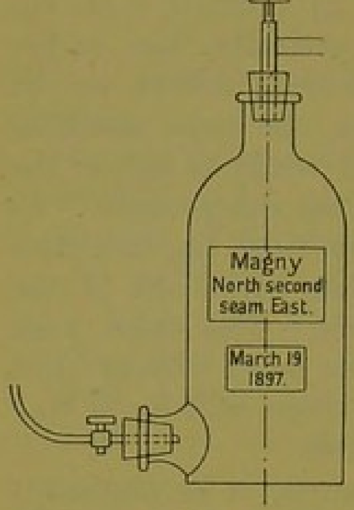

FIG. 30.

If the combustion is complete, the conclusion is that too much of the stock fire-damp was added; if there is no combustion, too little was added.

A fresh experiment is now made, adding a smaller quantity of fire-damp in the first case, a larger quantity in the second, and so approaching the limit gradually. It is found, for instance, that with 114 there is combustion, and none with 112. The limit of inflammability will therefore be 113.

If, instead of adding air from the sample, pure air had been added, 130 divisions of methane would have been required to reach the limit of inflammability; therefore the sample contains $130 - 113 = 17$ of stock fire-damp, or $17 \times \frac{122}{130}$ of pure fire-damp (6·1 per cent. being the limit of inflammability of this latter). The volume of the sample introduced was $2000 - 113 = 1887$ divisions.

As these 1887 divisions contain $17 \times \frac{122}{130}$ of pure methane, 1000 divisions will contain a quantity $x = 17 \times \frac{122}{130} \times \frac{1000}{1887}$.

This result may be generalised in a formula.

Let:—

Q be the number of cubic centimetres of stock methane which has to be mixed with air to make 200 c.c. of the mixture be at the limit of inflammability (Q is the figure representing the standard):

12·2 the limit of inflammability of pure methane for a volume of 200 c.c.:

$v$ the volume of stock methane which, when mixed with the sample and making a total volume of 200 c.c., brings the mixture exactly to the limit of inflammability:

P the percentage of fire-damp in the air to be analysed; then

$$P = \frac{Q - v}{200 - v} \times \frac{122}{Q} \times 100;$$

or

$$P = \frac{1220\,(Q - v)}{Q(200 - v)}.$$

(2) *The sample is inflammable.*

When an inflammable mixture has to be analysed, there are various ways of doing the work.

(*a*) The ordinary test tube has a circular mark denoting 100 c.c. A given volume of the sample is introduced (the standardised stock methane is useless), and then ordinary air up to the 100 c.c. mark. After mixing, the inflammability is tested successively until the limit of inflammability is reached. It is easy afterwards to calculate the proportion of fire-damp in hundredths. If 6·1 is the number of divisions necessary to reach the limit of inflammability with a total volume of 100 c.c. or 1000 graduations, it follows that the fire-damp tested was absolutely pure.

If, on the contrary, 20 c.c. or 200 divisions were required to arrive at this result, it follows that 20 c.c. contain 6·1 of pure fire-damp; consequently, 100 c.c. must contain 30·5.

As Le Châtelier's test tube does not allow quantities exceeding 20 c.c. to be measured with precision, no percentages save those between 100 and 30·5 can be determined by this method. As the method employed for non-inflammable mixtures enables percentages from 0 to 6 per cent. only to be ascertained, some further method is requisite for the mixtures of 6 to 30·5 per cent.

(*b*) This second method is applicable not only for mixtures between 6 and 30·5 per cent., but also for all inflammable mixtures. A cylindrical tube containing 100 c.c. is taken, and it is filled with the gas to be analysed; this is now transferred to a large bottle, and 10, 15, or 20 times its volume of air is added. The mixture is shaken, and it is analysed by the ordinary method for non-inflammable gases.

Knowing the proportion which the volume of the sample bears to the volume of the air mixed with it, it is easy to calculate the percentage of fire-damp in the sample.

SAMPLE PAGE OF TABLES.

Table of Proportions of Fire-damp. *Standard* 137.

| Gas Introduced. | Parts per 1000 of Fire-damp. | Gas Introduced. | Parts per 1000 of Fire-damp. |
|---|---|---|---|
| 137 | 0 | 114 | 11 |
| 136 | 0·5 | 113 | 11 |
| 135 | 1 | 112 | 12 |
| 134 | 1 | 111 | 12 |
| 133 | 2 | 110 | 13 |
| 132 | 2 | 109 | 13 |
| 131 | 3 | 108 | 13 |
| 130 | 3 | 107 | 14 |
| 129 | 4 | 106 | 14 |
| 128 | 4 | 105 | 15 |
| 127 | 5 | 104 | 15 |
| 126 | 5 | 103 | 16 |
| 125 | 6 | 102 | 16 |
| 124 | 6 | 101 | 17 |
| 123 | 7 | 100 | 17 |
| 122 | 7 | 99 | 18 |
| 121 | 8 | 98 | 18 |
| 120 | 8 | 97 | 18 |
| 119 | 8 | 96 | 19 |
| 118 | 9 | 95 | 19 |
| 117 | 9 | 94 | 20 |
| 116 | 10 | 93 | 20 |
| 115 | 10 | | |

To save the operator the trouble of working out the formula

$$P = \frac{1220(Q - v)}{Q(200 - v)}$$

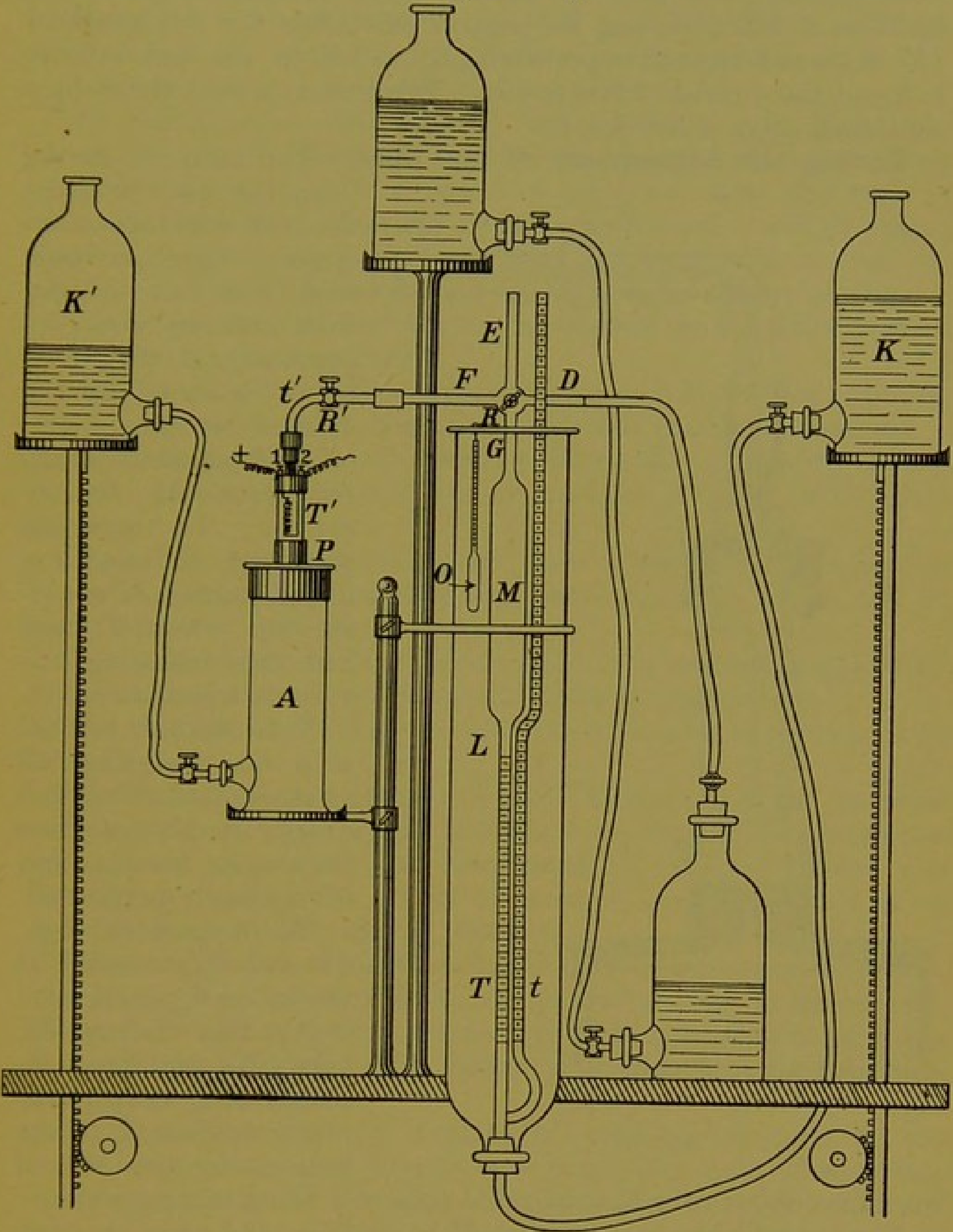

FIG. 31.—Apparatus for Estimating $CO_2$ and $CH_4$.

for each test, I have had a series of tables calculated for each standard; the percentages in the second column correspond to the number of tenths of a cubic centimetre of stock methane introduced into the test tube. Supposing that the standard is 137, for instance (137 tenths of a cubic centimetre for 200 c.c. of total volume), and that the sample to be analysed required the addition of 130 divisions, the page of the tables for the standard 137 is turned up, and opposite the figure 130 in the first column is found the number 3 (see p. 86). This indicates that the sample contained $\frac{3}{1000}$ of fire-damp.

**Testing the Atmosphere of the Goaf.**—The samples coming from the goaf or from the old workings often contain more carbonic acid and less oxygen than ordinary air; consequently, if they were to be analysed by the method of the limits of inflammability the results would be incorrect. In cases of this kind we employ a direct method of analysis, for which I have had the following apparatus constructed.

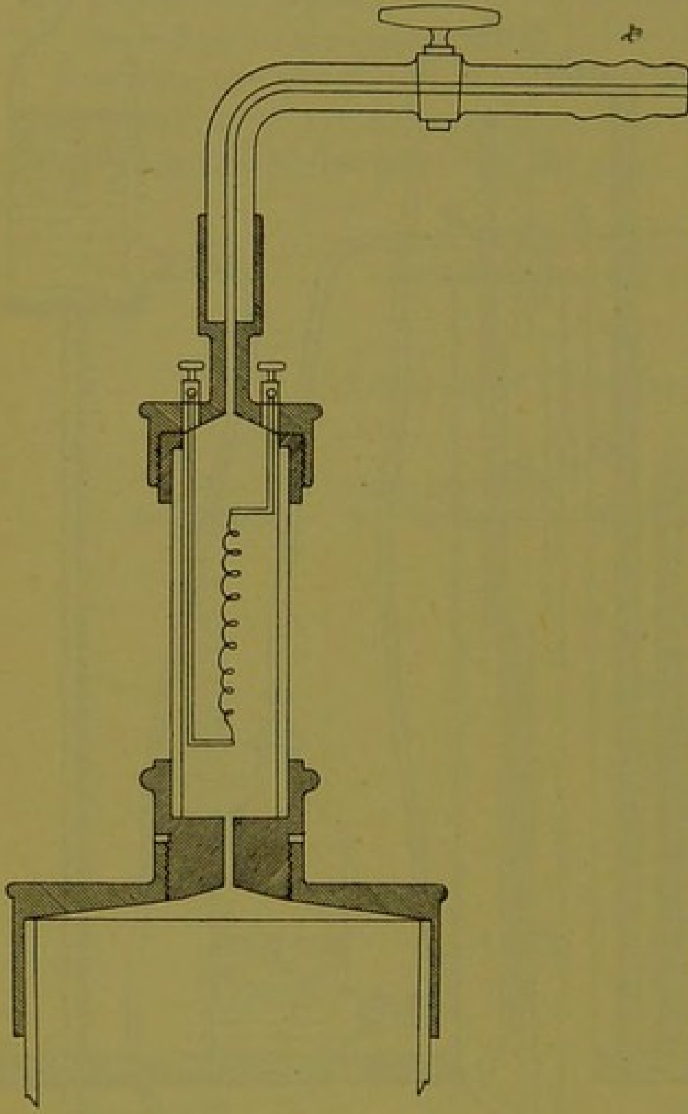

FIG. 32.

This method is suitable for analysing all mixtures containing fire-damp; it always gives very exact results, and is very easily performed.

The apparatus (figs. 31 and 32) consists of the following parts:—

(1) *The Burette.*—A tube T graduated in tenths of a cubic centimetre is joined at the bottom by the aid of an india-rubber tube to a movable reservoir K containing water.

The tube T has a wide part M at the top, and ends by a tap communicating with three branches (F, E, D) which is fitted with a two-way cock R, the barrel being so bored that any two tubes at right angles to one another can be made to communicate.

The burette holds altogether about 200 cubic centimetres, and the graduated part holds about 20 to 25 cubic centimetres. Below the graduated part a vertical tube *t* is fused on; it is graduated into millimetres, and serves to measure the pressure.

The whole of the burette is placed in a glass jacket L, through which water at a constant temperature is circulating.

A thermometer O indicates this temperature.

(2) *The Burner.*—This part of the apparatus is a glass tube about 15 mm. in diameter and 65 mm. long, with a metal cap at each end; it contains a spiral of platinum wire, the ends of which communicate with the screw connections 1 and 2 placed upon the upper cap. This has also a tube *t'* with a cock R', which is connected to the burner by thick india-rubber tubing.

The lower cap P of the burner is screwed on the third part of the apparatus, the scrubber A.

(3) *The Scrubber.*—The scrubber A is a hollow glass cylinder, with a tubulure near the bottom which communicates by a piece of india-rubber tube with a bottle K' containing caustic potash. It supports the burner, and it is filled with glass tubes.

The whole apparatus is placed upon a table, and the bottles K and K' stand upon shelves supported by racks, which can be easily raised or lowered.

Lastly, a battery of bichromate cells or a current supplied by some other source of electricity completes the apparatus.

The method of making an analysis with this apparatus is as follows:—

(1) While the two bottles K and K' are standing in their lowest positions, the tap R is turned so that F communicates with E. R' is opened, and the bottle K' is raised until the liquid just touches R'. R' is then shut, and the bottle K' is brought back to its original position.

(2) R is turned so as to bring D and G into communication. The bottle K is raised and the air of the burette is driven out. When the water arrives at the cock G, R is turned so as to make D and E communicate. The bottle K is then brought back into its original position.

(3) D is connected by a piece of india-rubber tube to the bottle containing the sample (see page 75), and when water under pressure is let into the lower tubulure, the gas contained in it is driven out. The whole tube is cleared out in this manner. R is next turned so as to put D into communication with the burette, and the sample passes into it. When about 200 cubic centimetres have passed over into it, the sample bottle is shut

off and F is put into communication with G by turning the cock R.

Time is given for the temperatures to equalise, and then the operator notes down the volume of air in the burette, the height of the water in the manometer *t*, and the temperature.

(4) The cock R′ is opened and the bottle K raised. The gas is driven, first into the burner and thence into the scrubber. When the water has come up to the cock R, the bottle K is lowered and the bottle K′ raised, then K is raised; and so on several times, allowing the gas to remain in the washer a short time on each occasion. Finally, things are brought back to what they were originally. The temperature, the pressure, and the volume are noted. From the data so obtained the quantity of $CO_2$ contained in the air submitted to analysis may be calculated.

(5) The procedure explained in the preceding paragraph is repeated, save that the electric current is turned on as soon as the platinum spiral is no longer bathed by the liquid. The fire-damp burns, and in proportion as the carbonic acid is formed, it is absorbed by the washer. Lastly, the current is shut off, and after the burner has been allowed to cool sufficiently to prevent its cracking, the liquid is brought back to R′, which is shut. The pressure, temperature, and volume are again read off. All the data for calculating the analysis have now been obtained.

The complete operation lasts about twenty minutes.

From the total loss in volume the amount of carbonic acid found in the first part of the analysis has to be deducted; the remainder of the loss is due to the fire-damp having been burnt into carbonic acid and aqueous vapour.

One volume of methane requires two volumes of oxygen for complete combustion; and as all the products are absorbed, the diminution in volume will be equal to three times the volume of methane.

It is evident that the process admits a great amount of precision, because the error, which cannot be large, will in any case be divided by three.

In order to have every guarantee that the analysis has been correctly performed, the operator must be certain that the air sample contains enough oxygen to burn the fire-damp which is in it. It may be necessary, therefore, to determine the percentage of oxygen. For this purpose we employ the very simple determination by the pyrogallate of potassium method.

The apparatus is a graduated burette G, ending in a bulb (fig. 33), the total capacity of the tube and bulb being 100 c.c.

At the bottom there is a tap; at the top also there is a tap, pierced not only by the ordinary hole, but also with an opening T following the longitudinal axis. Above the tap is a funnel; the bottom of this funnel can be made to communicate with the bulb by the ordinary passage through the tap, or with the external atmosphere through the tubulure T.

The burette is supported in a vertical position upon a stand. The part BG having been filled with water, the taps R and R′ are turned so as to shut off the bulb B from the atmosphere. The burette is placed on its stand, and the lower end K is made to dip a few centimetres into the pneumatic trough. T is then put into communication by an india-rubber tube with the screw-cock of the sample bottle.

Water is let into this bottle by the lower tubulure; the screw-cock is opened and the air in the india-rubber tube is driven out completely. R is now turned, so as to put B into communication with T. R′ is opened: the air of the sample enters into the burette, whilst the water contained in it sinks into the pneumatic trough. When a certain quantity has passed over into the burette, say 90 to 100 c.c., R is shut, so as to isolate B completely, and the connection of T with the sample bottle is shut off, after the end of the india-rubber tube has been closed by a pinchcock, and the screw-cock of the sample bottle turned down. All this time R′ remains open.

A stream of water from a reservoir in the laboratory is now allowed to play upon the bulb B, so as to bring the whole of the burette to a temperature which will be the same for all the operations.

When the volume in the burette remains stationary, it is read off, and the quantity and the pressure of the gas are noted. The tap R′ is closed; a concentrated solution of pyrogallic acid is poured into the funnel, and some pieces of caustic potash are put into it.

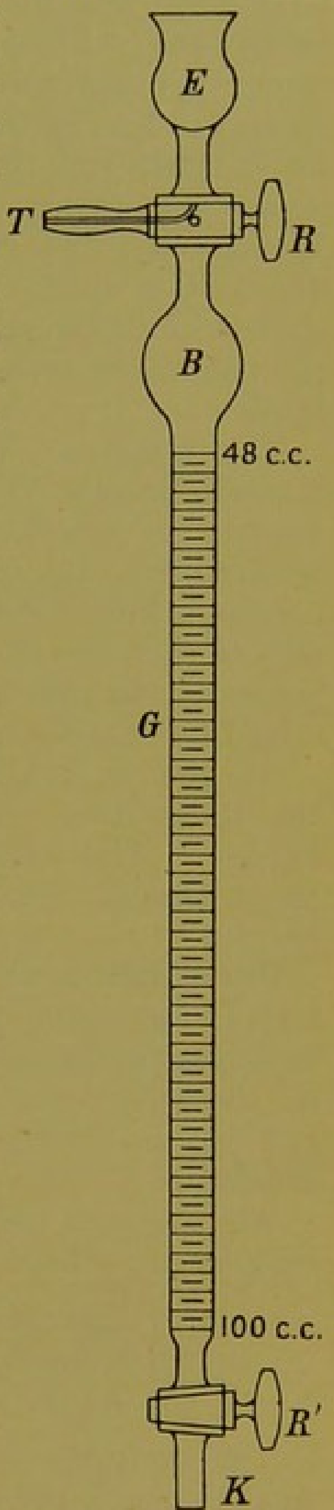

FIG. 33.—Burette for Estimation of $CO_2$ and Oxygen.

Then E is put into communication with B, and the pyrogallic acid flows down into the burette, saturating itself with caustic potash on the way. Pyrogallate of potassium is formed, and this absorbs the oxygen and turns brown. From time to time R′ is slightly opened to let out the coloured liquid from the burette, and draw in a fresh supply. Of course, fresh pyrogallic acid and fresh potash are put into the funnel in proportion as they are used up. When about two funnelfuls of pyrogallic acid have been introduced R is shut. The burette is removed from its stand, and shaken in all directions for an instant, and then put back upon the pneumatic trough. R′ is opened, and the water rises into the burette.

The funnel is filled with water, and this is allowed to run down into the burette ; this operation is repeated until the water in the burette is absolutely colourless. R is now shut and the bulb watered from the reservoir, in order to obtain the same temperature as before. When the volume remains stationary, it is read off and the pressure noted. After correction has been made for pressure, the true volume is ascertained and the diminution determined by subtraction.

As the pyrogallic employed contains an excess of potash, the diminution includes the carbonic acid as well as the oxygen. The amount of carbonic acid has to be determined by a similar operation, in which potash only is used as the reagent.

**Organisation of the Analytical Service.**—We have said the samples are taken by subordinate officials. The bottles, arranged in boxes, and according to districts, are sent to the laboratory in the evening. The samples are always taken towards the end of the shift, so as to have the highest percentages of fire-damp.

After a day's stoppage, or a stoppage of the fan, supplementary samples are taken :—

(1) Towards the end of the period of stoppage.
(2) Some hours after starting.
(3) At the end of the shift.

The analyst is any one of the employees whom we have trained to the work. The operations, furthermore, are so simple that anyone may be taught them in a day or two.

As soon as the analyses are finished, the analyst makes three copies of his report. One goes to the manager, another to the principal under-manager, and a third to the under-manager of the pit. If any sample shows a serious increase compared with that of the day before, he would at once advise the under-manager.

At the laboratory office a daily register is kept in which are written down all the operations day by day.

The standardising is done two or three times a day, and the results inscribed in the journal. The entries are made as follows:—

Date..........................................................

Standardising at..........................................o'clock A.M.

| | |
|---|---|
| Yes. | No. |
| 138<br>136 | 134 |
| | Mean 135 |

| | | | | |
|---|---|---|---|---|
| Magny pit: Return air from the first seam east | Yes | 130<br>128<br>Mean 127 | No 126 | $x=4$ |

This means:—

(1) That the experiments were made with the stock fire-damp of a standard of 135.

(2) That for the sample of air from Magny pit, combustion was obtained on adding successively 130 and 128 divisions of the stock fire-damp, and none with 126. The limit of inflammability is therefore 127, and the proportion $x$ of fire-damp in the sample is $\frac{4}{1000}$ (this figure is given by one of the tables).

With a person accustomed to the work, three or four experiments usually suffice to obtain a result. With a great deal of practice a person can tell by noticing the velocity with which the flame goes down the tube how much the quantity of fire-damp has to be diminished.

In addition to the daily journal, the analyst keeps up day by day another series of documents. Curves showing the percentages are constructed for each district, and these curves, of which the abscissæ represent days and the ordinates percentages found, are placed below the barometric curves.

At the end of each month, at the same time as the ventilating currents are being measured, samples are taken from the main return currents, in order to determine the total quantity of fire-damp issuing from the mine at that time.

For each district a special curve, of which the ordinates are proportional to the mean percentage of the month (result of the daily analyses) and the abscissæ represent months, enables a comparison to be made between the curve showing the output of the district and the curve representing the quantity of air sent into the district per ton of coal extracted.

# III.—THE EXAMINATION OF MINE AIR.

BY

J. S. HALDANE, M.D., F.R.S.

# THE EXAMINATION OF MINE AIR.

## I. METHODS OF ANALYSIS.

**Introduction.**—In the analysis of mine air it is frequently the case that the results, to be of real use, must be accurate to within very narrow limits. When the sample to be analysed differs considerably in composition from pure air, and when each of the constituent gases is present in considerable proportions, great accuracy is certainly not needed, and the ordinary "technical" methods of analysis are quite sufficient. But most samples are likely to be from air-ways, where the air usually differs very little in composition from pure air, so that what might at first sight appear to be only small errors are in reality very serious.

Let us suppose, for instance, that a gas-volumetric method is used which permits of the common margin 0·2 or 0·3 per cent. in either direction. As the deficiency of oxygen or excess of $CO_2$ in even the return air-ways of a mine is often less than 0·2 per cent., the determinations of these gases would only mislead, if they were made with a view to investigating such questions as the production of heat (see p. 137), or the mode of distribution of air in the mine. Similar determinations of other constituents, such as carbonic oxide or fire-damp, might easily be equally misleading.

It will be evident from what has been said that for mine air analysis a very exact method is generally needed. A second practical requisite, however, is that the method used should be rapid, so that a number of determinations can be quickly made one after the other—if necessary, in duplicate. A third requisite is that a convenient and reliable method of obtaining and transporting samples of mine air should be available, unless the determinations can be made on the spot underground.

The apparatus and methods described in the following pages have been designed with a view to fulfilling these conditions as far as possible.

**Determination of Oxygen, Carbonic Acid, Nitrogen, Firedamp, etc.**[1]—1. *Collection of Samples.*—The samples are collected in ordinary two-ounce stoppered bottles made of clear glass. These bottles hold about 70 c.c., which is enough of air for three analyses, in case it should be necessary to repeat any determination. A supply of bottles of this size can be carried in the pockets. The stopper of each bottle is greased with vaseline, and after the sample is taken should be turned round until no air-channels are visible in the vaseline. The stopper is held in position by a fairly stout elastic band passed over it, and a gummed label is placed on the bottle as shown in fig. 34.

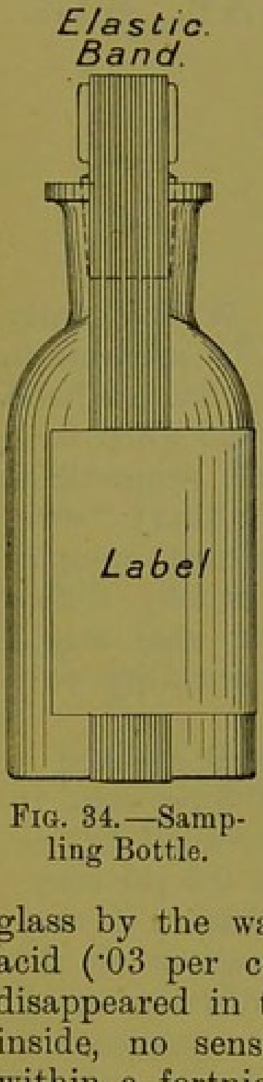

Fig. 34.—Sampling Bottle.

The bottles *must* be dry, and should also be clean. They should be cleaned with a brush, rinsed with clean (preferably distilled) water, and completely dried. If a bottle is wet and dirty an appreciable amount of carbonic acid may be produced, and of oxygen may disappear, by bacterial action. To quote an example, after four days the carbonic acid had increased by ·05 per cent., and after ten days by ·12 per cent., in a wet and dirty bottle. If, on the other hand, the bottle is wet and clean, the carbonic acid very gradually disappears, as it is absorbed by alkali dissolved out of the glass by the water. For instance, the whole of the carbonic acid (·03 per cent.) in a sample of pure atmospheric air had disappeared in twelve days. In *dry* bottles, even though dusty inside, no sensible alteration of the contained sample occurs within a fortnight or more.

The rubber band round the stopper is specially necessary in the

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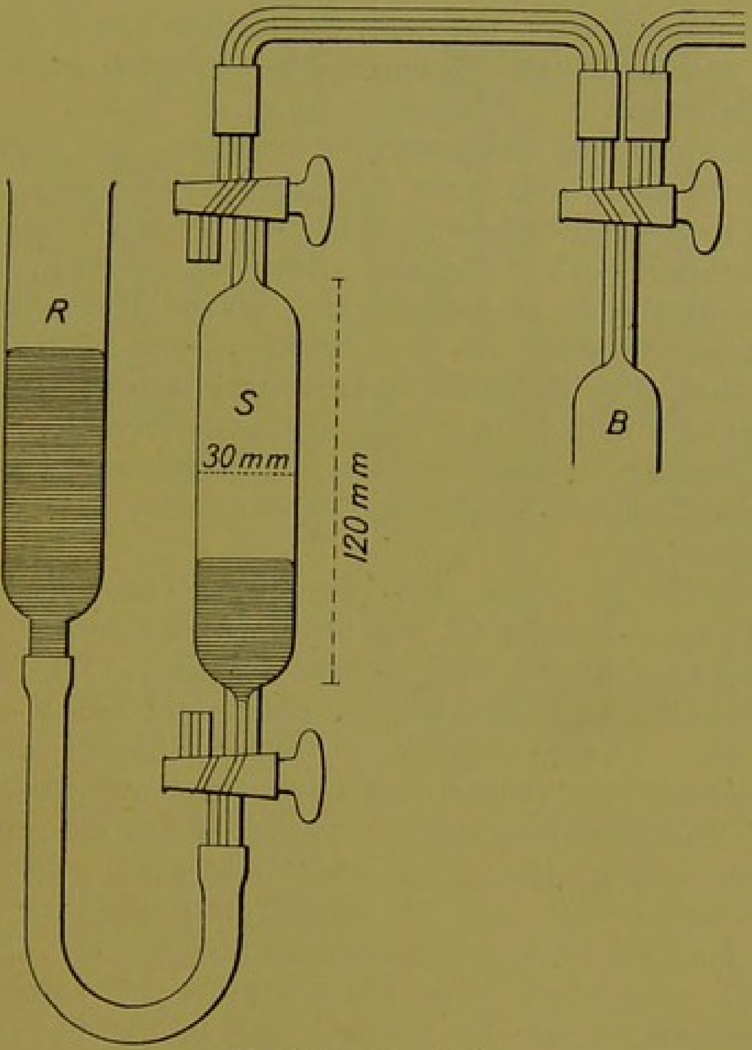
[1] The method here described is similar in principle to that which I originally published in the *Journal of Physiology*, vol. xxii. p. 465, 1898. As the result of further practical experience, however, a number of improvements have been introduced. The portable apparatus shown in fig. 38 has not hitherto been described.

case of samples taken in mines, as the stopper might otherwise be blown out in consequence of the diminution of atmospheric pressure during the ascent to the surface.

The sample is collected as follows. One end of a piece of rubber tubing about 2 or 3 feet long, and $\frac{1}{8}$ or $\frac{1}{4}$ inch in internal diameter, is introduced into the bottle, the other end being held in the mouth.



S = Sampling tube.
R = Mercury reservoir.
B = Gas-burette.

FIG. 35.—Sampling Tube, showing Mode of Connecting with Burette.

A deep breath of air is then sucked in through the tube, so that the bottle is completely washed out by the mine air. The tube is removed while the air is being still sucked in, so as to avoid any risk of the breath passing backwards into the bottle. The stopper is then inserted, turned round, and secured as already described, and the particulars written on the label. Care must, of course, be taken that the sample is not contaminated in any way through the presence of persons or lamps. When the gas to be examined is issuing from a pipe or bore-hole, a sample may be obtained by holding one end of the rubber tube inside the pipe (or attaching it to a glass tube passing through a cork or plug of clay fixed in the pipe), and placing the other inside the bottle. The gas then blows through the bottle, which should be inverted if, as is often the case, the issuing gas is lighter than air. The stopper must, of course, be inserted as soon as the tube is withdrawn.

When samples are collected over water, the carbonic acid percentage found is not quite reliable, as the water or the wet bottle may have absorbed some of the gas, or the water may have given up carbonic acid to the air. Samples collected in metallic vessels are unreliable as regards the oxygen if, as is often the case, there is oxidation of the metal going on inside. Glass sampling tubes, provided with a three-way tap at each end (see fig. 35), and of about 70 c.c. capacity, are convenient in certain cases, and render a mercury bath unnecessary; but for underground work they are fragile and troublesome to carry, besides being expensive.

2. *Description of Apparatus* (fig. 36).—The sample of air is measured in a gas-burette (A, fig. 36) about 32 inches (800 mm.) long, provided at the top with a three-way tap. The upper wide part is about 1 inch (25 mm.) in diameter, and has a capacity of about 15 c.c. The graduation, which is to ·01 c.c., extends down the narrow part (which is 3·5 mm. in bore) from about 15 to 21 c.c. There are also marks at the first five c.c. on the wide part. With such a burette it is possible to read without the aid of a telescope to ·001 c.c. A magnifying glass or a pair of spectacles may be required, however; and a good light behind the burette is needed. The burette must, of course, be most carefully graduated by the maker,[1] and should be checked by reversing the burette, filling with mercury, and weighing successive portions of about 1 c.c., which are allowed to flow out through the tap into a weighed vessel, any hanging droplet of mercury being carefully brushed down. In estimating the volume from the tap to the first graduation mark, it is necessary to add ·004 c.c. to the volume calculated from the weight of mercury which flows out between these points, as the mercury meniscus has its convexity towards the tap when the burette is in its natural position. During the whole operation the temperature

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[1] The apparatus here described can be obtained from Messrs Müller, Orme, & Co., 148 High Holborn, London, W.C.

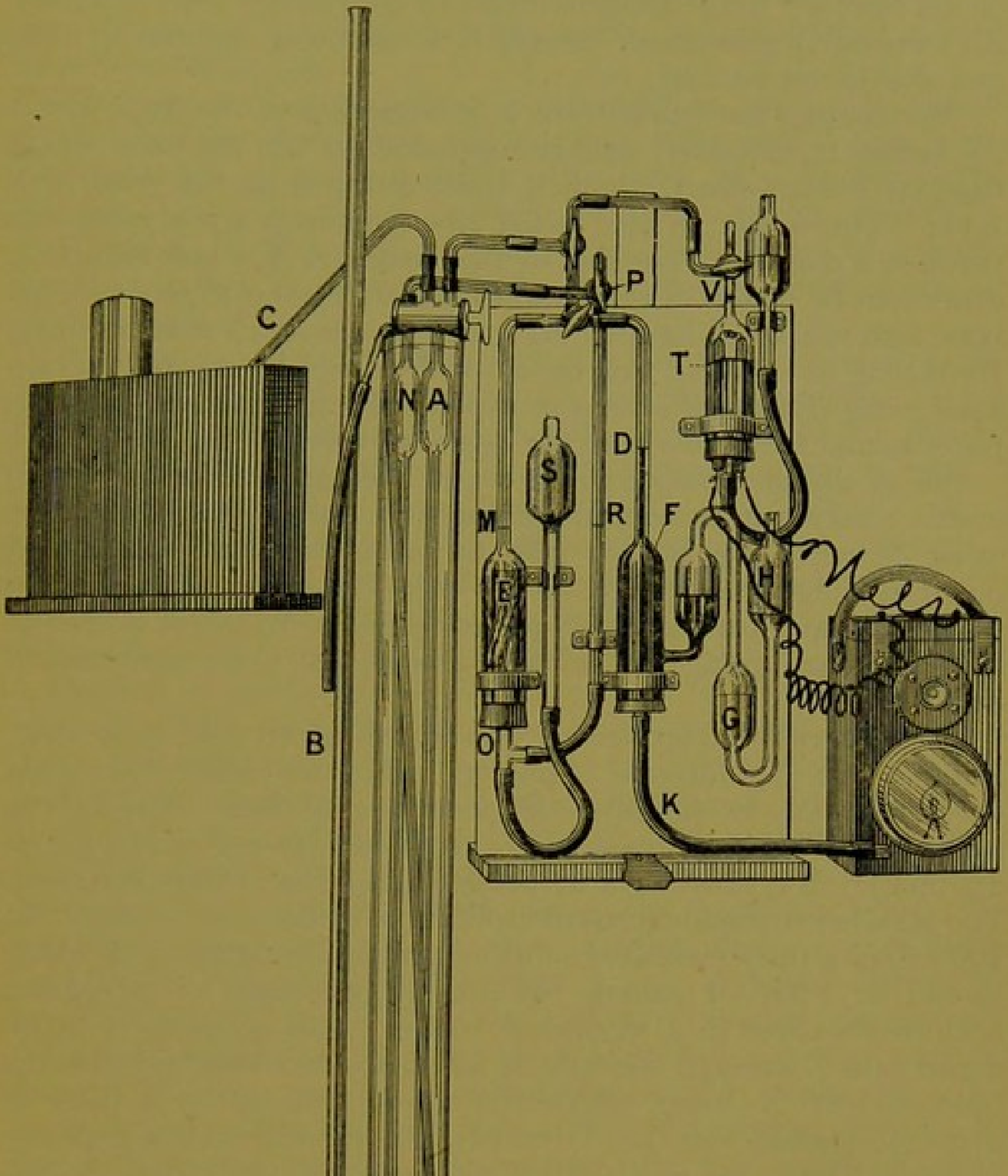

Fig. 36.—Apparatus for Air Analysis.

of the mercury in the burette must, of course, be kept constant. An irregularly graduated burette is a source of endless trouble, and should not be used.

Surrounding the gas-burette is a water-jacket, which is about 2½ inches in diameter, and is supported by an ordinary clamp fixed on a retort-stand, which is itself clamped to the front of a table. The water in the jacket can be mixed by blowing air through a glass tube passing to the bottom. The gas-burette is connected by means of thick-walled rubber tubing of about 3 mm. bore with the levelling-tube B, which is about 15 mm. in bore. By raising or lowering this tube, which is held by a spring clamp fixed to the retort-stand, gas is expelled from or drawn into the burette, and the pressure in the latter adjusted.

One of the three-way connections of the tap on the burette is used for taking in the sample through the curved tube C, and the other connects the burette with the absorption and combustion pipettes, which are arranged as shown. The connecting tubes are of about 2 mm. bore, and are joined together by short pieces of stout rubber tubing of the best quality and clean and smooth inside.

The absorption pipettes E and F are about 100 mm. long, and 30 mm. in internal diameter. They are filled with glass tubes in order to increase the absorbing surface. The tubing leading up from them must have a bore of about 2 mm. (1·8 to 2·2 mm.). E is filled with 20 per cent. solution of caustic potash. The alkaline pyrogallate solution filling F is made as follows. In 100 c.c. of a fully saturated solution (the specific gravity of which should be 1·55) of caustic potash, 10 grammes of pyrogallic acid are dissolved in a stoppered bottle. This solution is introduced into F through the tube K by means of a large pipette, the open end of K being afterwards securely closed by a piece of glass rod pushed well in. G and H, which have each a capacity of about 30 c.c., are partly filled with some of the strong potash solution. This not only protects the pyrogallate solution from the oxygen of the air, but also prevents the solution from becoming gradually diluted with water, as is the case when water is placed in G and H.

The solutions last for a very large number of analyses; but when it is found that the oxygen absorption is becoming at all sluggish the pyrogallate solution should be changed. It is particularly important that this solution should be made exactly in the manner described. If the potash is at all weak the absorption of oxygen is much slower, and such a solution ought to be at once rejected. The strong solution has the further advantage that its coefficient of absorption for gases is very low. It produces no trace of carbonic oxide, and is a most perfect absorbent for oxygen.

The pressure in the burette is adjusted by using the potash pipette as a pressure-gauge, and bringing the potash before every reading of the burette exactly to the mark M. As the potash solution has only about one-tenth of the specific gravity of mercury, and with a tube of 2 mm. bore the level can be adjusted very accurately, it is evident that the pressure-gauge is exceedingly sensitive.

In order to make the readings of the burette entirely independent of changes of temperature and barometric pressure during the analysis, a control tube N, which stands beside the burette in the water-jacket, is employed. The connecting tubes from N are of the same diameter as those from the gas-burette; and a three-way tap at P makes it possible to equalise the pressure in N with that of the atmosphere. By means of the T-tube O the potash solution is brought into connection with N. At the beginning of the analysis the potash is adjusted to the mark R by raising or lowering the potash receiver S, P being open to the air. P is now turned so that the control tube is connected with the potash tube only, and is not again opened till the analysis is complete. Each time a reading of the burette is made the potash is brought to the mark R by raising or lowering S. The potash in the absorption pipette is then brought to the corresponding mark M by adjusting the levelling tube. The readings of the burette are thus compensated by mechanical means for variations of temperature and pressure during the analysis, so that temperature and pressure may be disregarded. The lower part of the control tube is kept full of water, and the burette is also kept moistened sufficiently to make its inner surface wet without fouling the mercury meniscus, so that the air in both the burette and control tube is always saturated. The water used for moistening the inside of the burette should be slightly acidified with sulphuric acid, and occasional remoistening is necessary.

The use of a control tube in gas analysis was first described by Williamson and Russell,[1] who employed a mercury pressure-gauge. The same principle in a much improved form was applied in Petterson's apparatus,[2] in which the movement of a drop of oil in a horizontal tube connecting the burette with the control tube is used as a pressure indicator, and extreme accuracy

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[1] *Journ. of Chemical Society*, 1868, p. 238.

[2] *Zeitschr. f. analyt. Chem.*, vol. xxv. pp. 467, 479.

in the adjustment of the pressure in the burette to that in the control tube is thus attained. The Petterson apparatus is, however, difficult to manage, and possesses other disadvantages.

The combustion pipette T, which is filled with mercury, is about 80 mm. long by 30 mm. in internal diameter, and contains a spiral of three turns of very fine platinum wire, which can be heated by an electric current to a white heat, so as to completely burn any combustible gas present in the sample under examination. The current is led to the spiral through the two glass tubes shown, which are open above but sealed below and filled with mercury. Through the closed ends two pieces of stout platinum wire pass. These are connected by copper wires with a small accumulator or other convenient source of current. The spiral is fixed at the ends to V-shaped pieces of stouter platinum wire, which are thrust down the open ends of the glass tubes. It is thus easy to replace the spiral, should it by chance become fused by passing too strong a current.

To heat the wire, about three to four volts are needed; and a variable resistance should be provided, so that the current can be gradually increased until the spiral reaches a white heat. An ordinary hand electric lamp, arranged as shown in fig. 36, answers very well.

The method of burning combustible gases by means of a platinum spiral was first introduced by Coquillion[1] about twenty-five years ago for the estimation of fire-damp. It presents the advantage that, where the volume of combustible gas present is less than sufficient to form an explosive mixture with air, it is not necessary to add hydrogen or detonating gas, as in the older methods of analysis, since, however small the proportion of combustible gas present may be, the combustion occurs very rapidly in the presence of the heated platinum. The addition of hydrogen, oxygen, etc., can thus be entirely done away with in gas analysis, and only air need be added when oxygen is required for combustion. Since the composition of the outside air is practically constant, except during fogs in large towns, this is a great advantage, as errors arising from slightly impure oxygen, hydrogen, etc., or from the burning of nitrogen in exploding the sample, are entirely avoided, as well as the trouble of preparing pure oxygen and hydrogen.

For transferring a sample of air from a bottle to the gas-burette the mercury trough shown in fig. 37 is needed. It is made of two slabs of wood, which are so cut out that when they are screwed together a narrow slit, open at the top, is left between

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[1] *Comptes Rendus*, vol. lxxxiv. p. 458, 1877.

them. Into this slit, which is filled with mercury, passes a bent glass tube, as shown, by means of which the sample is transferred from the bottle to the burette. At one end of the upper part the slit expands into a rectangular space $2\frac{1}{2}$ inches long by $1\frac{1}{4}$ inches wide and $1\frac{1}{2}$ inches deep, in which the neck of the bottle is received. The slit itself is $\frac{1}{4}$ inch wide by 6 inches long and

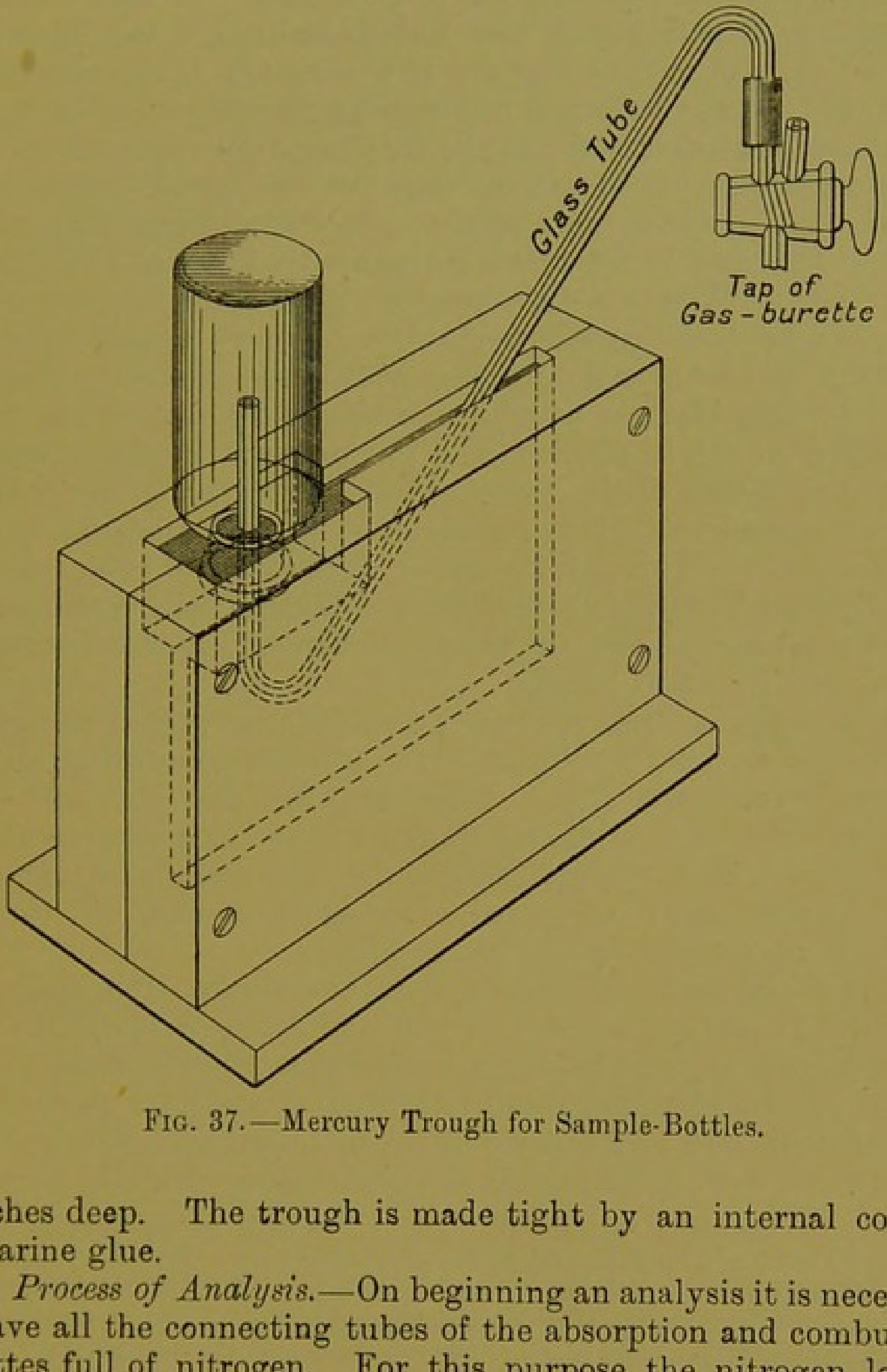

Fig. 37.—Mercury Trough for Sample-Bottles.

4 inches deep. The trough is made tight by an internal coating of marine glue.

3. *Process of Analysis.*—On beginning an analysis it is necessary to have all the connecting tubes of the absorption and combustion pipettes full of nitrogen. For this purpose the nitrogen left at the end of the previous analysis is always kept—preferably in the

pyrogallate absorption pipette—and the connections washed out with this gas, in case any oxygen should have diffused in through the rubber joints, as happens if the apparatus has stood for long. The pyrogallate, mercury, and potash are successively brought to the marks D, V, R, and M on the gauges of the absorption and combustion pipettes and of the control tube. The tap connected with the control tube is then closed to the outer air. The excess of nitrogen is now expelled through the bent tube attached to the top of the burette, mercury being allowed to follow till the bent tube is completely filled with it. The top of the burette is then closed and the levelling tube replaced.

The next step is to invert the neck of the sample-bottle under mercury and remove the stopper, care being taken that no air enters. This may be done most conveniently in a small Wedgwood mortar about 3½ inches in diameter. The bottle is now closed with a finger and transferred to the mercury trough, and the bent tube is introduced into the neck from below.[1] The tap of the burette is then turned, and about 20 c.c. of air taken in. After the tap has been closed the pressure inside is roughly adjusted by means of the levelling tube. The tap of the burette is then opened, so as to connect the burette with the potash pressure-gauge. This and the gauge of the control tube are then carefully readjusted, after blowing air through the water-jacket, and the volume of the air taken is read off on the burette to within ·001 c.c., and noted.

The sample is then passed over into the potash absorption pipette, the mercury in the burette, however, not being allowed to pass beyond the tap. After drawing the air backwards and forwards two or three times, so as to wash over any carbonic acid in the connecting tube, the sample is returned to the burette and re-measured, after again blowing air through the jacket and adjusting the two gauges.

If the sample is air containing only one combustible gas, such as fire-damp, and not more than will extinguish a lamp, the next step is to pass it over into the combustion pipette, turn on the current till the platinum spiral is white hot, and pass part of the air backwards and forwards for about half a minute, then shut off the current, and return the air to the burette, carefully bringing

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[1] When the sampling tube shown in fig. 35 is used no mercury trough is needed. The sampling tube and mercury reservoir are arranged as shown in the figure, and held in position by spring clamps. The air is first expelled from the connecting tubing through the free openings of the three-way taps of the sampling tube. The taps are then turned and the sample taken into the burette, the reservoir being at the same time raised or lowered so as to equalise the pressure.

the mercury in the pipette back to the mark. The pressure is then adjusted by means of the gauges of the potash pipette and control tube, and the volume read off. The $CO_2$ formed is then absorbed in the potash pipette (including the small portion left in the connection to the combustion pipette, which is washed out with air free from $CO_2$) and the volume again measured. As a small fraction of the fire-damp will have been left in the connections to the potash pipette when the combustion was made, and will thus have escaped combustion, the air is passed once more through the combustion process and the potash pipette, and any further diminution of volume noted. In exact experiments a little time should be allowed for the connecting tube to cool before adjusting the mercury level in the combustion pipette after it has been used.

The sample is now passed into the pyrogallate pipette, and backwards and forwards two or three times: the connections to the potash and combustion pipettes are washed out with nitrogen, which is passed back to the pyrogallate pipette, and after bringing back the pyrogallate to the mark, and adjusting the pressure in the burette as usual, the volume is again read off. The process should be gone through again, to make sure that no oxygen is left unabsorbed.

If, as is usually the case, some slight correction is needed in using the burette, this correction should be made. It will probably only affect sensibly the oxygen result.

The following is an example of an analysis of air from a colliery return air-way :—

| | |
|---|---|
| Volume of air taken . . . | 20·024 c.c. |
| After $CO_2$ absorbed . . . | 19·982 |
| ∴ $CO_2$ = | 0·042 = 0·21 per cent. |
| After combustion . . . . | 19·480 |
| ∴ contraction = | 0·502 |
| After $CO_2$ absorbed . . . | 19·230 |
| ∴ $CO_2$ formed = | 0·250 |
| After second combustion and $CO_2$ absorption . . . . | 19·206 |
| ∴ difference = | ·024 |
| Total difference (·502 + ·250 + ·024) = | 0·776 |
| ∴ $CH_4$ = ·776 × $\frac{1}{3}$ = | 0·259 = 1·29 per cent. |
| and $O_2$ used up = ·776 × $\frac{2}{3}$ = | 0·517 |

After $O_2$ wholly absorbed . . . 15·642

∴ $O_2$ = 3·564 + 0·517 = 4·081
= 20·38 per cent.

| Result:— | |
|---|---|
| Oxygen . . . | 20·38 |
| Carbonic acid . . | 0·21 |
| Fire-damp . . | 1·29 |
| Nitrogen . . . | 78·12 |
| | 100·00 |

In the above example ordinary fire-damp ($CH_4$) and no other combustible gas was present in the air. This is indicated, though not absolutely proved, by the fact that the contraction on combustion was, within the error of experiment, exactly double the $CO_2$ formed. To obtain absolute proof it would be necessary to make a second direct oxygen determination, without burning the fire-damp, and show that the oxygen result obtained in this way was the same as that found by the above method. This would prove that the oxygen used in the combustion was equal in volume to the contraction, and double the carbonic acid formed; and hence that the combustible gas was equal in volume to the carbonic acid formed, and could only be methane ($CH_4$).

A direct oxygen determination would also be necessary in any case in which the contraction on combustion, as compared with the carbonic acid formed, did not correspond to a gas or mixture of gases known to be present.

If the $CO_2$ formed were double the contraction, the only gas present would be carbonic oxide; and the combustible gas in air vitiated by gases from heated coal is sometimes nothing but carbonic oxide. The same remark applies to air vitiated by gases given off from a number of explosives, though a little hydrogen is in some cases mixed with the carbonic oxide. If more than three combustible gases be present, it is not possible to determine them separately by the combustion method, though the information obtained may often be sufficient for practical purposes.

The following is an example of an analysis of a sample of air vitiated by the products of combustion of gelignite and also by respiration, etc. The sample was taken in a "rise" in a metalliferous mine, five minutes after eight holes had been blasted.

*First Analysis.*

| | | |
|---|---|---|
| Volume taken | 20·298 c.c. | |
| After $CO_2$ absorbed | 19·740 | |
| ∴ $CO_2$ = | 0·558 = | 2·75 per cent. |
| After combustion | 19·707 | |
| ∴ contraction = | 0·033 = | 0·165 per cent. |
| After $CO_2$ absorbed | 19·659 | |
| ∴ $CO_2$ formed = | 0·048 = | 0·24 per cent. |
| After residual $O_2$ absorbed | 15·668 | |
| ∴ residual $O_2$ = | 3·991 = | 19·66 per cent. |

*Second Analysis.*

| | | |
|---|---|---|
| Volume taken | 20·294 | |
| After $CO_2$ absorbed | 19·736 | |
| ∴ $CO_2$ = | ·558 = | 2·75 per cent. |
| After $O_2$ absorbed | 15·719 | |
| ∴ $O_2$ = | 4·017 = | 19·795 per cent. |

From the two oxygen determinations it follows that the oxygen consumed in the combustion of the gas in the sample was 19·795 − 19·66 = 0·135 per cent. The contraction on combustion was 0·165 per cent., and the $CO_2$ formed 0·24 per cent.

In the explosion of gelignite and the combustion of the fuses the only combustible gases formed in appreciable quantities are CO, $H_2$, and traces of $CH_4$; and, as explained on pp. 13, 21, and 23, one volume of CO gives on combustion half a volume of contraction, consumes half a volume of oxygen, and forms one volume of $CO_2$; one volume of $H_2$ gives one and a half volumes of contraction and consumes half a volume of oxygen; and one volume of $CH_4$ gives two volumes of contraction and one volume of $CO_2$, and consumes two volumes of oxygen. Hence, if the symbols $CO$, $H_2$, and $CH_4$ represent the percentages present of these gases, we have the following equations :—

$$\begin{aligned} &(1)\ CO + CH_4 &&= 0{\cdot}24 \text{ per cent.}\\ &(2)\ \tfrac{1}{2}CO + 2CH_4 + 1\tfrac{1}{2}H_2 &&= 0{\cdot}165 \text{ per cent.}\\ &(3)\ \tfrac{1}{2}CO + 2CH_4 + \tfrac{1}{2}H_2 &&= 0{\cdot}135 \text{ per cent.} \end{aligned}$$

By subtracting (3) from (2) we find that $H_2 = 0{\cdot}03$ per cent. ; and by solving the other equations we find that $CO = 0{\cdot}24$ and $CH_4 = 0{\cdot}00$.

The result of the analysis is therefore as follows :—

| | |
|---|---|
| Oxygen | 19·795 |
| $CO_2$ | 2·75 |
| $CO$ | 0·24 |
| $H_2$ | 0·03 |
| Nitrogen | 77·185 |
| | 100·00 |

In routine determinations of fire-damp in mine air it is usually not necessary to determine anything else but the contraction on combustion; and this may be done in three or four minutes in all by passing the gas straight into the combustion pipette.

The above description applies only to samples of air in which a lamp will burn. In the case of other samples of mine gases the same procedure is possible if it is known that no combustible gas is present, or so little that the oxygen in the sample will suffice for the combustion. If, however, much fire-damp or other combustible gas be present, as in the case of samples from bore-holes, old workings full of fire-damp, etc., the gas must be diluted with air before combustion. In such a case the nitrogen present from the last analysis should be shunted into the explosion pipette. A sample of the gas is then taken in, measured, and the carbonic acid, and then the oxygen, determined in the ordinary way. From the result it will usually be possible to say approximately about how much fire-damp is probably present. The burette and absorption tubes are then thoroughly washed out with air, so as to remove all traces of fire-damp, after which the connections of the absorption pipettes are washed out with the nitrogen in the combustion pipette, and the gauges adjusted. A quantity of about 15 c.c. or more of pure air is then taken into the burette, deprived of $CO_2$, and measured. It is then completely shunted into the potash pipette, and mercury driven over so as to fill the curved tube, by means of which a small quantity of the gas from the sample-bottle is drawn into the burette. The quantity of gas required varies according to the proportion of combustible gas present, and should be chosen so that not more than about 6 per cent. of fire-damp shall be present when the gas is mixed with the air. To facilitate the proper estimation of the amount taken, it is convenient to have the rough graduation marks indicating the first five c.c. on the wide part of the burette.

The air is now returned into the burette, and the whole volume of the mixture of gas and air measured. From the previous measurement of the air the volume of gas taken is calculated. The amount of oxygen and $CO_2$ in this volume can also be exactly calculated from the previous analysis. The mixture is now passed straight over into the combustion pipette, the combustible gas burnt, and the contraction and $CO_2$ formed determined, after allowance has been made for the $CO_2$ already present in the gas. Finally, the oxygen is determined, and the oxygen used up in the combustion calculated by deducting what was left after the combustion from what was originally present.

The following example illustrates the method of calculation :—

*First Analysis.*

| | | |
|---|---|---|
| Volume taken . . | 19·962 | |
| After $CO_2$ absorbed . | 19·544 | |
| | ·418 | = 2·09 per cent. |
| After $O_2$ absorbed . . | 17·046 | |
| | 2·498 | = 12·51 per cent. |

From these results it follows that the gas contains 59·77 per cent. of air, together with probably about 15 per cent. of "black-damp," so that about 25 per cent. of fire-damp is likely to be present. The sample was therefore diluted to about a fifth with air for the combustion of the fire-damp.

*Second Analysis.*

| | | |
|---|---|---|
| Volume of air taken (freed from $CO_2$) | | 16·346 |
| + gas taken | = | 20·464 |
| ∴ gas taken | = | 4·118 |

| | | |
|---|---|---|
| After combustion . . . . | | 19·920 |
| ∴ contraction | = | 0·544 |
| After $CO_2$ absorbed . . . . | | 19·562 |
| ∴ $CO_2$ | = | 0·358 |
| After $O_2$ absorbed . . . . | | 16·166 |
| ∴ $O_2$ | = | 3·394 |

Of the $CO_2$ found, it is evident from the previous analysis that $4{\cdot}118 \times \frac{2{\cdot}09}{100} = {\cdot}086$ was present to start with in the gas taken; therefore $\cdot 358 - \cdot 086 = \cdot 272$ was produced by the combustion. As ·272 is just half the volume of the contraction on combustion (·544), the gas was presumably pure methane. The oxygen originally present in the mixture of gas and air was $\left(16{\cdot}346 \times \frac{20{\cdot}93}{100} = \right)3{\cdot}421 + \left(4{\cdot}118 \times \frac{12{\cdot}51}{100} = \right)0{\cdot}515 = 3{\cdot}936$; hence the oxygen consumed in the combustion was $3{\cdot}936 - 3{\cdot}394 = {\cdot}542$. This is almost exactly double the volume of $CO_2$ absorbed, so that the combustible gas was certainly pure, or all but pure, methane.

The result of the analysis was thus as follows :—

| | |
|---|---|
| Oxygen . . . . . . | 12·51 |
| Carbonic acid . . . . . | 2·09 |
| Methane (fire-damp) . . . . | 8·69 |
| Nitrogen . . . . . . | 76·71 |
| | 100·00 |

The percentage of fire-damp present is a good deal less than was roughly estimated from the first analysis, and the amount of black-damp correspondingly greater. The black-damp had been estimated on the assumption that it probably contained about 13 per cent. of carbonic acid, whereas it actually contained only 6·36 (see below, p. 124).

After each analysis the tap should be so turned as to disconnect the burette from the absorption apparatus and open the control tube to the air. Unless this precaution is taken, a fall of temperature or rise of barometric pressure may cause the potash to be sucked over, in which case the burette, etc., must be washed out with dilute sulphuric acid, and the taps cleaned, as otherwise they will probably jam.

4. *Testing the Apparatus.*—If a sample of air be taken into the burette, and deprived of $CO_2$, it will be found that, provided the precautions described above are carefully taken, the same reading, to within ·001 c.c., will be obtained again and again on passing the sample back and forwards into the potash or explosion pipette, although the temperature of the water-jacket may meanwhile have altered very appreciably. In other words, the gauges and compensating arrangement are so delicate that the readings of the burette are significant to the third decimal place. Some attention and practice will, however, be needed to obtain the best results, and the temperature of the room should be kept fairly steady, as the compensation is not quite perfect.

The accuracy of working of the apparatus may be easily checked by the analysis of a series of samples of pure outside air from a single bottle. The following, for instance, are the results of four successive analyses of the air from one bottle :—

| | Oxygen. | Carbonic Acid. |
|---|---|---|
| No. 1 | 20·930 | ·025 |
| „ 2 | 20·926 | ·030 |
| „ 3 | 20·931 | ·035 |
| „ 4 | 20·924 | ·030 |
| Mean | 20·928 | ·030 |

With the same burette the oxygen percentage in pure air was always found to be as nearly as possible 20·93 per cent. The graduation of this burette had been carefully checked in duplicate in the upright position (a glass tap having been fused on below for the purpose), and with moisture inside as during an analysis. Hence 20·93 may be taken to be the true percentage of oxygen in pure air. This figure agrees closely with the mean results of other observers using accurate methods.

If pure air be passed into the combustion pipette, and the wire heated, as in an analysis, there should be no difference whatever in the readings before and after. The traces of hydrogen present in air are thus quite inappreciable by this method.

The satisfactory working of the apparatus should be tested by blank experiments with the same air, and with the residual nitrogen. Any leakage in the connections will thus be detected, and can be further localised by putting pressure successively on different parts of the connections. The powder used for dusting the inside of rubber tubing is a fertile source of slight and very troublesome leakages at the joints. These leakages do not occur if the rubber is perfectly clean and smooth, or if the inside of each piece of tubing is coated with a thin layer of vaseline. Another source of slight error arises from the fact that when the potash pipette is first charged the potash may form a little potassium sulphide at the expense of sulphur present in the rubber. This potassium sulphide may then absorb an appreciable amount of oxygen when air is passed into the pipette, so that in successive blank experiments with air the readings are slightly lower each time. If the potash has turned yellow some sulphide is probably present, and the pipette should be re-charged with fresh solution.

Air to which ·047 per cent. of methane had been added gave in four successive determinations ·044 per cent., ·053 per cent., ·051 per cent., and ·040 per cent. It will be seen from these examples that with care results which are reliable to within ·01 per cent. may be obtained in ordinary analysis.

It seldom, if ever, happens that a gas-burette is graduated quite correctly all the way down to within ·001 c.c. The graduation ought, however, to be so close that for mine air analyses the irregularity is not sufficient to cause any appreciable error, except in oxygen determinations; and if the error in the oxygen percentage of pure outside air as given with the burette, starting at about some given graduation mark, be once determined, it is easy to make the requisite corrections. Supposing that a given burette always gives say 20·90 per cent. of oxygen, the result should be corrected to 20·93; and where lower oxygen percentages are obtained with mine air, a corresponding correction should be introduced. If, however, it is preferred to set down the result exactly as found, then the result obtained with pure outside air ought also to be stated. This result is by itself a most convenient check on the evenness with which any burette is graduated, and provided the burette is evenly divided, it does not matter whether the divisions marked on it correspond exactly to divisions of a cubic centimetre.

Pure, dry atmospheric air contains :—

| | | |
|---|---|---|
| Oxygen | | 20·93 |
| Carbonic acid | | 0·03 |
| Nitrogen | 78·10 | 79·04 |
| Argon | 0·94 | |
| | | 100·00 |

As in ordinary gas analyses it is not necessary to determine nitrogen and argon separately, these two gases together, along with the minute traces which are present of hydrogen and several of the recently discovered rarer gases, are usually referred to as "nitrogen," and are so referred to in the present work.

In summer the percentage of $CO_2$ in pure air, at about three feet from the ground (as determined by the far more delicate gravimetric method), varies from about ·025 per cent. by day to ·035 per cent. by night,[1] the mean being almost exactly ·030; and doubtless the oxygen percentage varies correspondingly. In large towns, particularly in winter, there is very commonly an increase of ·01 or ·02 per cent. in the $CO_2$ percentage; and in a fog in London Russell has found as much as ·14 per cent. of $CO_2$.

**Determination Underground of Carbonic Acid and Fire-damp or Carbonic Oxide.**—It is often desirable to be able to make accurate determinations on the spot underground of various impurities in the air. For instance, it may be desired to trace out the source and amount of some such impurity as carbonic acid or carbonic oxide, or to check by accurate determinations the cap indications of a lamp, or to ascertain whether fire-damp is present when a lamp gives no certain indications, or black-damp possibly containing fire-damp interferes with the lamp test.

With the object of meeting such cases I have designed the following method.

*Description of Apparatus.*—The apparatus, which is shown in fig. 38, is on the same principle as that already described, except that it is smaller and more compact, and does not afford a means of determining oxygen or any high percentage of other gases. It is enclosed in a wooden case, the internal measurements of which are 7 × 12 × $2\frac{1}{2}$ inches. The weight when the whole is ready for use is about $5\frac{1}{2}$ pounds.

The air-burette A, which is enclosed in a glass water-jacket, consists of a wide ungraduated and a narrow graduated portion. It holds about 10 c.c. from the top to the bottom of the scale. The graduated portion, which is 4 inches long, is divided into about 100 divisions. Two kinds of burette are supplied. In the first, which is more useful in metalliferous mines or non-fiery coal-mines, each division corresponds to $\frac{1}{5000}$th part of the volume of the burette. The lowest division is marked 0, and the highest 200, if exactly 100 divisions are present. Each division on the burette thus counts for two on the scale. Any difference between a reading at or near zero and a second reading is thus shown by the scale in volumes per 10,000, there being no calculations or

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[1] Haldane, *Journal of Hygiene*, vol. ii. p. 421, 1902.

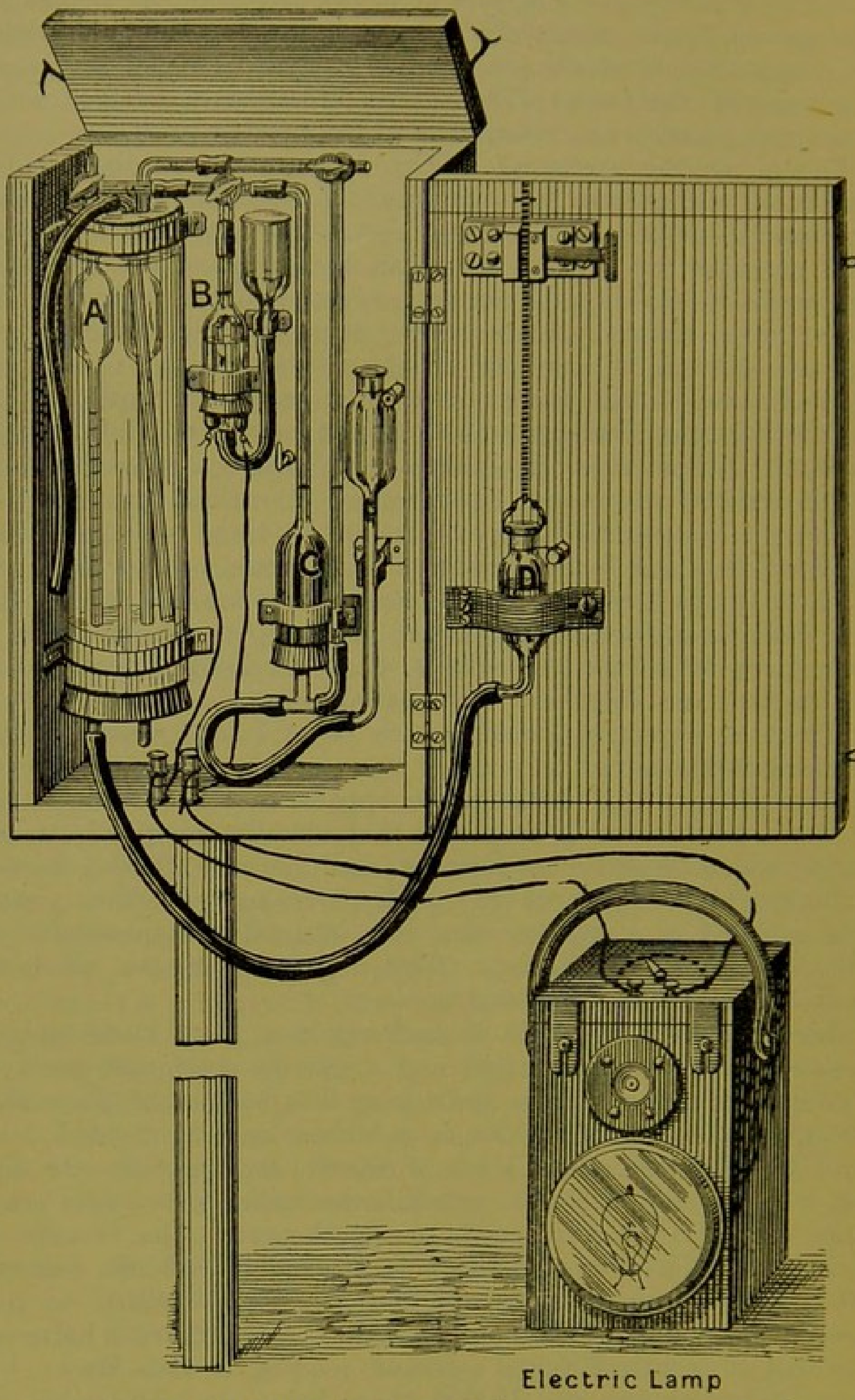

FIG. 38.—Portable Apparatus for Air Analysis underground.

corrections. In the second burette, which is meant for fiery collieries, each division corresponds to $\frac{1}{1000}$th part of the capacity of the burette. The lowest division is marked 0, and the highest 10, so that each division on the burette counts for 0·1 on the scale, which thus directly shows percentages of the capacity of the burette. The diameter of the potash pipette C, and the combustion pipette B, is 1 inch, and the length 2 inches. The connecting tubes leading to these pipettes and to the pressure-gauge of the control tube from above have an internal diameter of 1·8 to 2·2 mm., as in the larger apparatus; but the rubber and glass connecting tubes leading onwards from the pipettes to the corresponding reservoir tubes have an internal diameter of about 4 mm. The potash reservoir slides up and down on a spring clamp, and the mercury reservoir of the combustion pipette is also fixed by a spring clamp. The mercury reservoir D is suspended from a hook attached to the rack and pinion apparatus shown, by means of which the level of the mercury in the pipette can be accurately adjusted. The water-jacket, which is 8 inches long and 2 inches in diameter, is closed above by a split cork, fitting very loosely, so as to permit the free escape of air. A tube is provided for blowing air through the water of the jacket, so as to mix the water thoroughly before each reading of the burette. Both the burette and the control tube are kept moist inside, as in the larger apparatus. The burette should be washed out at first with very dilute sulphuric acid solution, so that the contained moisture, which should always be easily visible, remains acid. The calibration of the burette can easily be checked by weighing the mercury which flows out, as in the case of the larger apparatus.

In connection with work underground, it is particularly important to realise the importance of closing the connections between the potash and the gas burette and control tube at the end of each analysis. If this precaution be neglected, and the apparatus is meanwhile taken down a shaft, or from a return to an intake road, or from any very warm place to a cool one, the potash may be driven over into the burette, and the apparatus thus rendered useless until it has been thoroughly washed out, including all connections of the burette, with dilute acid. A little potash in the control tube is of no importance.

The efficient working of the apparatus is ascertained by depriving a sample of air of $CO_2$, and seeing that its volume as read off is not altered by as much as ·01 per cent. after it has been passed over into the potash pipette or combustion pipette, all adjustments being made as in an analysis. Any error due to leakage or obstructions in the connections, or failure from any cause of the potash to return exactly to its proper level in the gauge tubes, will thus be at once revealed (see p. 113).

As it is difficult to find convenient places underground on which to set the apparatus during an analysis, a brass socket is provided in the bottom of the case, into which the brass top of a wooden rod about 4½ feet long can be screwed. The apparatus can then be allowed to lean against the side of a road or working place during an analysis, and the readings can be made quite conveniently.

When it is desired to use the apparatus for analysing bottle samples of air above-ground, a mercury trough and curved tube must be employed, as in the case of the larger apparatus.

*Process of Analysis.*—The mercury reservoir is first raised, so as to expel all air from the burette to the outside. The tap of the burette is then closed by turning it a short way in the same direction as the hands of a clock turn, and the reservoir replaced on the hook at the right level for filling the burette. The apparatus is then carried open to the exact point from which the sample is required, and the tap opened to the outside, so as to allow the burette to fill. The tap is then again closed, and the apparatus placed in position for the analysis.[1] After roughly levelling the mercury in the burette and reservoir, the taps of the burette and control tube are opened towards the potash, and the levels adjusted to the marks after blowing air through the water-jacket. A reading is then taken, and ought of course to be close to the zero-point of the graduation. The $CO_2$ is then absorbed, as in the case of the larger apparatus, and a second reading taken after again carefully adjusting the levels and blowing air through the water-jacket, both these precautions being absolutely necessary. The difference between the two readings gives the proportion of $CO_2$ in percentage or in volumes per 10,000, according as the one or the other kind of burette is used.

The air is then passed into the combustion pipette, and the spiral heated by a current from a hand electric lamp, as described in the case of the larger apparatus. It is evident that this process must never be carried out at any place where there is any chance of the air being explosive; for although there will be no sparking if the wire connections are first made, and the current then gradually turned on, as ought always to be the case, through the

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[1] If the temperature at this point differs much from that at which the apparatus has just previously been, it is better to wait a few minutes before beginning the analysis, so as to allow the connecting tubes to the pipettes to reach the temperature of the air: otherwise the results are less accurate.

graduated resistance, yet a mistake might lead to there being a spark. An ordinary lamp must always be carried when the apparatus is used for gas-testing underground in fiery mines; and indeed it should be distinctly understood that the apparatus is not meant to replace in any way lamps for gas-testing purposes, since the latter, so far as they are capable of giving information, are far more convenient. The contraction on combustion having been noted, the $CO_2$ formed is likewise determined. The results indicate the proportion of fire-damp, carbonic oxide, or any other combustible gas, if such be present.

It is evident that if the $CO_2$ is determined first, as just described, a small part of the combustible gas will be left in the connections between the tap of the combustion pipette and the potash absorption pipette. This space can be determined once for all by filling the coarser burette with water, and passing water over first to the tap of the combustion pipette, and then to the mark on the potash pipette, and reading off on the burette the volume of the space in question. If, for instance, this space amounts to 7 per cent. of the capacity of the burette, it is evident that it is necessary to add about 7 per cent., or $\frac{1}{14}$th, to the proportion of fire-damp or CO found. The correction may also be determined once for all by making a determination of the combustible gas in a sample, without washing out the space, and then making a supplementary determination after the space has been washed out with air which has been freed from combustible gas and $CO_2$.

After an analysis the mercury reservoir is fixed to the case by a piece of elastic webbing, shown in fig. 38; and the rubber tube of the mercury reservoir is hitched over a hook, also shown in fig. 38. The taps having been turned so as to open the burette and control tube to the air, and at the same time shut off connection with the potash, the case is then closed up. Where there is a chance of the case being laid on its side, as in travelling, corks should be inserted in the potash and mercury reservoirs, or the mercury and potash poured out.

The following examples will serve to illustrate the calculation of the results:—

1. *Air from an "End" in a Metalliferous Mine, shortly after shot-firing. Finer burette used.*

| | |
|---|---|
| First reading of burette . . . . . . | 6 |
| After $CO_2$ absorbed . . . . . . . | 82 |
| $\therefore$ $CO_2$ in volumes per 10,000 = | 76 |

After combustion . . . . . . . . 86
∴ contraction = 4
After $CO_2$ absorbed . . . . . . . 92
∴ $CO_2$ produced in volumes per 10,000 = 6

Result :—$CO_2$ = 0·76 per cent.
CO = 0·06 „
$H_2$ = 0·007 „

As, however, an addition to the percentage of combustible gas of 7 per cent. needed to be made because some of the gas was left in the dead space beyond the combustion pipette, the corrected result was 0·064 per cent. of CO and 0·007 per cent. of hydrogen.

2. *Air from a "Return" in a Fiery Colliery. Fire-damp alone determined. Coarse burette used.*

First reading of burette . . 0·16
After combustion . . . . 2·72

∴ contraction = 2·56
∴ $CH_4$ = 1·28 per cent.

In the last determination there was no correction to be made, as the air was not passed into the potash pipette at all.

In the first determination the combustible gas was assumed to be CO and hydrogen, as no other gases could well be present; and in the second determination it was assumed that only methane was present, as previous analyses had shown that the contraction was always just double the volume of $CO_2$ formed.

A description will be found below (p. 147) of a physiological method of roughly determining very small percentages of CO in air, even when other unknown hydrocarbons are present.

**Determination of Stone Dust.**—In view of the disastrous effects produced in metalliferous miners by the habitual inhalation of air containing stone dust,[1] it is often important to determine the quantity of stone dust in the air of working places, particularly with a view to deciding whether the means taken to allay the dust are efficient. The determination can be conveniently made in the following manner :—

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[1] *Report by Haldane, Martin, and Thomas on the Health of Cornish Miners*, Parliamentary Paper [Cd. 2091], 1904. Also *Report of the Transvaal Miners' Phthisis Commission*, 1903; and *Report by Dr R. H. Makgill on Sanitary Conditions at Reefton Mines, New Zealand*, N.Z. Parliamentary Paper, 1904.

A piece of glass tube about 2½ inches long and ½ inch in diameter is prepared in the form shown in fig. 39. A small plug of cotton-wool is pushed firmly down to the constricted part. This filters off any dust in the air drawn through the tube. An additional guard plug or a cork at the wide end of the tube serves to prevent accidental contamination or loss of dust. At the place where it is desired to determine the dust, the cork or guard plug is removed, and the glass tube attached by a piece of rubber tubing about an inch long to the nozzle of a brass exhausting syringe taking about 200 c.c. or more of air at each stroke, and provided with thoroughly efficient valves. The glass tube should touch the nozzle of the syringe, so as not to require any support. The syringe is then held so that the tube points horizontally, and a sufficient quantity of air drawn through. The quantity is measured by counting the strokes of the syringe, the capacity of which has been calculated beforehand. Care must be taken that time is given at the end of each stroke for the full charge of air to enter, as the resistance of the cotton-wool and valve causes a slight delay. After the air has been drawn through the tube the guard plug is replaced. If any dust was present in the air, it will now be seen on the surface of the cotton-wool. The quantity present is determined by igniting the plug of wool in a platinum crucible, carefully weighed to decimilligrammes, with the usual precautions as regards cooling. The difference in the weight of the crucible before and after the ignition gives the weight of dust in the air. The weight of the ash from the cotton-wool is not appreciable.

FIG. 39.—Apparatus for Dust Determination.

The quantity of air needed for the analysis of course depends on the amount of dust present. In the air of an "end" or "rise" with a rock-drill at work boring dry holes, 10 litres would be sufficient, and would commonly contain from 5 to 10 milligrammes of dust. With an efficient jet or spray no appreciable quantity of dust is yielded by 20 litres of air. The absence of appreciable quantities of dust from the air can be inferred from the appearance of the cotton-wool, unless the dust is quite white. On the other hand, blackening of the wool might, in some cases, be due to smoke from explosives, the carbonaceous particles of which appear to be more or less harmless. The air of an end or rise just after blasting contains large quantities of dust if the rock blasted was dry; and the men ought not to return until there is less than 1 milligramme in 10 litres of air. The average air of a stope where men are working should not yield any weighable dust in 10 litres of air.[1]

**Determination of Moisture.**—The most convenient method of determining the moisture in air underground is by the readings of dry- and wet-bulb thermometers. Two good chemical Fahrenheit thermometers are selected. They must read together at all parts of the scale, and the graduation should be open and very plainly marked. A layer of thin muslin is tied with thread round the bulb of one of them, and this is wetted with water (carried in a small bottle) just before use. The thermometers are held in one hand, with the bulbs well separated, and vigorously waved about in the air to be tested, until the readings of both thermometers are perfectly steady. In reading the thermometers care must be taken that they are not affected by the heat of a candle or lamp. A pocket electric lamp is useful for making the readings. Unless the air is saturated, the wet-bulb thermometer will read lower than the dry-bulb. To calculate from the readings the weight of moisture per cubic foot of air, the percentage saturation, etc., Glaisher's well-known Tables[2] should be used.

Mine air is usually pretty moist, so that the difference between the dry- and wet-bulb readings is not very great. It is thus a useful rule to remember that for the first four or five degrees of difference between the dry- and wet-bulb thermometers each degree corresponds to about 7 per cent. of relative saturation at about 45° F., 6 per cent. at about 60°, and 5 per cent. at about 80°. Thus, if the dry-bulb reading was 80°, and the wet-bulb 75·5°, the relative saturation of the air with moisture would be $100 - 4{\cdot}5 \times 5 = 77{\cdot}5$ per cent.

The table on the following page gives the weight of moisture in grains per cubic foot of saturated air at different temperatures. With the help of this table, and the data given above as to the significance of dry- and wet-bulb observations, the weight of moisture in mine air at any part may be roughly calculated from the dry- and wet-bulb readings; though it is, of course, preferable to use Glaisher's Tables. In the above example, the number of

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[1] *Cf.* Thomas and Macqueen, *Trans. of the Inst. of Mining and Metallurgy*, 1904.

[2] *Hygrometrical Tables*, by James Glaisher, F.R.S. Published by Taylor & Francis, Red Lion Court, Fleet Street, London.

| Temperature, F. | Grains of Moisture per Cubic Foot of Air. | Temperature, F. | Grains of Moisture per Cubic Foot of Air. |
|---|---|---|---|
| 30° | 2·0 | 65° | 6·8 |
| 35° | 2·4 | 70° | 8·0 |
| 40° | 2·9 | 75° | 9·4 |
| 45° | 3·4 | 80° | 11·0 |
| 50° | 4·1 | 85° | 12·8 |
| 55° | 4·9 | 90° | 14·8 |
| 60° | 5·8 | 95° | 17·2 |

grains of moisture per cubic foot would be $11{\cdot}0 \times \frac{77{\cdot}5}{100} = 8{\cdot}5$. Glaisher's Tables give the results in grains and cubic feet (1 grain = 0·0648 gramme; and 1 cubic foot = ·0283 cubic metre).

**Recognition of Sulphuretted Hydrogen and Nitrous Fumes.**—Two very poisonous substances—namely, sulphuretted hydrogen ($H_2S$), and nitrous fumes from the combustion or imperfect detonation of nitro-explosives—are occasionally met with in formidable quantities in the air of mines (see pp. 134, 149). Fortunately, they are both easily recognisable by the senses.

Sulphuretted hydrogen in very great dilution is recognised by its characteristic smell of rotten eggs. When the proportion exceeds about ·01 per cent., the smell seems to be less distinctive, and irritation of the eyes begins to be produced—a warning symptom which should never be neglected. It may also be easily recognised by its blackening action on paper moistened with acetate of lead solution.

Nitrous fumes have an almost equally characteristic smell—that of fuming nitric acid. The presence of this smell after blasting should act as a warning to miners not to return till the air is clear. In higher proportions nitrous fumes have an irritant action on the air-passages; and air which produces this effect is decidedly dangerous. A simple chemical test for nitrous fumes is to expose paper soaked in a solution of starch and iodide of potassium. The starch is quickly turned blue by the liberation of iodine if nitrous fumes are present.

## II. INTERPRETATION OF MINE AIR ANALYSES.

It is of little use to have a complete analysis of mine air, unless the significance of the results is equally completely understood. The following section will therefore be devoted to a discussion of the significance of the various results which may be obtained.

### Methods of Stating the Results.

Every analysis of mine air should be stated in terms of the actual chemical constituents found, as in the analyses quoted above. It is usually, however, of advantage also to state the results in another form. In nearly every case a greater or less amount of air is present in the mixture analysed. As (apart from the very small quantity of oxygen which might be liberated in the detonation of dynamite) atmospheric air is the only source of oxygen in a mine, it is clear, in the first place, that the proportion of atmospheric air in the sample may be calculated from the oxygen percentage by multiplying by $\frac{100}{20 \cdot 93}$. The residue left after deducting the oxygen, nitrogen, and $CO_2$ of the air consists of nitrogen, $CO_2$, and possibly methane (fire-damp), CO, etc. The methane, and also the CO, or any other combustible constituent, ought evidently to be stated separately, so that what is still left over consists of nitrogen and $CO_2$. Now it will be found that in the great majority of mine air analyses (see pp. 125–128) the composition of this residue corresponds more or less closely to that of the "black-damp," or "choke-damp," met with in unventilated parts of the mine from which the sample comes. Hence the residue in question may be set down in the analysis as "black-damp."

By black-damp, or choke-damp, a miner practically understands any sort of gas or air which will extinguish a candle or lamp without at the same time being capable of causing an explosion, and which will not cause symptoms of poisoning, asphyxiation, or serious discomfort when mixed with just sufficient air to allow a candle to burn. Pure black-damp, free from air, is very commonly confused with carbonic acid, but is really a mixture of nitrogen with a relatively small proportion of carbonic acid.[1]

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[1] For experiments on the nature, source, and properties of black-damp, see Haldane and Atkinson, *Trans. Inst. of Mining Engineers*, vol. viii. p. 549; Haldane, *ibid.*, vol. xi. p. 265; Haldane and Meachem, *ibid.*, vol. xvi., 1899; also *Report to the Home Secretary on the Health of Cornish Miners*, 1904, p. 82.

It is simply the gaseous residue resulting from the slow oxidising action of air on oxidisable substances in a mine (see p. 129). Hence it consists chiefly of nitrogen; and a mixture of black-damp and air has very different physical and physiological properties from a mixture of carbonic acid and air. For instance, pure black-damp is much lighter than carbonic acid, and is even lighter than air if, as may happen, it contains less than 5·25 per cent. of carbonic acid. A small admixture of fire-damp, which is very common in collieries, will easily make black-damp lighter than air.

The following examples illustrate the mode of statement of an analysis in terms of air, black-damp, etc., and at the same time show that this mode of statement is justifiable:—

1. *Gas issuing into a Return Air-way from Old Workings through a pipe in a brick stopping, Podmore Hall Colliery, North Staffordshire.*

| | |
|---|---|
| Oxygen | 0·72 |
| Carbonic acid | 11·03 |
| Methane ($CH_4$) | 7·47 |
| Nitrogen | 80·78 |
| | 100·00 |

*Otherwise expressed.*

| | | | |
|---|---|---|---|
| Air | Oxygen | 0·72 | 3·44 |
| | Nitrogen | 2·72 | |
| Black-damp | Nitrogen | 78·06 | 89·09 |
| | Carbonic acid | 11·03 | |
| Fire-damp | | | 7·47 |
| | | | 100·00 |

2. *Air from Main Return of same Colliery.*

| | |
|---|---|
| Oxygen | 20·34 |
| Carbonic acid | 0·305 |
| Methane ($CH_4$) | 0·65 |
| Nitrogen | 78·705 |
| | 100·00 |

*Otherwise expressed.*

| | | | |
|---|---|---|---|
| Air | Oxygen | 20·34 | 97·18 |
| | Carbonic acid | 0·03 | |
| | Nitrogen | 76·81 | |
| Black-damp | Nitrogen | 1·895 | 2·17 |
| | Carbonic acid | 0·275 | |
| Fire-damp | | | 0·65 |
| | | | 100·00 |

In these analyses the percentage composition of the black-damp was—

| | No. 1. | No. 2. |
|---|---|---|
| Nitrogen | 87·6 | 87·3 |
| Carbonic acid | 12·4 | 12·7 |

### 3. *Gas issuing through a Pipe from Old Workings, Hamstead Colliery, South Staffordshire.*

| | |
|---|---|
| Oxygen | 3·35 |
| Carbonic acid | 5·25 |
| Nitrogen | 84·03 |
| Methane | 7·33 |
| Carbonic oxide | 0·04 |
| | 100·00 |

*Otherwise expressed.*

| | | | |
|---|---|---|---|
| Air | Oxygen | 3·35 | 16·00 |
| | Nitrogen | 12·65 | |
| Black-damp | Nitrogen | 71·38 | 76·63 |
| | Carbonic acid | 5·25 | |
| Fire-damp ($CH_4$) | | | 7·33 |
| Carbonic oxide | | | ·04 |
| | | | 100·00 |

### 4. *Air from Main Return, same Colliery.*

| | |
|---|---|
| Oxygen | 20·55 |
| Carbonic acid | 0·13 |
| Methane | 0·06 |
| Nitrogen | 79·26 |
| | 100·00 |

*Otherwise expressed.*

| | | | |
|---|---|---|---|
| Air | Oxygen | 20·55 | 98·19 |
| | Nitrogen | 77·61 | |
| | Carbonic acid | 0·03 | |
| Black-damp | Nitrogen | 1·65 | 1·75 |
| | Carbonic acid | 0·10 | |
| Fire-damp ($CH_4$) | | | 0·06 |
| | | | 100·00 |

In these analyses the percentage composition of the black-damp was—

| | No. 3. | No. 4. |
|---|---|---|
| Nitrogen | 93·2 | 94·3 |
| Carbonic acid | 6·8 | 5·7 |

5. *Sample from a Disused "End," Dolcoath Tin Mine, Cornwall.*
*A candle would scarcely burn.*

| | |
|---|---|
| Oxygen | 17·99 |
| Carbonic acid | 3·18 |
| Nitrogen | 78·83 |
| | 100·00 |

*Otherwise expressed.*

| | | | |
|---|---|---|---|
| Air | Oxygen | 17·99 | 85·96 |
| | Carbonic acid | ·03 | |
| | Nitrogen | 67·94 | |
| Black-damp | Nitrogen | 10·89 | 14·04 |
| | Carbonic acid | 3·15 | |
| | | | 100·00 |

6. *Sample from Top of Corresponding Upcast Shaft.*

| | |
|---|---|
| Oxygen | 20·86 |
| Carbonic acid | 0·10 |
| Nitrogen | 79·04 |
| | 100·00 |

*Otherwise expressed.*

| | | | |
|---|---|---|---|
| Air | Oxygen | 20·86 | 99·67 |
| | Carbonic acid | 0·03 | |
| | Nitrogen | 78·78 | |
| Black-damp | Nitrogen | 0·26 | 0·33 |
| | Carbonic acid | 0·07 | |
| | | | 100·00 |

In these analyses the percentage composition of the black-damp was—

| | No. 5. | No. 6. |
|---|---|---|
| Nitrogen | 77·6 | 79·1 |
| Carbonic acid | 22·4 | 20·9 |

In the author's experience, black-damp in different English mines contains from about 78 to 95 per cent. of nitrogen, and 22 to 5 per cent. of $CO_2$. In New South Wales collieries black-damp with as little as 4 per cent. of $CO_2$ has been found,[1] and black-damp of similar composition has been found by the writer in a well in England. Black-damp which was nothing but pure nitrogen has recently been observed in a metalliferous mine in Colorado.[2]

There are certain cases where it would be clearly incorrect to include a residue of nitrogen and $CO_2$ as "black-damp." These gases may, for instance, be partly derived from an explosive (see p. 131) or from respiration; and it may be possible to say to what extent this is the case if the sample is from some confined space in a mine. As a general rule, however, the products of respiration, lights, and explosives have such a minute effect on the air in the air-ways of a mine that they may be neglected, at any rate in the case of collieries. For instance, in the colliery from which samples 3 and 4 were taken, the men, horses, and lights would only account for, at most, one-fiftieth of the consumption of oxygen in the mine; and in the case of Dolcoath tin-mine, for about one-eighth. The products of combustion of a colliery explosion ("after-damp") or of an underground fire are also difficult to distinguish from ordinary black-damp. After an explosion, for instance, the ventilation of a colliery is interrupted, and the workings become filled with a mixture of after-damp,

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[1] Guthrie and Atkinson, *Proc. Royal Society of New South Wales*, vol. xxxv, p. 52 (1901).

[2] Lee, *Mining Journal*, August 27, 1904.

black-damp, fire-damp, and air. The former always contains carbonic oxide—probably about 3 or 4 per cent. The products of combustion from heated or burning coal likewise contain carbonic oxide in varying proportions.

In English mines, no perfectly clear case seems yet to have been recorded where nitrogen or carbonic acid, not traceable directly or indirectly to the action on air of substances in coal or other minerals, has been given off underground. Small quantities of nitrogen and carbonic acid are, it is true, commonly present in samples of fire-damp from bore-holes, etc.; but even this may perhaps be derived from air. It is well, however, to bear in mind cases such as that of the Grotto del Cane, where pure $CO_2$ is given off, or that of the hot springs of Bath, where large quantities of nitrogen, mixed with a little carbonic acid, issue with the hot water. Similar cases may occur in mines.

Instead of stating the results in terms of air and black-damp, it may be simpler to state them in terms of diminution of oxygen and increase of $CO_2$. Where there is no fire-damp present, this is the simplest method of statement; but when fire-damp is present it becomes necessary to distinguish between the diminution of oxygen due the presence of the fire-damp, and that due to processes of oxidation in the mine.

## Sources of the Impurities in Mine Air.

The sources of the impurities found in mine air have just been referred to generally; but a somewhat more detailed discussion is needed as regards some points.

With respect to the actual chemical process by which black-damp is formed, the author's observations have led him to the conclusion that in all probability black-damp is chiefly produced by the action of the oxygen of the air on iron pyrites ($FeS_2$) contained in coal and other minerals. In samples of coal which have been kept undisturbed, and protected from water, though exposed to air, it will be observed that crystals of sulphate of iron, accompanied by a very acid reaction, are formed in and on the coal at the expense of iron pyrites. The coal itself, on the other hand, seems to remain unaffected, although it is more or less crumbled to pieces by the formation of the crystals. If carbonates are present along with the pyrites, the iron is deposited as ferric hydrate, and calcium sulphate crystals are formed. The same process may be observed in metalliferous mines. Drops of strongly acid water, giving the reactions of sulphuric acid and iron salts, may often be observed on the roof of a level, or else abundant crystals of calcium sulphate and deposits of ferric hydrate. The sulphuric acid in the water from mines has even been known to produce hydrogen inside iron water-pipes, besides corroding pumps, etc. It seems natural to conclude from these observations that black-damp is formed by the following reactions:—

$$4FeS_2 + 15O_2 + 8H_2O = 2Fe_2O_3 + 8H_2SO_4;$$

and

$$8H_2SO_4 + 8CaCO_3 = 8CO_2 + 8CaSO_4 + 8H_2O.$$

In this process 8 volumes of $CO_2$ are produced for every 15 volumes of oxygen which disappear, and the black-damp formed would consequently consist of 12·4 per cent. of $CO_2$ and 87·6 per cent. of nitrogen. This corresponds fairly well with the composition of the black-damp commonly found in coal mines, ironstone mines, and some metalliferous mines. It is evident, however, that sulphuric acid or acid iron salts may come in contact with bicarbonate instead of carbonate of lime, in which case the black-damp might contain about 22 per cent. of $CO_2$. The second part of the reaction may, also, not occur at all, or may occur at a different place from the first part, so that different samples of black-damp will vary a good deal in the percentage of $CO_2$ present. Black-damp may also be formed by the decomposition of such substances as copper pyrites or carbonate of iron, although in ironstone mines where the latter substance is mined the black-damp does not seem to have the composition which would be expected from the oxidation of carbonate of iron to ferric hydrate. Thus, samples from two ironstone mines in the Cleveland district, and one in North Staffordshire, contained on an average 13·9 per cent. of $CO_2$ and 86·1 per cent. of nitrogen.

In consequence of the chemical changes just described, which may go on for many years in coal and other minerals exposed to the air, any unventilated part of a mine tends to become charged with black-damp, which in collieries is commonly mixed with fire-damp given off by the coal. On a fall of barometric pressure there is an outflow of this gas into the workings, and a corresponding inflow of air with a rise of barometric pressure. Strata which are porous, and have been drained of water, may contain in their pores extensive reservoirs of black-damp formed from air, and if the ventilation is at all deficient inconvenience or danger may arise with every fall of barometric pressure. In the case of ordinary wells this danger is a common one. Thus a well in which the air was perfectly pure in the morning may be full of black-damp (or choke-damp) in the afternoon, in consequence of a fall of barometric pressure; and fatal accidents often occur from well-sinkers neglecting to test the air with a candle before each descent. With a falling barometer the black-damp may not only fill a well, but also issue in large quantities from the top. The gas is similar in composition to the black-damp of mines.[1]

The effects of respiration and burning of lights on the air of a mine can seldom be calculated directly from analyses of the air, as they are masked by the formation of black-damp from the oxidation of minerals. Hence they can only be roughly estimated by calculation. A miner at work probably produces about 1·5 cubic feet of $CO_2$ per hour, a candle about ·5 cubic feet, and a horse at work about 4 cubic feet. If the rate of ventilation in a mine is known, the effects on the air of respiration and lights may thus be estimated. To take an example, in one district of the Eston ironstone mine, there were 52 men and 5 horses, who would produce, along with 52 candles, about 125 cubic feet of $CO_2$ per hour, or 2 cub. ft. per min. In addition, about 0·5 cub. ft. of $CO_2$ per min. were produced by combustion of gunpowder. The ventilation was 20,000 cub. ft. per min., so that the percentage of $CO_2$ in the return air would only be increased and the oxygen diminished by ·0125 per cent. in consequence of respiration, lights, and blasting. Actually the $CO_2$ in the return air was increased by ·31 per cent., and the oxygen diminished by ·55 per cent.

In the case of confined spaces, such as an "end" or "rise" in a metalliferous mine, it may, however, be quite easy to determine by analysis the effects of respiration, explosives, etc., on the composition of the air. If, for instance, the air is analysed before and after shot-firing, the difference due to the products of the explosion may be very striking. The following examples will illustrate this :—

| | Oxygen diminished per cent. | $CO_2$ increased per cent. | CO per cent. | $H_2$ per cent. |
|---|---|---|---|---|
| In rise, Dolcoath Mine, just before blasting . . . | 0·56 | 0·43 | 0·00 | 0·00 |
| Same rise, just after blasting with gelignite . . . | 1·18 | 2·72 | 0·24 | 0·03 |
| In end, same mine, just before blasting . . . | 0·17 | 0·17 | 0·00 | 0·00 |
| Same end, just after blasting with gelignite . . . | 0·515 | 1·08 | 0·14 | 0·01 |

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[1] *Cf.* Haldane, *Trans. Inst. of Mining Engineers*, vol. xi. p. 265 ; also Lee *Mining Journal*, August 20 and 27, 1904, who describes a case in which parts of the workings of a metalliferous mine were flooded with pure nitrogen at every fall of barometric pressure.

Where there is an underground fire, or heating of coal or shale in a goaf, analyses of the return air, especially if repeated from time to time, may afford valuable information. The existence of fire or heating may be assumed with considerable certainty if any appreciable amount (more than, say, ·02 per cent.) of carbonic oxide be discovered in air in which a light will burn, provided there is no other source of the carbonic oxide. Although even smaller traces of carbonic oxide would justify suspicions of heating in a goaf, yet there is not the slightest doubt that coal which is not heated in any way may, under certain circumstances, produce small quantities of carbonic oxide. Thus, the author found in experimenting with a sample of coal which was brought straight from the mine to the laboratory, and had never been heated in any way, that when this coal was pounded and left in a closed flask at the laboratory temperature of about 60° F., about 0·18 per cent. of carbonic oxide was present in the residual nitrogen, etc., left in the flask after all the oxygen had been absorbed by the coal. In another experiment ·11 per cent. was found, although there was still as much as 8 per cent. of oxygen left in the air of the flask. The carbonic oxide was determined both by the platinum spiral method and by means of blood solution, so that there was not the smallest doubt as to its presence.[1] If the gas in the flask had been diluted with air to such an extent that a light would have just burned in it, there would still have been present about ·03 per cent. of carbonic oxide in the air. The coal was from the thick coal-seam at Hamstead Colliery in South Staffordshire. Cases are on record where carbonic oxide was present in the air, and even produced fatal poisoning, although no heating could be discovered. In such cases heating may or may not have really existed; and further observations must decide whether carbonic oxide in really formidable amount is ever given off by coal or other minerals which are not heated. In various samples of ordinary black-damp from different collieries the writer has been unable to detect carbonic oxide, except in cases where heating was probable; and there does not seem to be much doubt that, as a general rule, the presence of appreciable quantities of carbonic oxide in air points with great certainty to fire or heating.

Determinations of $CO_2$ or CO in air often give valuable indications as to the progress or subsidence of a fire. Thus, in the case of a recent fire at Dolcoath Mine, determinations were made of the $CO_2$ in the air of the upcast shaft leading from the fire. Under normal conditions the air issuing from this shaft contained

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[1] *Trans. Inst. of Mining Engineers*, vol. xvi., 1899.

about 0·11 per cent. of $CO_2$. Two days after the fire had broken out the $CO_2$ in the air issuing was ·68 per cent. at 11 a.m., and ·66 per cent. at 5 p.m. Next day it was ·54 per cent. at 11 a.m., and ·60 per cent. at 5 p.m.; next day, ·42 per cent. at 11 a.m. and ·36 per cent. at 5 p.m.; and next day, ·24 per cent. at 11 a.m. At the first testing the CO was ·09 per cent., so that, allowing for the $CO_2$ normally present in the air of the shaft, there was about 1 volume of CO to 5 of $CO_2$ in the gas produced by the fire. In a sample from the Snaefell Mine fire there was about 1 volume of CO to 4 of $CO_2$ (see p. 168).

In colliery explosions CO is formed in large amounts, and in all probability most commonly in the proportion of about 1 volume of CO to 4 of $CO_2$.

In metalliferous mines the most common source of CO in formidable quantities is the imperfect explosion of the dynamite used in blasting. In the perfect explosion of any of the various forms of dynamite or blasting gelatine no CO, or only a very small quantity, is formed. When, however, from any cause, such as unskilful handling, or defective fuses, detonators, or dynamite, the explosion is imperfect, and the dynamite partly burns instead of exploding, carbonic oxide and nitric oxide are formed in place of $CO_2$ and nitrogen. Danger and inconvenience are thus caused, as well as waste of dynamite and of time. With good dynamite, properly handled, the air of an "end" just after blasting ought not to contain more than small proportions of CO, such as those shown in the analyses quoted above (p. 131). The proportion of CO ought not to exceed about a tenth of that of $CO_2$. A much higher proportion indicates some defect. Nitrous fumes arising from the accidental ignition of boxes of dynamite underground have occasionally caused the death of a number of men in gold-mines.

The following table, compiled from analyses by Sarrau and Vieille, and Noble and Abel, shows the composition by volume of nitro-glycerine (the main constituent of the various varieties of dynamite), and also of different kinds of gunpowder:—

| | $CO_2$. | CO. | $N_2$. | NO. | $CH_4$. | $H_2$. | $H_2S$. | $O_2$. |
|---|---|---|---|---|---|---|---|---|
| Nitro-glycerine detonated . . | 63·2 | .. | 31·6 | .. | .. | .. | .. | 5·2 |
| ,, burnt in presence of its own gases . | 12·7 | 35·9 | 1·3 | 48·2 | 0·3 | 1·6 | .. | .. |
| Blasting powder . . . . . | 32·15 | 33·75 | 19·03 | .. | 2·73 | 5·24 | 7·10 | .. |
| Gunpowder (Curtis & Harvey, No. 6) . . . . . . . | 50·22 | 7·52 | 34·46 | .. | 2·46 | 3·26 | 2·08 | .. |

Of these gases, CO, $H_2S$, and NO (which latter immediately combines with the oxygen of the air to form the well-known red fumes consisting of $NO_2$ and other oxides of nitrogen) are all intensely poisonous (see pp. 144–151). Explosives which for any reason give off large proportions of poisonous gases are unfit for use in places which are not very freely ventilated; and analyses of the air after blasting will afford valuable information on this point. On account of the ease with which nitrous fumes are condensed, CO is usually the best index of these impurities.

The presence of $H_2S$ in mine air may be due either to heating of coal (when this gas is often given off along with CO), or to blasting with gunpowder. It occasionally happens, however, that $H_2S$ is given off from some other cause—probably either through contact of acid water with sulphides, or through the reducing action on sulphates of bacteria in foul and stagnant water. A fatal accident, due to the disturbance of some water in which $H_2S$ had probably accumulated in one of these ways, occurred recently in a New Zealand gold-mine.[1] $H_2S$ is very soluble in water, and is also readily given off if the water is disturbed: hence great care is needed in dealing with water which contains this gas. In sewers accidents with $H_2S$ are frequently caused by the disturbance of foul sewage.

With regard to the sources of fire-damp in mine air very little need be said here, as the facts are so well known. It may be given off from shale as well as from coal, and it is occasionally met with in the course of mining operations in other strata. It may also be formed in small quantities during the decomposition of wood, etc., under water, in the absence of free oxygen. This source of fire-damp is very rare in mines, however, and even the fire-damp found in the goaf in collieries is, practically speaking, all derived from coal.

## Inferences as regards Risks of Fire-damp Explosions.

It is scarcely necessary to refer here to the inferences which may be drawn from the presence of percentages of fire-damp which can be easily detected by means of a lamp in fiery mines, as these inferences are necessarily familiar to every colliery engineer. It is perhaps, however, worth while to point out that there is considerable advantage in occasionally checking by gas analysis the cap indications of the testing lamp employed. By this means the range and definiteness of the information given by flame-cap

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[1] Aitken, *New Zealand Mines Record*, May 16, 1904.

tests may certainly be greatly increased. In the author's experience, there is a great deal of difference among different persons as to the interpretation of flame-cap indications; and the very distinct though imperfectly formed caps shown by an oil lamp with from 1 to 2 per cent. of fire-damp in the air are often either disregarded or taken to indicate much higher percentages. The portable gas-analysis apparatus described above affords a ready means of determining the correct interpretation of all cap indications, whether obtained from ordinary oil lamps or from the much more sensitive alcohol or hydrogen gas-testing lamps.

In cases where much black-damp is mixed with fire-damp, air analyses may often give warning of a danger which it is difficult to detect with an oil lamp. Where black-damp and fire-damp occur together in the proportion of about 1 volume of fire-damp to from 3 to 7 parts of black-damp, the mixture will not be explosive if just sufficiently diluted with air to enable a lamp to burn. The lamp will go out when the oxygen of the air is diminished by about 3 per cent. (see below), or when the mixture just referred to is diluted to about a seventh with air. If, however, the mixture is less diluted with air, it becomes explosive,[1] since more than 6 per cent. of fire-damp, and more than 12 per cent. of oxygen, both of which are required in order to constitute an explosive mixture, may be present. It follows that what is taken by a miner for ordinary black-damp may under certain circumstances prove explosive; and probably many accidents, particularly in collieries where naked lights and gunpowder are used, have been due to this cause. A miner may, for instance, have his light extinguished by a mixture of this kind, and may strike a light after going further into the mixture, and thus cause an explosion. A probable case of this kind was reported by Mr W. N. Atkinson,[2] and he has recently informed me of another case. Even if the mixture, when sufficiently diluted with air to allow a lamp to burn freely, be tested for a cap, nothing distinct may be noticed, though very careful testing would nearly always reveal indications of a cap, even with an ordinary oil lamp, and a hydrogen lamp would show a long cap. The Clowes hydrogen lamp is invaluable in testing suspicious mixtures of this kind, as the flame is not extinguished till the oxygen percentage falls to about 10 or 11 per cent.

Black-damp of this dangerous sort would always be lighter than

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[1] Haldane and Atkinson, *Trans. Inst. of Mining Engineers*, vol. viii. p. 560, 1895.

[2] *Annual Report of the Inspector of Mines for the Staffordshire District*, 190, p.

air; and any such black-damp should be regarded with the greatest suspicion, and most carefully examined. Occasional analysis of samples of the black-damp from a mine will put a manager on his guard against dangers of this kind.

The following is an analysis of a sample of black-damp collected by Mr W. N. Atkinson at a place where an explosion had recently occurred in a mixture of the kind just referred to:—

| | |
|---|---|
| Oxygen | 14·65 |
| $CO_2$ | 1·96 |
| Methane | 7·07 |
| Nitrogen | 76·32 |
| | 100·00 |

*Otherwise expressed.*

| | | | |
|---|---|---|---|
| Air | Oxygen | 14·65 | 69·96 |
| | Nitrogen | 55·29 | |
| | $CO_2$ | 0·02 | |
| Black-damp | Nitrogen | 21·03 | 22·97 |
| | $CO_2$ | 1·94 | |
| Fire-damp | | | 7·07 |
| | | | 100·00 |

It will be seen from the analysis that the mixture was explosive. If diluted to about half with pure air it would probably just support a flame, and would also show a distinct cap. If, as might well happen underground, the dilution were with return air containing 5 or 6 per cent. of black-damp, the addition of nearly twice as much air would be needed for the support of a lamp flame, and the cap might easily be overlooked.

## Inferences as regards Effects on Lights.

With increasing diminution of the oxygen percentage and increase of the $CO_2$ in air the light given by a candle gradually diminishes. Angus Smith[1] estimates the diminution in light for an upright candle as being nearly 5 per cent. of the full illuminating power for every 0·1 per cent. of $CO_2$ in the air, when the $CO_2$ is produced by respiration or combustion of candles, and is therefore accompanied (as is commonly the case in mine air) by

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[1] Appendix B to the *Report of the Commission on Metalliferous Mines in Great Britain*, p. 254, 1864.

a somewhat greater diminution in the oxygen percentage. The result is considerably affected by the percentage of moisture in the air. It must always be remembered that the results of air analyses are stated as for dry air, whereas the air itself contains varying percentages of moisture, which have marked effects in diminishing the light from a candle. Angus Smith found that the rate of burning is proportional to the light given. If a candle be placed horizontally, or the wick of a lamp be turned up, the effects of the vitiated air in diminishing the light may be to a considerable extent counteracted. Addition of carbonic acid to air has more effect on a flame than addition of nitrogen; hence a light is somewhat more or less affected with a given diminution of the oxygen percentage according as the accompanying increase of $CO_2$ is greater or less. A given percentage of black-damp in air will thus affect a light more if the percentage of $CO_2$ in the black-damp is higher.

When the vitiation of the air reaches a certain point a candle or lamp will no longer burn. The point of extinction is, however, somewhat different according to the time given for the vitiated air to affect the candle or lamp. If the candle is left for some time in the vitiated air it will gradually go out with about 1 per cent. more oxygen in the air than if it is only left in the vitiated air for a few seconds. When the air is vitiated with black-damp of about the average composition met with in English collieries, an upright tallow candle gradually goes out at about 17·6 per cent. of oxygen and 2·2 per cent. of $CO_2$. If held horizontally it goes out at about 17 per cent. of oxygen and 2·6 per cent. of $CO_2$. An open colza lamp went out at 17·4 per cent. of oxygen, and a bonneted Clanny safety lamp at 17·2 per cent. of oxygen. The hydrogen flame in a Clowes safety lamp, on the other hand, was only extinguished at 10 per cent. of oxygen and 7·6 per cent. of $CO_2$.[1] In air containing less than 16 per cent. of oxygen a candle or oil lamp is instantly extinguished.

A safety lamp is of course also extinguished when the percentage of fire-damp inside the lamp approaches or reaches the explosive limit (6 per cent.). There may or may not be a slight explosion inside the lamp before the flame is extinguished.

## Relation of Air-impurities to Heat-production in Mines.

In deep mining one of the most formidable difficulties to be contended with is the high temperature met with underground.

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[1] Haldane and Atkinson, *Trans. Inst. of Mining Engineers*, vol. viii., p. 558.

It is often of great practical importance to know the cause of the high temperature; and the results of air analyses may throw considerable light on this. A high temperature met with at any part of a mine may be due either to the natural temperature of the strata or to causes dependent on mining operations. The only considerable source of heat-formation in connection with mining operations is, however, oxidation of one kind or another. If explosives are largely used, or if men and lights are crowded together at one point in a mine, they may have a considerable local influence on the temperature. As a general rule, however, as already shown above, the oxidation of minerals by the action of the air is much more extensive than the oxidation due to lights, respiration, and the use of explosives. It follows from this that by far the most important cause of heat-production in a mine is the oxidation of minerals. Reasons were given above for concluding that the mineral substance chiefly oxidised in mines is iron pyrites. The heat-production in a mine may therefore be calculated on the assumption that this is the case. The result would, however, be very little different if the combination of the oxygen were with organic or other substances.

The actual heat of combustion of iron pyrites does not seem to have been experimentally determined as yet, but it can be calculated approximately from the heats of combustion of iron and sulphur. The heat of formation of ferrous sulphide (FeS) is exceedingly small ($Fe + S = 24,500$),[1] and it may be assumed that the same is true for iron pyrites ($FeS_2$). The equations for the heats of combustion of iron and sulphur are as follows :—

$$2Fe + 3O = Fe_2O_3 = 197,700\,;$$

and $$S + 3O = SO_3 \text{ (solution)} = 141,000.$$

Combining these equations, so as to obtain the heats of combustion of iron and sulphur in the proportions in which they exist in iron pyrites,

$$2Fe + 4S + 15O = Fe_2O_3 + 4SO_3 = 197,700 + (4 \times 141,000) = 761,700.$$

A small addition would be necessary to represent the further heat liberated in the decomposition of calcium carbonate by

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[1] The data quoted are from Berthelot's *Thermo-Chimie*, vol. ii. The figures given indicate the number of unit weights of water raised 1° C. for each unit weight of either of the elements entering into the reaction, multiplied by the atomic weight of the element, and by the number of atoms of it required to form a molecule of the resulting substance. Thus, in the above reaction $1 \times 56$ grammes of iron give 24,500 gramme-calories.

sulphuric acid; but this may be left out of account, as the decomposition may only occur partially, and the heat of formation of iron pyrites, which would probably tell as much in the opposite direction, has not been allowed for.

From the above equation it follows that, as the atomic weight of oxygen is 16, for every $(15 \times 16 =)$ 240 grammes of oxygen consumed in oxidising iron pyrites, sufficient heat is liberated to raise 761,700 grammes of water 1° C.: or for every gramme of oxygen consumed about 3170 gramme-calories of heat are liberated. If, therefore, we know the amount of oxygen consumed per minute in a mine, we can calculate the heat-production.

The amount of oxygen consumed can be calculated from the volume of air passing into the mine, and the percentage loss of oxygen which this is shown by analysis to have undergone when it reaches the upcast shaft. It is evident, however, that the percentage loss of oxygen by the air in passing through the mine is not the same thing as the diminution in oxygen percentage in the return air as compared with the intake air: for, on the one hand, part of this diminution may be due to the addition of fire-damp to the air, and, on the other hand, the real loss of oxygen may be partly masked by the fact that (as seems to be always the case in coal-mines) the air has been diminished in volume by the oxidation process, the volume of $CO_2$ formed being much smaller than the volume of oxygen which disappears. Hence it is necessary to calculate from the nitrogen percentage the volume of oxygen corresponding in the original intake air to the percentage of oxygen found in the return air.

To take an example, the air from a main return air-way in a Staffordshire colliery had the following composition:—

| | |
|---|---|
| Oxygen . . . . . | 19·80 |
| $CO_2$ . . . . . . | 0·45 |
| Methane . . . . . | 1·35 |
| Nitrogen . . . . . | 78·40 |
| | 100·00 |

The volume of oxygen which would correspond, in pure air, to 78·40 c.c. of nitrogen would be $20{\cdot}93 \times \frac{78{\cdot}40}{79{\cdot}04} = 20{\cdot}76$, since pure air contains 79·04 per cent. of nitrogen. Hence $20{\cdot}76 - 19{\cdot}80 = 0{\cdot}96$ per cent. of oxygen had disappeared from the air as it passed through the workings. If 50,000 cubic feet of air per minute were passing into the district drained by the return, the total volume of oxygen absorbed would be $50,000 \times \cdot 0096 = 480$ cubic feet per minute. As, however, 1 cubic foot of oxygen at standard pressure and temperature weighs 40·6 grammes, and would weigh nearly as much at the temperature and pressure of the mine, the weight of oxygen absorbed in the district per minute was $480 \times \cdot 040 = 19 \cdot 2$ kilogrammes, and the heat formed was $19 \cdot 2 \times 3170 = 60,860$ kilogramme-calories. In other words, the heat-production in this district of the colliery was sufficient to raise 6 cwts. of water per minute from freezing-point to boiling-point, or was about equal to that produced by a furnace burning 10 tons of coal per day. The specific heat of air is about 0·24; and as 1 cubic foot of air weighed in the mine about 36 grammes, there were $50,000 \times \cdot 036 = 1800$ kilogrammes of air per minute passing through the district. Hence, if the whole of the heat formed had been expended in warming the air, the latter would have been raised in temperature by $\frac{60,860}{1800 \times \cdot 24} = 141^\circ$ C., or 254° F. Actually, the air in the intake had a temperature of about 60° F. (15·5° C.), and in the return about 80° F. (27° C.), so that, even allowing for the large amount of heat carried off in the latent form through evaporation of moisture, only about a fifth of the heat formed by oxidation in the district was being carried off by the air-current. The rest of the heat was being expended in gradually warming up the strata surrounding the workings. The amount of heat carried off by the ventilation was, in fact, relatively so small that it would have made very little difference to the *average* temperature of the workings if the ventilation had been greatly reduced.

The example just given illustrates well the use of a complete and accurate analysis of mine air where a question of the mine temperature is concerned; and it is evident that temperature becomes more and more important as mining is carried on at greater and greater depths.

For practical purposes it will often be convenient to calculate, not the absolute heat-production in a mine or any part of it, but the relation between the heat carried off by the ventilating current and that formed in the workings. For this purpose only the analysis is needed, and not the rate of ventilation. In the example given above it was shown that with a disappearance in the air-current of 0·96 per cent. of oxygen sufficient heat is formed to raise the temperature of the air by about 254° F.: hence for every ·01 per cent. of oxygen disappearance sufficient heat is formed to raise the air-temperature about 2·65° F., or 1·5° C.

In a mine, however, the return air is always more highly charged with aqueous vapour than the intake air, and the latent heat thus carried away usually exceeds greatly the heat carried off by the mere warming of the air. The difference between the weights of aqueous vapour in 1 cubic foot of the intake and the return air may be conveniently calculated with the help of Glaisher's well-known *Hygrometrical Tables* from the readings of the dry- and wet-bulb thermometers. The latent heat of aqueous vapour at an ordinary mine temperature is about 590 Centigrade units. Hence for every grain[1] of increase in the weight of aqueous vapour in a cubic foot of air, the heat carried off by 1000 cubic feet of air is $\frac{1000}{15{,}400} \times 590 = 38{\cdot}3$ kilogramme-calories. From the data already given, this would be equal to the heat required to warm the air 8° F., or would be equal to the heat produced in the disappearance of ·03 per cent. of oxygen.

An example will illustrate the mode of application of this method of calculation. The temperature both by the dry- and wet-bulb thermometer at the top of the main upcast shaft at Dolcoath tin-mine in Cornwall was found to be 72° F., and to be nearly constant. The disappearance of oxygen in the air of the shaft was ·07 per cent. The mean temperature of the outside air was about 52° F. by the dry bulb and 49° by the wet bulb. There was thus a difference in temperature of 20° F., and in moisture of 5 grains per cubic foot of air, between the two shafts. The moisture would carry off latent heat equivalent to that produced by the disappearance of $5 \times {\cdot}03 = {\cdot}15$ per cent. of oxygen; and in the rise of temperature between the two shafts the air would carry off heat equivalent to that produced by the disappearance of ${\cdot}01 \times \frac{20}{2{\cdot}65} = {\cdot}075$ per cent. of oxygen. Hence the heat carried off was equivalent to that produced in the disappearance of ${\cdot}15 + {\cdot}075 = {\cdot}225$ per cent. of oxygen, while the actual disappearance of oxygen was only ·07 per cent. The air-current was thus on the whole cooling the mine, and carrying off thrice as much heat as was produced in the mine, its action in this respect being in striking contrast to that of the air-current in the case of the colliery previously quoted. As a matter of fact, the temperature (79° F.) near the bottom of the main upcast shaft at Dolcoath (2600 feet below surface) was about 15° F., lower than the natural temperature (94° F.) of the rock at this depth. In coal-mines it appears to be seldom the case that the corresponding

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[1] In Glaisher's Tables the weights are in grains. 15·4 grains = 1 gramme.

position is not considerably above the natural temperature of the strata.[1]

## Effects of Air-impurities on Men.

The gaseous impurities present in the air of a mine may affect men, either in virtue of the diminution which they cause in the percentage of oxygen present, or because some gas which is in itself positively injurious is present. An analysis of the air will often give very useful information as to the presence or absence of gaseous impurities in injurious amount. Work underground ought to be, and in collieries and ironstone mines in this country usually is, extremely healthy; but cases often occur in which the men in a mine, or part of a mine, are found to be suffering in health. Rightly or wrongly, the gaseous impurities in the air are usually blamed; but for want of definite information as to their nature and effects, the real cause, whatever it may be, remains uncertain.

**Deficiency of Oxygen.**—The effects of deficiency of oxygen in the air have been found both by laboratory experiments and by experience in mines, mountain-climbing, balloon ascents, etc., to be the same whether the percentage of oxygen, or its pressure, is diminished. Thus the effects produced on a miner by simple deficiency in the percentage of oxygen in the air are the same as those produced by the great diminution in atmospheric pressure at high altitudes. In mines at high altitudes these effects will be combined; but, as a general rule, in mines the increased depth, and consequent increased pressure, compensates to a greater or less extent for diminished percentage of oxygen. As will be explained below, there is another physiological cause which increases the supply of oxygen to the lungs of a miner; and, as a matter of fact, the supply is nearly always more abundant underground than above ground, even though the air is considerably vitiated. It is a matter of common observation that a diminution of even as much as a fourth or more in atmospheric pressure, as is the case, for instance, at various health resorts in mountainous districts, produces no discomfort at all; and similarly a diminution of a fourth in the oxygen percentage of the air in a mine near sea-level—*i.e.* a diminution from 20·93 per cent. to about 15 per cent.—is by itself practically

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[1] For investigations on the factors determining air-temperatures in mines, see Haldane and Meachem, *Trans. Inst. of Mining Engineers*, vol. xvi., 1899; also *Report by Haldane, Martin, and Thomas to the Home Secretary on the Health of Cornish Miners*, Parliamentary Paper [Cd. 2091], 1904, Appendix 3.

without effect on men, though a candle would be instantly extinguished in such air. As the diminution increases further certain effects begin, however, to be produced. The first symptoms usually noticed are that any great muscular exertion is less easy, and that it is apt to cause slight dizziness and unusual shortness of breath. A person not exerting himself will as a rule not notice anything unusual until the oxygen percentage has fallen to 10 per cent. The breathing then usually begins to become deeper and more frequent, the pulse more frequent, and the face somewhat dusky. At 7 per cent. there is usually distinct panting, accompanied by palpitations, and the face becomes of a leaden blue colour. At the same time the mind becomes confused, and the senses dulled, although the person breathing the air may be quite unaware of the fact. Muscular power is also greatly impaired. At a slightly lower percentage there is complete loss of consciousness; and to judge from the records of balloon accidents, life is in imminent danger at any lower percentage, or at a less pressure than about a third of an atmosphere, corresponding to a height of about 30,000 feet. In air containing no oxygen loss of consciousness occurs within forty seconds or less, without any previous warning symptom. Since the discomfort produced by simple deficiency of oxygen is comparatively slight, there is very little to indicate the danger due to want of oxygen; and it is most dangerous to venture into places where the oxygen is very deficient. In places where this is the case, not only is a lamp instantly extinguished, but often a good deal of $CO_2$ is also present, and this produces physiological effects sufficient to give warning; but in certain cases—for instance, where the deficiency in oxygen is due to the presence of fire-damp, or to black-damp containing very little $CO_2$ (see above) —there is not sufficient $CO_2$ to give any warning. A miner who puts his head into a collection of fire-damp in the roof, or ventures too far into workings filled with fire-damp, will probably fall down unconscious without previously feeling anything to indicate danger. Fire-damp itself, like nitrogen, has no definite action, except such as it produces by diminishing the oxygen percentage of the air.

**Excess of $CO_2$.**—An excess of $CO_2$ in air produces no very noticeable effect until the percentage rises to about 3, which is more than is often met with in mine air just extinctive to lights. With an increasing proportion the breathing becomes very noticeably deeper and more frequent: at about 5 or 6 per cent. there is marked panting, accompanied by increased frequency of the pulse. At about 10 per cent. there is violent panting, throbbing, and flushing of the face. Headache is also produced, especially noticeable on a return to fresh air. Beyond 10 per cent. $CO_2$ begins to have a narcotic effect, and at about 25 per cent., death may occur after several hours; but as much as 50 per cent. may be breathed for some time without fatal effects, to judge from experiments on animals. Air which contains any considerable percentage of $CO_2$ may be at once recognised by the marked panting which it causes; and as in mine air deficiency in oxygen is usually due to the presence of black-damp, which contains, as already seen, a good deal of $CO_2$, it follows that air deficient in oxygen can usually be recognised by the effects of the $CO_2$ present in it. It has recently been found by the author and Mr J. G. Priestley that under normal conditions the depth and frequency of the breathing are so regulated that the pressure exercised by the $CO_2$ percentage in the air of the air-cells in the lungs remains constant (at about 6 per cent. of an atmosphere). Thus, if the percentage of $CO_2$ in the air is increased, however slightly, the breathing becomes just sufficiently deeper and more frequent to compensate for the difference; and the pressure of $CO_2$ of the air in the lungs thus remains normal. This method of regulation is extraordinarily delicate. We have, for instance, found that at the bottom level of Dolcoath Mine in Cornwall (2600 feet) the *percentage* of $CO_2$ in the air of the air-cells of the lungs was very distinctly lower than at the surface, and much lower than at the top of Ben Nevis (4400 feet). The *pressure* of $CO_2$ per square inch was, however, the same at each of these places. It follows from this observation that the percentage, and still more the pressure, of oxygen in the air-cells of the lungs is greater down a mine than on the surface, unless the oxygen percentage of the air is greatly diminished without a corresponding increase in $CO_2$, or so greatly diminished that the increased breathing cannot compensate in any way for the deficiency. Such slight increases in $CO_2$ (up to about 1 per cent.) and deficiencies in oxygen as are ordinarily met with in air where a light will burn well are evidently therefore of no physiological importance in themselves, although their effects have often been supposed to be very serious.

**Carbonic Oxide.**—This gas is of great importance, from its very serious effects on men: it is often met with in mines, and it is responsible for many deaths. Thus CO poisoning is the cause of nearly all the deaths in colliery explosions and in underground fires;[1] and the occurrence of CO in connection with heated coal and

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[1] See Report by the author on the Causes of Death in Colliery Explosions, Parliamentary Paper [C. 8112], 1896.

the use of unsuitable or improperly handled explosives in ill-ventilated parts of a mine, often gives rise to much trouble (see above, p. 133). To understand the significance attaching to the presence of varying proportions of this gas in the air, it is necessary to give some account of its mode of action.

The oxygen absorbed by the lungs from the air is normally taken up by the blood in the form of an unstable chemical compound with the red colouring matter (hæmoglobin) of the blood, and so carried by the circulation to the tissues, where it is used up. Hæmoglobin not only combines with oxygen, but also forms a far less unstable compound with CO; and hæmoglobin which is saturated with CO cannot take up oxygen. In proportion, therefore, as CO-hæmoglobin is formed the blood loses its power of carrying oxygen to the tissues, and death from want of oxygen finally ensues. It will be readily understood, however, that, since oxygen as well as CO has an affinity for hæmoglobin, the extent to which the latter substance can become saturated with CO will depend on the relative proportions in which oxygen and CO are present in the air. The one gas tends to drive the other out from the hæmoglobin, and the final result is an expression of the balance struck between the two conflicting processes. If the percentage of CO in the air is so high that too little of the oxygen compound is left to support life, then death ensues. If, on the other hand, the person is removed to fresh air before death occurs, then the carbonic oxide is in the course of several hours turned out of the hæmoglobin and passes off in the breath; and this process may be greatly hastened by artificial respiration where required, and by the administration of oxygen. If, finally, the person remains exposed to a moderate percentage of CO, the blood ceases after a time to take up more CO. In the case of the living body it may be roughly stated that with about ·08 per cent. of CO in the air the hæmoglobin will finally become about half saturated with CO, while with ·04 per cent. it will become a third saturated, and with ·16 per cent. two-thirds saturated,[1] etc.

A further point of importance is that with the small percentages of CO which are commonly met with in mines it may take a considerable time for the blood to become sufficiently charged with CO to produce symptoms of poisoning. A man may thus

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[1] In experiments made by Lorrain Smith and myself on man (*Journal of Physiology*, vol. xx. p. 297, 1896), lower saturations than this were observed, but in subsequent experiments we have found that the period of experiment was probably too short.

go a long way into a poisonous atmosphere without experiencing any effects; and it may then be impossible for him to return. The volume of blood in a man of average weight has been found to be about 3 litres, or 5¼ pints, and it is capable of entering into combination with about 600 c.c. (1 pint) of CO. Supposing that he is breathing air containing 0·2 per cent. of CO, and that he is at rest, when he will only be breathing about 7 litres of air per minute, of which only about 5 litres will reach the air-cells of his lungs, he will evidently not be able to absorb more than $50 \times \cdot 2 = 10$ c.c. of CO per minute; and it will thus be at the least half an hour before his blood becomes even half saturated with CO. If he is moving about or working he will breathe more air, and probably absorb more CO; but in any case it will take some time for the blood to become so charged with CO that he feels the effects of the poison. In an actual experiment made during rest it was found that with 0·2 per cent. of CO in the air the hæmoglobin did not reach 50 per cent. saturation till after 70 minutes, so that, as might be expected, most of the CO breathed during this period was not absorbed.

The symptoms of CO poisoning are essentially the same as those produced by air deficient in oxygen, and vary according to the degree of saturation of the hæmoglobin with CO. With 20 per cent. saturation the only symptom is a slight tendency to dizziness and shortness of breath on exertion. As the saturation increases, however, the symptoms of want of oxygen become more and more pronounced, until at 50 per cent. saturation it is scarcely possible to stand, and even slight exertion causes temporary loss of consciousness. The onset of the symptoms is very insidious, there being only slight shortness of breath and palpitations, but hardly any discomfort; and the senses, power of judgment and of movement, are commonly much impaired before the person is aware of anything being wrong. In some cases there is much excitement, but often there is simple drowsiness and stupidity. The symptoms are in some respects similar to those produced by alcohol. One curious fact is that in CO poisoning, as in alcoholic poisoning, sudden exposure to cool fresh air may greatly increase the symptoms. Death seems often to be immediately brought about by muscular exertion, as in attempts to escape rapidly up ladders, inclines, etc. If death occurs gradually, the hæmoglobin is usually about 80 per cent. saturated with CO. In the case of persons who have been rescued alive, but still unconscious, after long exposure to CO, death often occurs later in consequence of damage to the tissues during the exposure.

The dangers of CO poisoning, and the symptoms which accompany it, are very graphically described in the Report to the Home Secretary of Sir Clement Le Neve Foster on the fire at Snaefell Mine in 1897. The main passages from this report are reproduced in the Appendix at the end of this book.

The percentage of CO which is fatal, if sufficiently long inhaled, to men and animals seems to vary a good deal in individual cases. As little as ·17 per cent. is sometimes fatal to animals, though usually about ·4 per cent. is required to cause death within a moderate time. Anything above ·15 per cent. must, however, be regarded as distinctly dangerous, and probably anything above ·03 per cent. would in time produce symptoms distinctly felt on any exertion.

A miner's lamp, or his senses, will give him warning of the presence in air of any other dangerous impurity except CO; and in view of the difficulty of recognising by ordinary means the presence in poisonous amount of this gas, the author proposed the plan of making use of a small warm-blooded animal (a mouse or very small bird) as an indicator of CO. In very small warm-blooded animals the respiration and chemical changes in the body occur far more rapidly than in a man. Consequently the small animal absorbs CO correspondingly more rapidly, and thus shows symptoms of poisoning much sooner than a man does in the same atmosphere. Hence, if a miner, going into air which may contain CO, carries a mouse with him in an open cage, and watches to see whether it shows signs of sluggishness or exhaustion, it will give him timely warning of the presence of a dangerous amount of CO. It must, however, be borne in mind that this test is not a very delicate one. Symptoms sufficient to cause in a man dizziness, etc., on exertion, would hardly be observed in a mouse; and consequently much caution is necessary in going down ladders, steep inclines, etc., when trusting to the indications of a mouse, as the exertion in returning might produce serious symptoms if even a moderate percentage of CO were present.

A mouse may also be used for detecting the presence of even very small percentages of CO in mines. If it is left for about ten minutes at the place where the air is to be tested, and is then killed at the same place, one can tell approximately by an examination above ground of its blood how much CO was present in the air. A very dilute solution is first made of normal blood, which may be obtained from a prick in the finger. This is placed in two test tubes of equal diameter, and should be of such a dilution that the solution has a yellow tinge. The solution in one of the test tubes is then shaken up with ordinary lighting gas till the hæmoglobin is saturated with CO, when its colour changes to pink. A preliminary experiment will readily decide whether the dilution is sufficient to show fully the difference in tint. In another test tube of the same diameter is placed a solution of the mouse's blood, a drop of which may easily be obtained by opening the heart, and this solution is cautiously diluted till its *depth* of tint is the same as that of the other two solutions. On now comparing the tints of the three tubes, it will be found that that which is saturated with CO has a full pink colour, which contrasts markedly with the yellow of the normal blood solution. If CO was present in the air the blood solution from the mouse will be intermediate in tint, and it is possible to estimate roughly, according as the mouse's blood solution approximates in tint to the one or other of the two first solutions, to what extent the mouse's hæmoglobin was saturated with CO. From this the percentage of CO in the air may be roughly estimated, since the blood of the mouse will be about half saturated with ·08 per cent. of CO in the air, a third saturated with ·04 per cent., a fifth saturated with ·02 per cent., two-thirds saturated with ·16 per cent., etc. The tints should be compared by holding the test tubes against the light from the sky, and they should be changed from side to side during the comparison. The colorimetric test is far more delicate and more suitable for quantitative estimations than the spectroscopic or any other known method of examining small samples of blood for CO. This method requires daylight, however, though a lamp, or better, an incandescent gas burner, with a blue glass chimney and opal globe may also be used, or else blue glass spectacles. The test is very useful for such purposes as tracing the position of heated coal in a goaf, or exploring a mine after a fire or explosion.

If a mouse is not available, a similar test may be carried out as follows with a sample of the suspected air :—The sample is collected in a perfectly clean bottle of about 100 c.c. capacity. The cork of the bottle is removed under a dilute (about ½ per cent.) solution in distilled water of normal blood (obtained either by squeezing a prick from the finger or from any animal) in a small basin. About 5 c.c. of the air in the bottle is then allowed to bubble out, and a corresponding volume of blood to enter. The cork is then replaced, and the bottle covered with a cloth to keep off the light, which interferes with the reaction, and shaken continuously for ten minutes, when the hæmoglobin will have reached a point of saturation dependent on the percentage of CO present. The solution is then poured into a test tube and its percentage saturation estimated by the eye in the manner just described.

The percentage of CO ($p$) present may be calculated by the following formula from the percentage saturation ($s$):—

$$p = \frac{s \times \cdot 07}{100 - s}.$$

Thus, if the estimated saturation be 20 per cent., the percentage of CO will be $\frac{20 \times \cdot 07}{100 - 20} = \cdot 017$. It is evident, however, from what has been said above as to the relative influences of oxygen and CO in determining the percentage saturation of hæmoglobin with CO, that if the oxygen percentage of the air be much diminished the calculation as given will be incorrect, the result being too high. Thus, if the oxygen percentage be diminished to half, the result will be twice as high as it ought to be, and must be correspondingly corrected. In ordinary samples of mine air, where a light will burn, this source of error may, however, be neglected. Where only very small percentages of CO are present in air the method just described is often very useful, particularly where other combustible gases are present. No other gas will turn the blood solution pink, so that the test, like that with the mouse's blood, is a perfectly certain and extremely delicate one for CO. A more exact but also less easy colorimetric method of estimating the percentage saturation of the blood with CO was described by me in the *Journal of Physiology*, vol. xxii. p. 478 (see also vol. xviii. p. 465, and vol. xxii. p. 233).

**Sulphuretted Hydrogen.**—The circumstances (blasting with gunpowder, spontaneous heating of coal, decomposition of sulphides, etc., under which this very poisonous gas may occur in mines have been already alluded to (p. 134). The action of $H_2S$ on men and animals has been carefully investigated by Lehmann.[1] He concluded that air containing about ·07 per cent. is just sufficient to cause death after an exposure of about an hour or more in the case of various animals, and also of man. In one of his experiments on man alarming symptoms were produced within a few minutes by air containing ·05 per cent. The frequently quoted statement that a man can breathe 1 or even 3 per cent of $H_2S$ for a short time without injury is quite erroneous. Such percentages would cause almost instantaneous death. Lehmann found that 0·2 per cent. was sufficient to kill dogs and cats within one and a half minutes.

The symptoms are those of an intense poison, acting both locally as an irritant, and after absorption on the brain and other

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[1] *Archiv für Hygiene*, vol. xiv. 1892, p. 135. See also Haldane, *Lancet*, 1896, vol. i. p. 220.

parts. Except in great concentration, it causes no characteristic change in the blood. With very small proportions the first symptoms noticed are irritation of the eyes and air-passages. The action on the eyes may only produce slight discomfort, and a feeling as if some dust were present. Symptoms really due to sulphuretted hydrogen have sometimes been attributed to dust. With somewhat more $H_2S$ in the air, eye inflammation (conjunctivitis), accompanied by intense pain, particularly during the next night, is produced. There may also be slight bronchitis. When as much as ·05 per cent. of the gas is present, alarming symptoms, such as giddiness, vomiting, etc., are quickly produced, besides catching of the breath and other signs of irritation.

In accidents from $H_2S$ men are usually rendered helpless or unconscious with great suddenness; and sometimes one man after another is struck down during efforts to save the first man affected. In one case investigated by me five men lost their lives in a manhole leading to a sewer, the last four having descended one after another in vain attempts at rescue. As in the case of carbonic oxide poisoning, death often occurs afterwards in men who have been rescued unconscious from air containing $H_2S$. It seems to be the case that when formidable proportions of $H_2S$ are present the sense of smell for this gas becomes no longer a reliable guide. 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 $H_2S$. The smell was easily perceptible, however, when I opened, in the fresh air, a bottle containing a sample of the gas.

**Nitrous Fumes.**—When nitro-glycerine or nitro-cellulose explosives burn or fume off quietly instead of detonating, they give off, as explained above (p. 133), carbonic oxide and nitric oxide in place of carbonic acid and nitrogen. The nitric oxide immediately combines with the oxygen of the air to form red fumes consisting chiefly of nitric peroxide ($2NO + O_2 = 2NO_2$).

Nitrous fumes have an irritant action on the air-passages, and are extremely dangerous when present in appreciable proportions, and have caused many deaths. In the case of several other irritant gases, such as sulphurous acid, there is very little danger in breathing for some time percentages which are extremely unpleasant and irritating to the throat, nose, and eyes. The only after-effect is a temporary catarrh. With nitrous fumes, however, there is very great danger, as the after-effect produced is frequently an intensely acute bronchitis, which is often fatal. Persons who have been exposed for some time to an irritant atmosphere of nitrous fumes often notice very little wrong just after the exposure; but after a few hours the bronchitis begins to develop, and is often fatal within forty-eight hours. As many as twenty lives have been lost at a time from the nitrous fumes produced by a box of dynamite which has caught fire underground, and where bad fuses, unsuitable detonators, or bad dynamite are used, miners are often severely, and sometimes fatally, injured by nitrous fumes. I have found that animals are affected in the same way as men. Thus mice exposed for half an hour to air containing as little as ·05 per cent. of nitrous fumes (*i.e.* air to which ·05 per cent. of NO had been added) died, within twenty-four hours, of bronchitis. The animals seemed to be only slightly inconvenienced by the gas at the time, and were apparently quite well when first removed from the gas. It would appear from this experiment that nitrous fumes are even more poisonous than sulphuretted hydrogen; and no gas met with in mines is so treacherous in its effects.

In the case of other irritant gases, persons who have often been exposed before acquire a considerable tolerance; and this may probably be the case with nitrous fumes.

Fortunately, nitrous fumes, even in very great dilution, are easily detected by their characteristic smell of fuming nitric acid; and great care should be taken in returning after a blast if this smell is distinct. Air containing enough nitrous fumes to produce feelings of irritation in the nose or air-passages is very dangerous.

**Moisture.**—So long as the temperature of a mine is moderate the percentage saturation of the air with moisture is practically without any direct influence on the comfort or health of miners. When, however, as is frequently the case, the temperature is high, moisture in the air is of great importance. In still and saturated air at a temperature above about 80° to 85° it is hardly possible for men to do continuous hard work, even when stripped to the waist. At higher temperatures in saturated air the amount of work possible becomes less and less, and the body temperature may rise rapidly, though men accustomed to the heat can bear it much better than others. At temperatures above about 90° by the wet bulb it is only possible to work for short periods, and it becomes difficult even to remain without working. Thus at a temperature of 93° in still and saturated air I found that though I was stripped to the waist, and doing practically no work, my temperature rose 5° in two hours, and was still rising rapidly when I found it necessary to come out.[1] On the other hand, it is a

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[1] *Report on the Health of Cornish Miners*, 1904, p. 94.

common observation that if the air is dry much higher temperatures can be borne with ease and comfort. In collieries where the air is fairly dry and in motion, men can work quite well at a dry-bulb temperature of 90°, or even 100°; and in hot climates with very dry air much higher temperatures are not oppressive. Men working rock-drills driven by compressed air have the great advantage, if the mine is hot, of being in fairly dry air during much of their time, since the air which escapes from the drill is only about 20 per cent. saturated with moisture when it assumes the mine temperature.

**Dust.**—It has been known for long that the death-rate among English metalliferous miners above middle age is far higher than among colliers or ironstone miners, and that the excess of deaths is due to phthisis and other lung diseases. Until lately, however, there was a good deal of difference of opinion as to why metalliferous mining has been so unhealthy. The observation that men engaged in boring dry holes with rock-drills are extremely liable to phthisis, and the investigations of the recent Transvaal Miners' Phthisis Commission,[1] and Home Office Committee in England,[2] all go to show that the real cause is the inhalation of air containing dust from hard stone. An exhaustive examination, during the Home Office inquiry, of the conditions underground in Cornish mines showed that, although ankylostomiasis (worm disease) was found to be prevalent, all the facts pointed to stone-dust inhalation, and this alone, as the cause of the excessive mortality.

The following tables from the Home Office Report will give an idea of the extreme seriousness of the effects produced by stone-dust inhalation. It will be seen that the proportional loss of life from this cause entirely dwarfs that from accidents and all other causes. The recent rise in the death-rate has been entirely caused by the use of rock-drills without water-jets or other means of stopping dust, and by the large number of rock-drill men who have returned to Cornwall from the Transvaal and other countries.

From personal inquiries carried out for the Home Office Committee by the registrars in the Redruth district of Cornwall, it was found that out of 142 deaths of men who had at any time worked rock-drills, 133, or 94 per cent., were from lung disease,

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[1] *Report of the Transvaal Miners' Phthisis Commission*, 1903.

[2] *Report to the Home Secretary on the Health of Cornish Miners*, by J. S. Haldane, Joseph S. Martin, and R. Arthur Thomas [Cd. 2091], 1904. See also discussion on Miners' Phthisis in *Trans. Inst. of Mining and Metallurgy*, 1904.

the average age at death being 37·2 years. Out of 178 deaths of miners who had never worked rock-drills, 116, or 65 per cent., were from lung disease, the average age at death being 53. Of 47 men who died, and had worked rock-drills in the Transvaal only, the average duration of the work was only 4·7 years.

The dust to which metalliferous miners are exposed is produced :

TABLE I.—DEATHS FROM ALL CAUSES PER 1000 LIVING AT EACH AGE.

| | AGES. | | | | | |
|---|---|---|---|---|---|---|
| | 15–20. | 20–25. | 25–35. | 35–45. | 45–55. | 55–65. |
| All occupied Males, England and Wales, 1890–1892 . . . . | 2·55 | 5·1 | 7·3 | 12·4 | 20·7 | 36·7 |
| Coal Miners, England and Wales, 1890–1892 . . . . . . | 3·8 | 5·6 | 6·3 | 9·6 | 19·4 | 43·8 |
| Ironstone Miners, England and Wales, 1890–1892 . . . . | 3·4 | 4·6 | 5·9 | 8·2 | 17·0 | 33·3 |
| Lead Miners, England and Wales, 1890–1892 . . . . . . | 3·0 | 6·45 | 9·45 | 13·5 | 23·9 | 66·6 |
| Tin Miners, Cornwall, 1890–1892 . | 3·0 | 7·0 | 8·1 | 14·3 | 33·2 | 66·1 |
| ,, ,, ,, 1900–1902 . | 1·55 | 5·8 | 13·4 | 27·9 | 39·85 | 66·8 |
| All Miners (including Gold Miners) living in Cornwall, 1900–1902 . | 1·7 | 5·8 | 20·9 | 39·0 | 44·6 | 70·5 |
| Cornish Miners, 1849–1853 . . | 8·9 | | 9·0 | 14·3 | 33·5 | 63·2 |
| All Males, England and Wales, 1849–1853 . . . . . . | 8·1 | | 10·1 | 13·0 | 19·0 | 34·8 |

TABLE IIA.—DEATHS FROM LUNG DISEASES PER 1000 LIVING AT EACH AGE.

| | AGES. | | | | | |
|---|---|---|---|---|---|---|
| | 15–20. | 20–25. | 25–35. | 35–45. | 45–55. | 55–65. |
| All occupied Males, England and Wales, 1890–1892 . . . . | 0·95 | 2·6 | 3·8 | 5·9 | 8·5 | 13·0 |
| Coal Miners, England and Wales, 1890–1892 . . . . . . | 0·9 | 2·0 | 2·1 | 3·5 | 7·8 | 18·7 |
| Ironstone Miners, England and Wales, 1890–1892 . . . . | 1·6 | 1·5 | 2·1 | 3·2 | 6·5 | 13·0 |
| Lead Miners, England and Wales, 1890–1892 . . . . . . | 2·0 | 3·3 | 5·1 | 8·7 | 13·2 | 32·0 |
| Tin Miners, Cornwall, 1890–1892 . | 1·3 | 3·7 | 3·9 | 9·5 | 23·0 | 40·7 |
| ,, ,, ,, 1900–1902 . | 0·5 | 2·6 | 10·5 | 23·2 | 29·6 | 42·8 |
| All Miners (including Gold Miners) living in Cornwall, 1900–1902 . | 0·7 | 2·7 | 17·3 | 33·2 | 32·2 | 42·6 |
| Cornish Miners, 1849–1853 . . | 3·05 | | 4·4 | 8·5 | 24·3 | 44·5 |

TABLE IIB.—DEATHS FROM ACCIDENT PER 1000 LIVING AT EACH AGE.

| | AGES. | | | | | |
|---|---|---|---|---|---|---|
| | 15–20. | 20–25. | 25–35. | 35–45. | 45–55. | 55–65. |
| All occupied Males, England and Wales, 1890–1892 | 0·5 | 0·6 | 0·7 | 0·9 | 1·1 | 1·4 |
| Coal Miners, England and Wales, 1890–1892 | 1·5 | 1·5 | 1·8 | 2·25 | 2·9 | 3·1 |
| Ironstone Miners, England and Wales, 1890–1892 | 0·9 | 1·1 | 1·2 | 1·3 | 1·7 | 1·9 |
| Lead Miners, England and Wales, 1890–1892 | 0·0 | 0·9 | 1·1 | 0·3 | 0·7 | 0·5 |
| Tin Miners, Cornwall, 1890–1892 | 1·0 | 2·1 | 0·9 | 0·3 | 0·3 | 4·4 |
| ,, ,, ,, 1900–1902 | 0·5 | 1·8 | 0·9 | 0·6 | 1·4 | 0·0 |
| All Miners (including Gold Miners), Cornwall, 1900–1902 | 0·5 | 1·7 | 0·8 | 0·55 | 1·25 | 0·5 |
| Cornish Miners, 1849–1853 | 2·0 | | 2·1 | 1·9 | 2·4 | 1·5 |

TABLE IIC.—DEATHS FROM ALL OTHER CAUSES PER 1000 LIVING AT EACH AGE.

| | AGES. | | | | | |
|---|---|---|---|---|---|---|
| | 15–20. | 20–25. | 25–35. | 35–45. | 45–55. | 55–65. |
| All occupied Males, England and Wales, 1890–1892 | 1·1 | 1·8 | 2·9 | 5·6 | 11·8 | 19·3 |
| Coal Miners, England and Wales, 1890–1892 | 1·4 | 2·1 | 2·4 | 4·3 | 8·7 | 22·0 |
| Ironstone Miners, England and Wales, 1890–1892 | 0·9 | 2·0 | 2·6 | 3·7 | 8·9 | 18·4 |
| Lead Miners, England and Wales, 1899–1892 | 1·0 | 2·15 | 3·2 | 4·5 | 9·9 | 34·0 |
| Tin Miners, Cornwall, 1890–1892 | 0·7 | 1·2 | 3·3 | 4·5 | 9·9 | 21·0 |
| ,, ,, ,, 1900–1902 | 0·5 | 1·4 | 2·0 | 4·2 | 8·9 | 24·0 |
| All Miners (including Gold Miners), Cornwall, 1900–1302 | 0·5 | 1·4 | 2·8 | 5·25 | 11·15 | 27·4 |
| Cornish Miners, 1845–1853 | 3·85 | | 2·45 | 3·9 | 6·8 | 17·2 |

(1) in the drilling of all holes in an upward direction when a jet or spray is not used; (2) at the beginning of downward holes before the hole will hold the water poured in; (3) in blasting; (4) in moving dry ore, *i.e.* shovelling it, sending it down ore-shoots, etc.; (5) at rock-breaking machines and dry crushing mills. In drilling by hand much less dust is produced

than with a rock-drill; but, unless water is used from the beginning, the amount is, nevertheless, considerable.

A large number of dust determinations in the air of Dolcoath Mine in Cornwall have recently been published by Thomas and Macqueen.[1] They found that in drilling dry holes with a rock-drill the amount of dust in the air inhaled by the men averaged 4·6 milligrammes in 10 litres of air, and varied from 0·5 to 11·4 milligrammes. In drilling downward holes, into which water was thrown from a can, the average was 2·2 milligrammes in 10 litres, the dust being produced before the hole was deep enough to hold water, and remaining in suspension afterwards. When a jet or spray was used properly from the beginning there was no weighable dust in 20 litres of air. In hand-drilling 0·1 to 4·1 milligrammes in 10 litres were found in the case of dry holes and at the beginning of holes into which water was afterwards poured. In filling waggons with dry ore 0·6 to 3·4 milligrammes were found; and at a rock-breaker when the water-sprinkler was not used 9·2 milligrammes were found. In ends and rises, within three to five minutes after blasting, 1·6 to 9·0 milligrammes were found, and it usually took about half an hour for the quantity to fall below 1 milligramme; but when the dust was drowned down by a water-blast the amount was reduced at once to less than 1 milligramme, and was frequently not weighable.

The dust in the Cornish mines is mostly derived from very hard granite, while that in the Transvaal and other gold-mines is from the quartz reef. Dust from flint, sandstone, ganister, and other similar stone is also known to be extremely prone to produce phthisis. On the other hand, coal dust, even in the considerable quantities which are commonly inhaled by colliers, seems to be relatively harmless, as shown by the tables quoted above, although after the age of about fifty colliers suffer somewhat in excess from lung affections. Dust from the mechanical disintegration of less hard varieties of stone, such as slate, etc., is probably intermediate in its effects. The particles of smoke from explosions, candles, etc., do not seem to be injurious, and ironstone miners, who work in an atmosphere containing much gunpowder smoke, are relatively very healthy, as also are the men employed in the very smoky atmosphere of the Metropolitan Railway.

Most metals are fortunately met with as ores in a very insoluble form, so that the presence of actually poisonous dust in metalliferous mines is exceptional. Much trouble is, however, caused by the dust from lead ore in the form of carbonate; and where

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[1] *Trans. Inst. of Mining and Metallurgy*, 1904.

lead carbonate is present the strictest precautions are needed to prevent the occurrence of symptoms of lead-poisoning (colic, anæmia, various forms of paralysis, etc.), either from inhalation of lead dust, or from ingestion of lead dust by the mouth from dirty hands, etc. In mines where mercury is mined still stricter precautions are necessary to prevent symptoms of poisoning by the inhalation of air containing cinnabar dust or vapour of mercury. Dust or vapour containing mercury is so poisonous that it is even said that symptoms of mercurial poisoning (salivation, etc.) have been noticed in the case of men exposed much to the smoke from blasting, the mercury coming from the fulminate in the detonators.

Where the mineral smaltite ($CoAs_2$) is mined, cancer of the lungs is somewhat frequent, and this appears to be due to some chemical action of the arsenic or cobalt of the decomposed mineral on the lungs.[1]

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[1] Many references to the subject of metallic poisoning, etc., in the mining and smelting of ores will be found in Le Neve Foster's *Text-book of Ore and Stone Mining*, 1904.

# APPENDIX.

## THE EFFECTS OF CARBONIC OXIDE IN CONNECTION WITH AN UNDERGROUND FIRE AT SNAEFELL MINE.

THE accident here referred to occurred in May 1897. Sir Clement Le Neve Foster was at that time Chief Inspector of Mines for the district within which the accident occurred, and it was thus his duty to go to the mine and report upon all the circumstances.

Snaefell lead-mine is situated on the flank of the mountain in the Isle of Man from which it takes its name. It is a small and somewhat primitive mine, only employing about fifty men at the time of the accident. As is shown by the sections (Plates I. and II.), the mine is worked by a main shaft, which follows the dip of the vein, and was 171 fathoms deep. The shaft, which is rectangular, is divided into three compartments, the middle one being the ladderway, and those on either side being used respectively for winding ore, and for the pump and the compressed air pipes. The ore was wound up in a rough wooden bucket or "kibble."

In the main the ventilation was "natural," being due to the higher temperature underground than above ground. The general tendency of the air-current was down the shaft to the bottom of the mine, and up through the various winzes (intermediate shafts) to the adit level. The open end of this had been connected to a sloping wooden chimney on the hillside, by which means the draught was increased. The mine had been officially inspected three days before the accident, and the ventilation was in its normal state, though on several previous occasions it had been found to be defective.

The time spent upon the ladders by the young and active men was about a quarter of an hour in descending and half an hour in ascending. The older men would take longer.

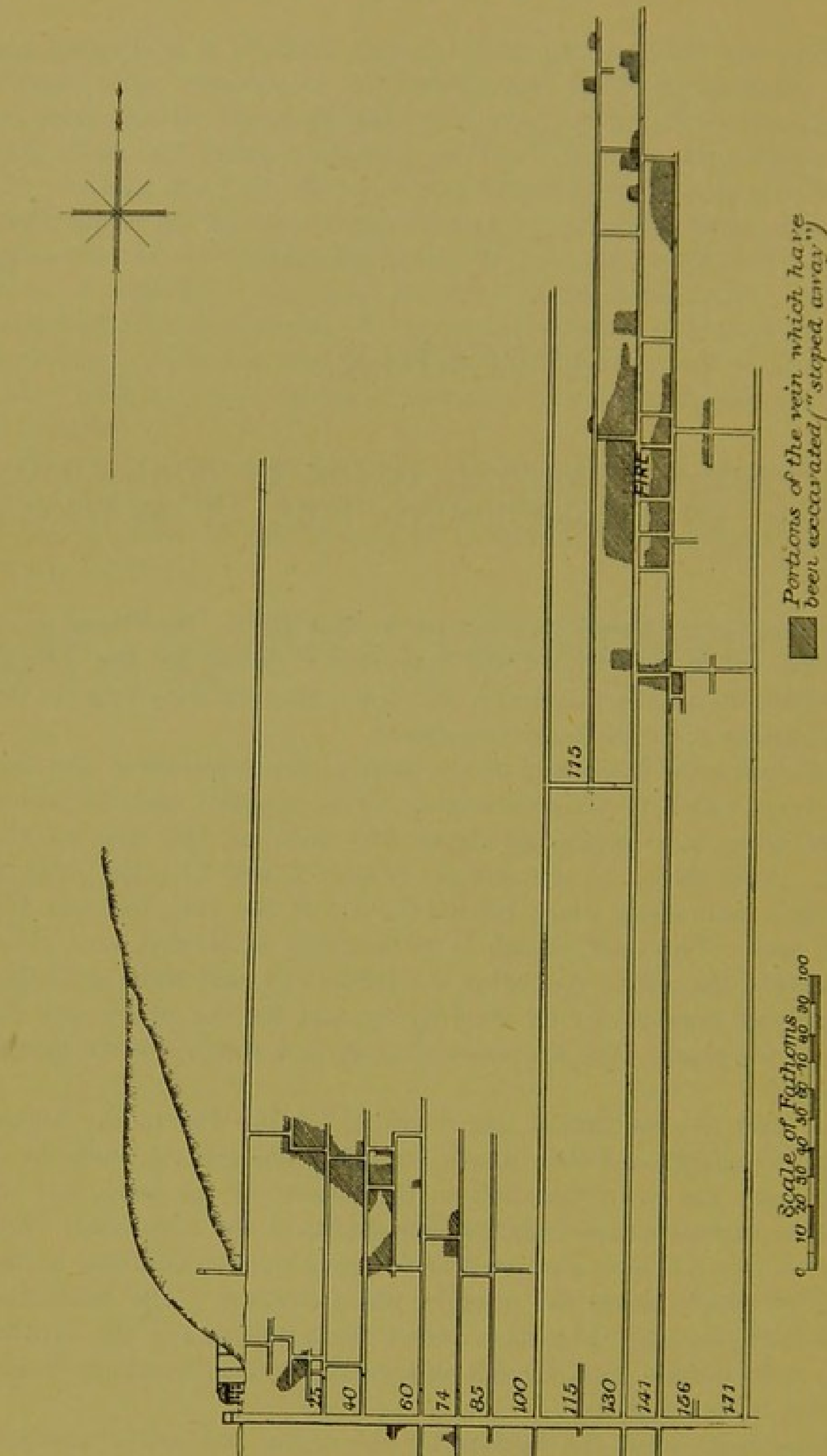

Plate I.—Snaefell Mine.

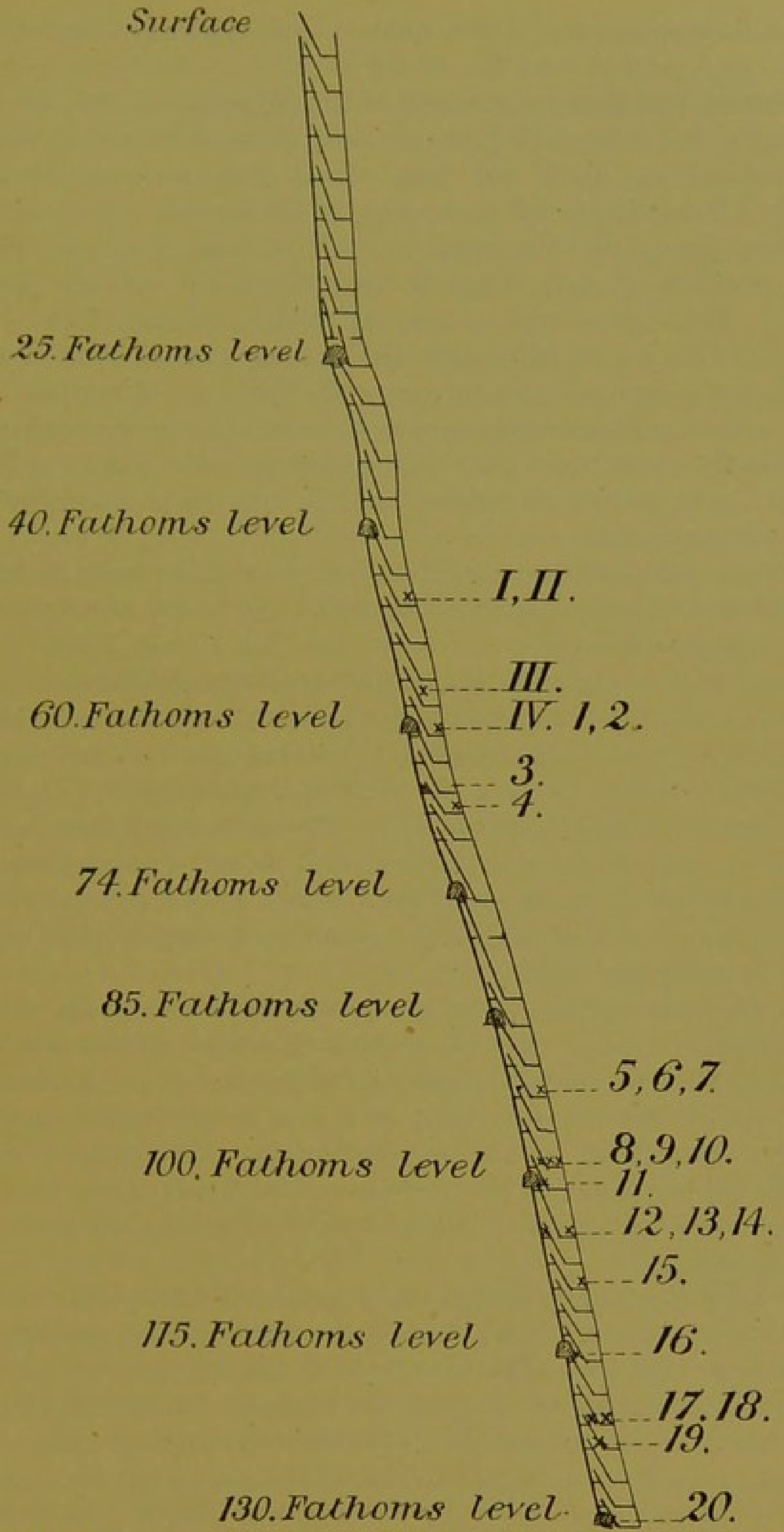

Plate II.—Diagrammatic Section of Ladderway of Shaft of Snaefell Mine to 130-fathoms level. The Roman numerals indicate the positions at which rescued men were found: the Arabic numerals show the positions of the bodies.

The following account of the accident and subsequent exploration of the mine is reprinted from the official Report.[1]

**Accident, and Rescue of some of the Miners.**—A little after 6 a.m. on Monday, the 10th of May, the morning shift, consisting of thirty-five men, entered the shaft and began their descent down the ladders. Shortly afterwards several men came to the surface in an exhausted condition, saying that the mine was full of some foul gas, which so deprived them of their strength that they could scarcely climb the ladders. These facts were at once reported to Captain Kewley; after sending to Laxey for assistance, he immediately descended the shaft with the object of ascertaining the true state of affairs, and of rescuing the men below, who were stated to be more or less overcome by the noxious gases. He met a few men almost dead-beat, trying to make their way up, and between the 45 and the 60-fathoms level he came upon others, still alive, but quite unconscious.

With the object of improving the atmosphere of the mine, he had holes punched in the pipes conveying compressed air to the boring machines, and this gave some relief.

If one tries to imagine the exact condition of affairs in a shaft such as has been described, it is evident that the task of the rescuers was no easy one. Persons unaccustomed to mining can best understand the state of the case by picturing the shaft as a rectangular well, having a ladderway in the middle (Plate II.). The unfortunate men had to be dragged up from platform to platform with the aid of ropes, through the "manholes," which measure only 22 inches by 19 inches, whilst the rescuers themselves were breathing a poisonous atmosphere, and beginning to feel its paralysing effects.

I have mentioned that ore and waste rock are drawn up the shaft in a bucket (*kibble*); but in cases of severe accidents, a special receptacle is used in its place for conveying the injured persons to the surface. It is a rectangular box six feet long, and just deep enough and broad enough to take a man. This was called into requisition a little later, and, with the aid of volunteers who had come from Laxey mine, three of the survivors were successively put into it and dragged up the shaft by the winding engine.

The work of rescue proceeded under great difficulties until five o'clock in the afternoon, when James Kneale, the last survivor, was brought to the surface. By this time the rescuers themselves were thoroughly exhausted, and barely able to climb the ladders. Captain Kewley, whose pluck has in no way suffered from his sixty-five summers, had gone down

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[1] *Report to the Home Secretary on the Circumstances attending the Underground Fire at the Snaefell Lead Mine in the Month of May* 1897, by C. Le Neve Foster, Esq., D.Sc., F.R.S., one of H.M. Inspectors of Mines [C. 8880].

no less than ten times, risking his own life again and again, in the hope of bringing succour to his men.

Dr Miller, of Laxey, on hearing of the disaster, immediately proceeded to the mine and gave medical aid to the sufferers, several of whom were still unconscious on reaching the surface.

Fortunately for all concerned, my assistant, Mr Williams, was still in the island ; and, upon receiving notice of the disaster through the foresight of Mr Samuel Harris, High Bailiff of Douglas, he hastened to the mine, which he reached about six in the evening. In the hope of finding further survivors underground and being able to save them, he at once organised another rescue party with Captain Kewley, and descended the shaft to the 74-fathoms level, passing three dead bodies. Mr Williams and a miner named Frederick Christian then made their way nearly to the 100-fathoms level, passing other dead bodies, some of which impeded their progress. The obstruction of the manhole just above the 100-fathoms level by three bodies was so great, that they decided to proceed no further ; and it is fortunate that they did so, for on commencing their ascent, they found that their strength was failing them, and that they had a difficulty in climbing the ladders. In time they reached the 60-fathoms level, and rejoined Captain Kewley and the rest of the rescuing party, who had commenced the ascent and were complaining of weakness and of inability to climb. It was then that Mr Williams applied a remedy, in a fashion hitherto untried in mining accidents, as far as I am aware.

On hearing at Douglas that the accident was probably due to foul gases, Mr Williams tried to procure some cylinders of compressed oxygen. As none could be obtained, he thought that possibly he could effect his purpose by generating the health-giving gas on the spot, and he bought about a pound and a half of potassium chlorate. This he carried with him down the mine, and made use of it while he and the rest of the rescue party were waiting to commence their ascent from the 60-fathoms level. He set light to a heap of newspapers on the floor of the level, and kept throwing the potassium chlorate, little by little, on to the fire. On leaning over it and inhaling the fumes, the party experienced decided relief, and to some extent regained their strength. I imagine that the deflagration of a portion of the chlorate furnished heat enough to cause another portion to give off its oxygen ; but, be the explanation what it may, I am assured by Mr Williams and Captain Kewley that the improvised remedy was unquestionably of service in enabling the rescue party to reach the surface. By this time they had been forced to the conclusion that no one remained below alive.

Before going underground, Mr Williams had telegraphed a brief notice of the disaster to me ; but, unfortunately, I was engaged officially at Newhaven, and the telegram did not reach me till after the last train had left for London. I was consequently obliged to defer my departure until the following morning, and then it was impossible for me to reach Liverpool in time to catch the mail steamer leaving that port for Douglas. I was unable to start from Liverpool until the morning of the 12th.

**Recovery of the Dead Bodies.**—After the last unsuccessful attempt to find and rescue any possible survivors, a consultation was held between Captain Kewley, Captain Reddicliffe, Mr Williams, and Dr Miller, and it was thought desirable to bring up the corpses from underground as soon as possible, as the work of removal would certainly become more difficult, sickening, and noxious each day it was delayed. On this account Mr Williams again descended the mine with a party of men, and was engaged till eleven o'clock at night in sending three bodies to the surface.

Early on the following morning the work of recovery was continued, under the superintendence of Mr Williams, as Captain Kewley was suffering from the effects of the poisonous atmosphere in the mine on the previous day, besides having ample work to do in superintending the disposal of the bodies as they were sent up to the surface. The working parties had further the aid and advice of Captain W. H. Kitto, the manager of Foxdale Mine, and my friend Mr H. Wynne-Finch, who happened to be staying with him when the news of the disaster arrived; they at once proceeded to Snaefell, descended the mine, and threw themselves into the work energetically.

Early in the afternoon, Mr Williams was so exhausted by his exertions, that he became unconscious for a few minutes, and had to be sent up to the surface in the "box." By this time ten bodies had been recovered, making, with the three brought up on the previous day, thirteen in all. Work was then suspended for the day. About six o'clock in the evening, a party of volunteers from Foxdale Mine, summoned by telegram from Captain Kitto, reached Snaefell, and would have descended at once if they had not been told that their services would not be required until the following day.

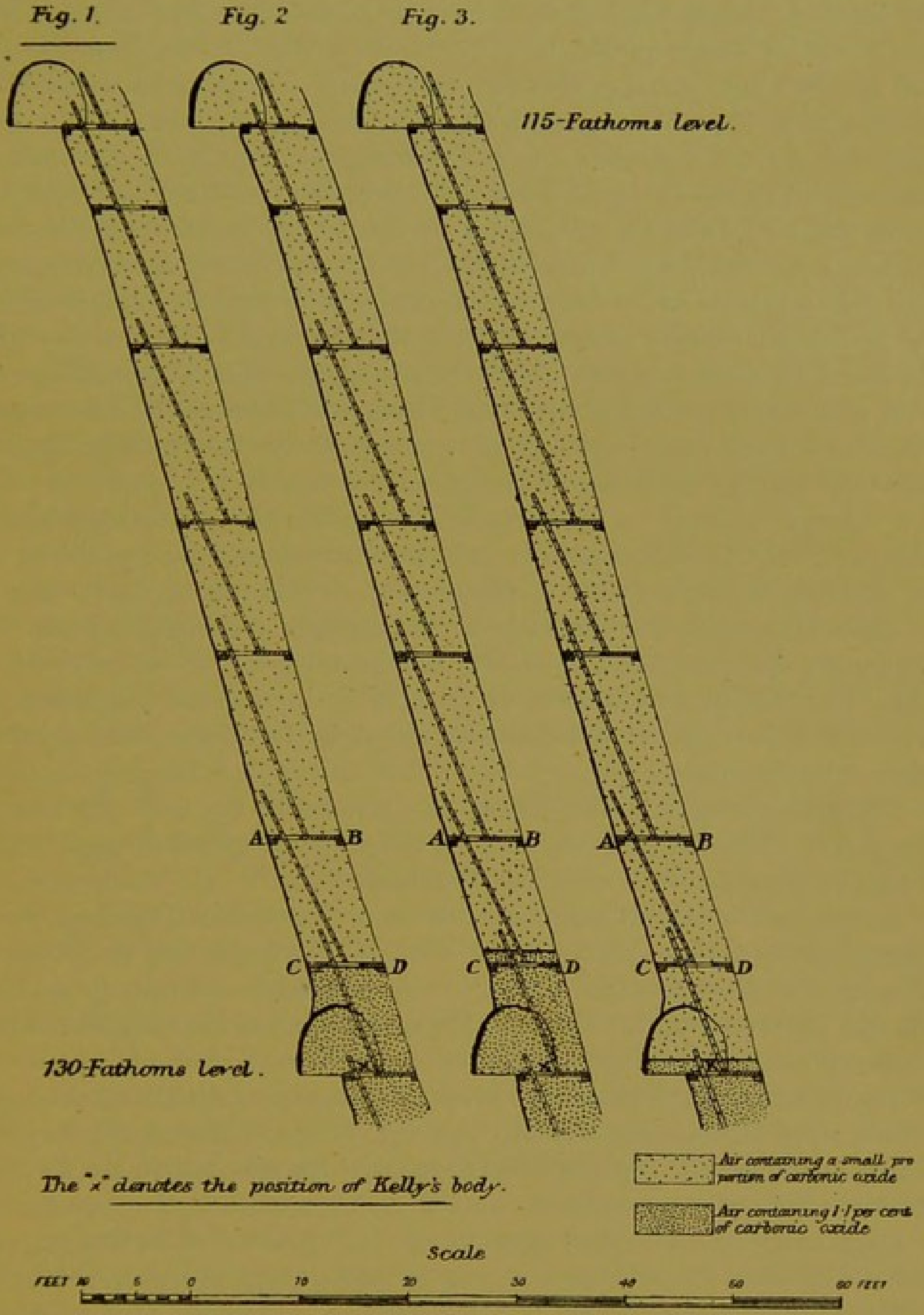
My other assistant, Mr Jones, who had started from Chester as soon as he received telegraphic instructions from me, reached Laxey in the evening.

On the Wednesday morning a party of volunteers, headed by Mr Williams and Mr Jones, descended the mine, and recovered five more bodies, which were found on different platforms near the 115-fathoms level, some above and some below.

By this time, they had descended as far as the platform immediately above the 130-fathoms level (CD, Plate III, fig. 1). One of the miners kneeling upon this platform put his candle through the "manhole" in order to look for the last body, when he found that it was at once extinguished. Knowing the importance of ascertaining the exact nature of the poisonous

## LADDER-WAY IN SNAEFELL MINE.

*From the 115-fathoms level to the 130-fathoms level.*



The "x" denotes the position of Kelly's body.

PLATE III.

gas, Mr Williams sent a note to the surface asking to have some bottles, filled with water, and well corked, sent down to him for the purpose of securing samples for analysis. When the bottles arrived, he stood upon the second rung of the ladder below the platform, and, keeping his head well up, he held one of them under the platform, allowed the water to run out, and re-corked it. A second sample was obtained in a like manner, but while he was emptying the water from a third bottle, he suddenly, and without any warning, became unconscious. There is no doubt that he inhaled a big whiff of gas which came through the "manhole" when disturbed by the operation of taking samples. The effect was instantaneous, but it must be recollected that his blood was already affected by his having been down the mine for some hours. As he knew that he was running some risk, he had wisely taken the precaution to put a rope round him before beginning his dangerous task, and it is most fortunate that he did so, for otherwise it is almost certain that he would have lost his life. Mr Jones and some miners who were holding the rope dragged him up from platform to platform, for a total distance of 80 feet, still in an unconscious state ; and their work was not accomplished without difficulty, for they were feeling the effects of the poisonous atmosphere, and had only just strength enough to lift their living burden. On reaching the 115-fathoms level, Mr Jones held his colleague's mouth to a hole punched in an air-pipe, through which a strong current was issuing, and worked his arms backwards and forwards in the manner recommended for the apparently drowned, and before long he was rewarded by seeing signs of life. Mr Williams was then at once sent up in the "box," and on arrival at the surface he was brought round by Dr Miller, who injected ether subcutaneously.

Mr Jones managed with difficulty to climb to the top with the rest of the party. There is no doubt that by his presence of mind, under very trying circumstances, he saved Mr Williams' life.

Undeterred by Mr Williams' narrow escape from death, Captain Kitto descended the mine in the afternoon with Mr Wynne-Finch and a party of volunteers from Foxdale, with the object of endeavouring to recover the last body, leaving his assistant, Captain Lean, to direct matters at the surface if necessary. They penetrated as far as the platform which Mr Williams had reached when he took his sample, and reported that they saw a body upon the landing some 10 feet below it. While one of the men was punching the air-pipe, in order to improve the ventilation, Mr Wynne-Finch became unconscious, and was sent to the surface in the "box."

Captain Kitto and his men then ascended the ladders, all feeling more or less the effects of the poisonous atmosphere which they had been breathing.

Travelling by the earliest possible steamer, I was not able to reach Douglas until the afternoon of the Wednesday (12th of May), and on proceeding at once to the mine I found Dr Miller, who took me to see the eighteen corpses laid out in the carpenter's shop. He pointed out the signs of poisoning by carbonic oxide, telling me also that these had been more apparent on the Monday and Tuesday. I was also able to congratulate Mr Williams upon his escape and hear from him and Mr Jones some details concerning the condition of the mine. I then went to see my friend Mr Wynne-Finch, who was lying down in his mining clothes, still feeling bad. Later on he was brought down to the inn at Laxey and was put to bed with hot bottles. The next day he was sufficiently well to return to Foxdale.

As the men who had been underground were tired or exhausted, and as there was nothing to be gained by an immediate descent, I postponed my visit underground until the following day. I then considered it my duty to test the air very carefully for fear of risking any more lives. I had come to the conclusion from Mr Williams' first telegram, and from newspaper accounts, which told me that the disaster was caused by fire or foul gas, that probably carbon monoxide was at the bottom of the mischief, and therefore in passing through Liverpool I had bought a supply of mice, with the object of employing them as indicators of the poison in case it should still be present.

A mouse was put into an improvised receptacle made from the revolving part of its cage, and this was attached to the "clevis" or spring-hook of the winding rope, whilst a lantern and lighted candles were placed inside the kibble. By the aid of this testing apparatus it was easily ascertained without any risk that the air was not bad as far as the 115-fathoms level, and that it became poisonous and deadly at the 130. The mice showed precisely the same symptoms as human beings; for, if not completely dead on arriving at the surface, they had lost all power in their legs, whilst pinkness in the snout recalled the pink lips of the dead bodies of the unfortunate miners. I then decided to descend the mine and learn by further personal examination the precise condition of affairs. Accompanied by Mr Williams, Mr Jones, Captain Kewley, and several miners, I went down the ladderway as far as the 115-fathoms level, and on descending deeper took the precaution to test the air with a mouse and candle before going below each platform. By means of a string I lowered the cage, with the mouse inside and the candle affixed by a lump of clay (see fig. 40), from one platform to the next, and left it for a couple of minutes before drawing it up. Testing carefully in this manner from stage to stage, we arrived all right at the bottom of the fourth ladder (AB, Plate III., fig. 2); but when, standing upon the platform at the foot of this ladder, I lowered the mouse to the fifth, I found that the light went out and that the little animal showed signs of much distress. The air was evidently worse than it had been on the previous day, for then a light would burn brightly on the platform, although it was extinguished below. On Thursday, the day of my visit, there was very bad air above the platform. One of the miners begged me to be allowed to go down with an air-hose in his mouth ; but of course I refused, saying that I was responsible, and that no one should go down lower. We all climbed up again without difficulty ; though, after an hour at the surface, I began to have a violent pain across the forehead which lasted some time.

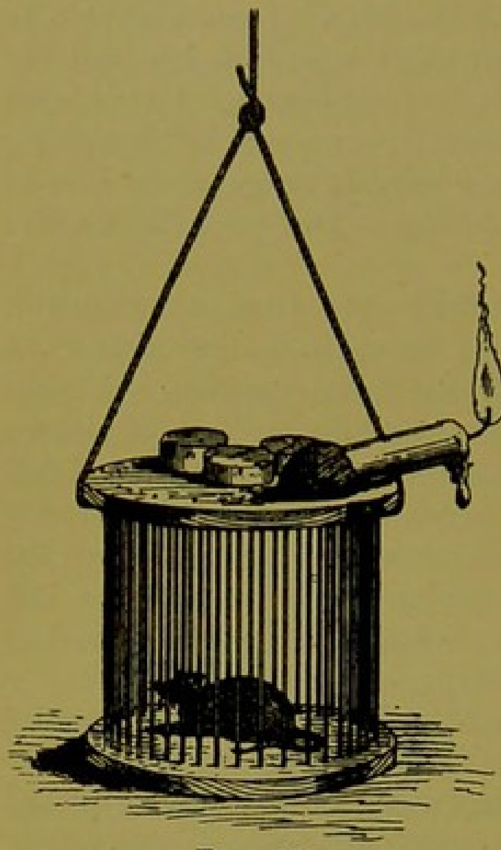


FIG. 40.

In order to improve the ventilation of the mine, I had a fire lighted at the bottom of the wooden chimney, and I was glad to see that it created a good draught.

On the following day my tests made from the surface showed me that the level of the bad air in the mine had not gone down as I expected. I therefore concluded that some of the ventilating doors, which I had been told were shut, must be open. Captain Kewley offered to send down men to see, but I thought that it was better that I should go myself. Mr Williams, Mr Jones, and Captain Kewley came down with me to the 100 level, and we found two doors open. These I helped to shut, and we came up, hoping to find a great improvement on the morrow.

On the Saturday morning, my tests with mice proved that things were much in the same condition ; and it then seemed to me probable that the door at the 130-fathoms level was open, allowing the air going down the main shaft to escape through this level to the succession of intermediate shafts which formed the upcast, without going to the lower levels at all. I was of opinion that this door should be closed if possible, and there was naturally a desire on all sides that the last body should be brought up.

Mr Williams, Captain Kewley, Captain Reddicliffe, and I, with a party of miners, went down all right to the 115-fathoms level ; and before descending any further I tested the air, by lowering a tame rat in a cage, from platform to platform. Leaving most of the miners at the 115, Mr Williams, Captain Kewley, Captain Reddicliffe, I, and

Henry Clague reached the fifth platform (CD, Plate III.) in safety, from whence, when I lowered my testing apparatus with its candle alight, I could see the body of the poor miner, lying in the position described by the Foxdale men. Just at the level of the body, the candle went out. I let the cage with the rat remain down five minutes by my watch, and when brought up it was not dead, though visibly affected. Captain Kewley and Clague said they would go down and get up the body. I had to tell them plainly that they should do no such thing. No doubt it looked easy, for the body was not more than 10 feet below us. I was firm in refusing permission, but said that I thought we might grapple for it easily and bring it up in a very few minutes. One of the men who was higher up came down with the grappling iron, and, in order to use it more conveniently, he pushed aside the short ladder leading from the platform CD to the 130 level. Moving the ladder seems to have disturbed the body of gas, for almost immediately afterwards Captain Kewley said he was feeling ill, so I shouted, "All up at once." We all climbed to the 115 level, where the "box" was in readiness. Captain Kewley was put into it, and we signalled to have him wound up. Those who had been as far down as the platform CD were decidedly affected by the poisonous atmosphere, and as they felt they could climb no higher, they sat down in the 115 "lodge" or "plat," that is to say, the enlargement of the mouth of the level where it joins the shaft.

The miners who had remained at the 115-fathoms level, or had descended but little below it, started off by the ladders, and in time reached the top of the shaft in a somewhat exhausted condition. In the meanwhile the "box" in which Captain Kewley was being raised to the surface stuck in the shaft, owing to a link of the chain, by which it was attached to the winding rope, getting caught between two of the planks in a defective part of the wooden trough up which it was sliding. The "box" would go neither up nor down, and poor Captain Kewley was kept in this trying position for about an hour. At last his son went down with some men and set the "box" free, and another party came to the 115-fathoms level to rescue those who were unable to climb. The "box" was sent down to that level, and one after another we were brought to the surface. After this misadventure it was evident that it would be unwise to venture down the mine again until the ventilation had considerably improved.

**Further Examination of the Mine and Inquest.**—At the adjourned inquest, evidence was given by Captain Reddicliffe, myself, Mr Williams, and one of the miners, and our examination occupied no less than eight hours. My most important duty was communicating the result of the analyses of two samples of gas which Mr Williams had obtained just above the 130 level, at the risk of his life, in the manner already described. Dr John Haldane, F.R.S., Lecturer in Physiology, University of Oxford, to whom the samples had been submitted, had made the following report to you :—

"OXFORD, *May* 19*th*, 1897.

"SIR,—I beg to report as follows on the articles transmitted to me for examination in connection with the Snaefell disaster.

"The articles which had been forwarded to the Home Office by Dr Le Neve Foster, H.M. Inspector of Mines, consisted of two dead mice, and two samples of air contained in bottles. The bottles were closed by corks, which had been sealed and were found to be perfectly air-tight.

"The first mouse examined was labelled as follows :—'Snaefell Mine, No. 1, 13th May. Mouse lowered into the mine in a kibble as far as 130-fathom level, came up alive, but legs paralysed ; killed on reaching the surface.'

"The blood on dilution with water was found to have the pink tint characteristic of carbon monoxide poisoning. Judging roughly by the tint, I estimated that the hæmoglobin was about 80 per cent. saturated with carbon monoxide. An exact determination could not be made, as the light was failing at the time when the articles for examination were received.

"The second mouse was labelled—'Snaefell Mine, No. 2, May 13th, 1897. Mouse taken down into the mine and lowered by me from the platform at the foot of the 4th ladder below the 115-fathoms level to a platform some 25 feet below it. Mouse had suffered and was killed at once.'

"The blood of this mouse had also the characteristic tint of carbon monoxide poisoning. The saturation of the hæmoglobin was exactly determined and found to be 78·3 per cent.

"The bottles containing the samples of air were both labelled as follows :—'Sample of air from shaft of Snaefell Mine just above 130-fathoms level, 12th May 1897, C. Le Neve Foster.'

"The composition of the sample in the first bottle opened was found to be as follows :—

| | Per cent. |
|---|---|
| Oxygen | 15·48 |
| Carbon dioxide | 4·22[1] |
| Carbon monoxide | 1·07 |
| Hydrogen | 0·48 |
| Nitrogen and Argon | 78·75 |
| | 100·00 |

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[1] A duplicate determination also gave 4·22 per cent.

"The gas in the second (larger) bottle had the following composition :—

| | Per cent. |
|---|---|
| Oxygen | 15·52 |
| Carbon dioxide | 4·26 |
| Carbon monoxide | 1·10 |
| Nitrogen, Argon, Hydrogen | 79·12 |
| | 100·00 |

"As the second sample was evidently the same in composition as the first, the hydrogen was not determined separately. The carbon monoxide was in each case determined colorimetrically with blood solution, and the hydrogen by passing over a glowing platinum spiral. The carbon dioxide formed by contact with the platinum corresponded exactly to the carbon monoxide known to be present, so that no appreciable proportion of methane or other hydrocarbons can have been present.

"The composition of the sample corresponds to a mixture produced by the combustion of wood or other similar material. Inhalation of air of this composition would produce helplessness (in a man) within about seven or eight minutes at most, and would soon cause death. A candle would not burn in such air, but would just do so on the addition of a third of its volume of fresh air. The mixture would then still be intensely poisonous, and would still be if diluted with four times its volume of fresh air. When diluted with nine times its volume of fresh air it would still be capable of rendering a man incapable of walking.—I am, Sir, your obedient servant, JOHN HALDANE.

"The Under Secretary of State,
Home Department."

Although, after the statement of Dr Miller and the appearance of the corpses, there was no doubt about the cause of death, it nevertheless was extremely satisfactory to find such ample confirmation by Dr Haldane, and it is worthy of remark that upon no occasion, as far as I am aware, has a sample of such a terribly poisonous character ever been taken in a mine.

The whole of the evidence confirmed me in the opinion which I had formed on the very first day I heard of the accident—that it resulted from an underground fire.

It was found on testing the air, day after day, by lowering mice and candles from the surface, that the atmosphere of the mine was improving gradually under the influence of the natural ventilation, and on the 7th of June it was considered that the descent to the 130-fathoms level could be made with perfect safety. A party of men went down the mine and sent up the last body—that of Robert Kelly.

Owing to official work at Petty Sessions in Wales and in the southern portion of my district, my next visit to the island was not until the 16th June; I was then fortunate enough to be accompanied by Dr Haldane, who made a visit at his own expense in order to investigate the circumstances of such an important disaster from the poisonous gas, with which, more than any other scientific man, he is so thoroughly familiar. A very stormy passage prevented our reaching the mine until late in the afternoon, and by that time Mr Williams and Captain Kewley had been down the mine and had discovered the seat of the fire. They then accompanied Dr Haldane, Dr Miller, Captain Reddicliffe, and me to the 130-fathoms level, and at a point about 630 yards north of the shaft we found that the level was completely blocked by rubbish, which had fallen from workings above, as the supporting timbers had been destroyed by fire. The pieces of charred timber left no doubt about the origin of the disaster.

A sample of the air taken by Dr Haldane gave him the following results on analysis :—

| | |
|---|---|
| Carbonic acid gas . . . . . . . | 0·64 |
| Oxygen . . . . . . . . . | 20·17 |
| Nitrogen and Argon . . . . . | 79·19 |
| | 100·00 |

No trace of carbon monoxide could be detected in the sample.

**Cause of the Accident and Remarks.**—Though Professors Dewar,[1] Tilden,[2] and Bedson[3] have discovered that carbonic oxide occurs occluded in certain rocks and minerals, the gas has never, I believe, been found as a natural constituent of the atmosphere of mines. It was evident, therefore, from the first, that I had to seek for some artificial source of the poison when investigating the accident, and I think that it is now

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[1] "Recent Researches on Meteorites," *Proc. Roy. Inst.*, vol. xi., London, 1886, p. 546.

[2] "On the Gases enclosed in Crystalline Rocks and Minerals," *Proc. Roy. Soc.* vol. lx., 1897, p. 453. Since my report was written, I find that Prof. Ramsay and Mr Travers, in their paper upon Fergusonite, state that a small quantity of carbonic oxide is given off by the mineral gadolinite when heated (*Proc. Roy. Soc.*, vol. lxii., 1897, p. 329), whilst Behrens notes the occurrence of the gas in the coal of Upper Silesia ("Die Kohlenstaubgefahr und ihre Bekämpfung," *Glückauf*, vol. xxxiv., 1898, p. 316).

[3] "A Contribution to our Knowledge of Coal Dust," *Trans. Fed. Inst. Min. Eng.*, vol. vii., 1893-94, p. 28.

perfectly certain that the deaths of the twenty victims of the Snaefell disaster were due to carbon monoxide, produced by timber burning in the mine. The next point for consideration is how the timber became ignited. Before the workings could be entered, I suggested two possible explanations: (1) A lighted candle stuck up against one of the timber supports; (2) the spontaneous combustion of cotton waste impregnated with oil, which had been in use by the men who were working rock drills. As the inspection of the mine revealed the fact that the seat of the fire was at the 130-fathoms level, where men had been engaged in putting in fresh timber, and not in the 171-fathoms level, or in the "stopes" above it, where machine drills were being employed, I naturally at once abandoned the second theory, and I feel convinced in my own mind that the first is the true solution of what was thought by some persons to be a mystery.

The timber in parts of the 130-fathoms level is very dry, and would easily take fire. It will, then, be asked how the ignition of the timber could escape the knowledge of the men employed at the place.

To answer this question one must explain a common practice of miners. When his candle, held in its clay socket, is nearly burnt out, the workman very frequently sticks up the end against the side of his working place, whether timbered or not, takes a fresh candle from his bundle, and lights it at the flame of the old one; he then blows out the flame of the candle-end, or puts it out with his fingers, with the intention of using it as a "snuff" for igniting the fuse of some future shot. Careless miners may sometimes leave a candle-end to burn away of itself, whilst in other cases the snuffing out may be imperfectly performed and the wick may go on smouldering, and eventually ignite inflammable material with which it is in contact. It is quite easy, therefore, to account for the ignition, and some facts which I extracted at the inquest fully confirmed me in my belief. In answer to my question, "Have you ever known timber used in a mine take fire accidentally from a candle being left near it?" Captain Reddicliffe stated that he thought he could recollect no less than five cases of the kind—three in Laxey Mine and two at other mines.

Once started upon a timber prop, the fire would naturally spread to the adjacent supports, and no doubt it burnt well and thoroughly for a time, as long as plenty of air was available; but when the combustion of the supporting frames so weakened them that they gave way under the weight of the waste material lying upon them and caused a block in the level, the condition of things was somewhat altered. The timber was then burning in a sort of *cul-de-sac*, and did not get all the oxygen necessary for the perfect combustion of the carbon; the result was that carbon monoxide was generated in addition to carbon dioxide.

It is rather startling to find how small a quantity of timber need be burnt to pollute to a dangerous extent the passages of a mine. According to Mills and Rowan,[1] air-dried wood may be considered as consisting of

40 parts of carbon (inclusive of 1 part ash),
40 „ „ oxygen and hydrogen in the proportion in which they unite to form water,
20 „ „ hygroscopic water.

Taking the weight of a cubic foot of larch, which was the kind of timber employed at Snaefell, at 34·5 lbs.,[2] the quantity of carbon in it will be

$$\frac{39 \times 34{\cdot}5}{100} = 13{\cdot}455 \text{ lbs.}$$

12 parts by weight of carbon combining with 16 parts by weight of oxygen will produce 28 parts by weight of carbon monoxide. Therefore, 1 cubic foot of larch will produce

$$\frac{28 \times 13{\cdot}455}{12} = 31{\cdot}395 \text{ lbs.}$$

of carbon monoxide. At a temperature of 60° F., and under a barometric pressure of 30 inches, 1 cubic foot of carbon monoxide weighs about 520 grains. 31 lbs. of carbonic oxide will therefore occupy 417 cubic feet of space. Taking an ordinary mine tunnel or level as being 7 feet high by 5 feet wide, each yard of length would contain 105 cubic feet, and therefore it is easy to see by calculation that 417 cubic feet of carbon monoxide would furnish 1 per cent. of the contents of a gallery about 400 yards long. Of course 1 per cent. of this noxious gas is quite sufficient to cause almost immediate loss of consciousness, followed speedily by death.

The total capacity of all the levels, shafts, and excavations in the Snaefell Mine was stated in evidence at the inquest to be a little over a million cubic feet; therefore 25 cubic feet of timber contain carbon enough to produce sufficient carbon monoxide to give an atmosphere with 1 per cent. of the noxious gas all through the mine.

I have not taken into account the alteration in the volume of the gas which would be caused by differences of temperature and pressure, because these would not affect the gist of my statement that a very small fire may suffice to produce very disastrous results, unless the air-currents traversing the workings are sufficiently strong to sweep out the

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[1] *Fuel and its Applications*, London, 1889.

[2] *Pocket-book of Engineering Formulæ*, by Molesworth, 22nd edition, 1888, p. 18; 34·5 is the mean of the two values given. Karmarsh, quoted by Mills and Rowan (*op. cit.* p. 7) gives 0·565 as the specific gravity of air-dried larch, which is equivalent to 35·3 lbs. per cubic foot.

foul gases as quickly as they are produced. At Snaefell the block in the level, produced by the rubbish falling when the supporting frames were burnt away, stopped the air-current in that part.

I will now for a moment consider the question of carbon dioxide.

Calculating in the same manner as before, we find that the perfect combustion of 1 cubic foot of larch would produce 49·335 lbs. of carbon dioxide. As 1 cubic foot of carbon dioxide, under the same conditions as before, weighs about 820 grains, the above quantity of 49·3 lbs. would occupy a space of 420 cubic feet. A hundred cubic feet of larch would give 12,000 cubic feet of carbon dioxide, or enough to impregnate a million cubic feet to the extent of 4 per cent.; therefore we see that the combustion of 125 cubic feet of timber might have added sufficient carbon dioxide and carbon monoxide to bring the whole atmosphere of the mine into the condition of the poisonous sample so often referred to, whilst its noxious properties were strengthened by the exhaustion of the life-sustaining oxygen. However, it is not likely that the whole of the mine was ever full of such an atmosphere, and the combustion of a very much smaller quantity of timber than that which has been mentioned would have sufficed to produce the poisonous atmosphere in the 130-fathoms level and in the shaft. If we take a timber supporting frame (*sett*) in a level, consisting of two side props (*legs*), each measuring 6 feet 6 inches in length and 9 inches in diameter, and a horizontal beam (*cap* or *head-tree*) 6 feet long, and of the same diameter, we have at once more than 8 cubic feet of wood. The frames were placed very close to each other; in fact, there were nearly three to the yard. In addition, the covering pieces of timber placed upon the "caps" were 4 inches thick, and were again overlaid by other timber, so that one may safely assume that in each yard of level there were more than 35 cubic feet of timber. An examination of the 130-fathoms level has shown that the fire extended for 11 yards along it, because it is blocked for that distance. Under these circumstances, though the extent of the fire may not have been very great, still there is evidence of a sufficient amount of burning to account for the disaster.

It may be a matter of surprise to some persons that the miners should have gone to their fate without any suspicion of the danger ahead. If the fire had taken place on any day except a Saturday, the men of the afternoon shift would probably have become aware of it before it had attained very dangerous proportions, and before the lack of oxygen had been the means of causing the generation of the supremely poisonous lower oxide of carbon. The intervening Sunday, when no one was down the mine, gave time for the gases to cool and the odour of burning to subside, and consequently warnings were lacking which would have been present if the mine had been entered sooner. Besides, it must not be forgotten that the miner usually considers that his candle is a sufficient indicator of the state of the air: if it burns dimly, he becomes suspicious; if it goes out, he feels that there is danger. At Snaefell the candles continued to burn brightly, and though some of the men evidently noticed a little smell and a feeling of warmth in the air, there was nothing to make them apprehend that their lives were in jeopardy, until they began to be overcome. Probably no miner in the island had ever heard of carbon monoxide and its noxious qualities.[1]

A question often asked is, "Why did not the men start to climb up the ladders the moment they began to feel the effects of the poison?" This is easily answered by those who have suffered from its effects and escaped with their lives. Carbon monoxide is a most insidious enemy, for, whilst it is easy to go on descending ladders while inhaling the poisonous atmosphere, the limbs seem to be incapable of action when the exertion of climbing upwards has to be encountered. The position in which the bodies were found confirms this view of the case.

**The Mouse as an Indicator of Carbonic Oxide.**—It will be seen from what I have already said, that the mice employed as indicators of carbonic oxide did render useful service, as I was able, whilst standing on the surface, to determine, without the slightest risk to anybody, the depth at which the air in the mine really began to get very bad, and to obtain proof of the presence of carbonic oxide in it. A mouse was also of use to me underground in testing the air below the 115-fathoms level from platform to platform, and enabled me to say without hesitation that no one should descend beyond a certain point. However, it gave no indication of the small proportion of carbonic oxide in the air above the highly poisonous parts (Plate III.), either on the Thursday or on the Saturday. It is necessary to recollect that I was using the mouse for the first time, and that consequently I may not have been so keenly alive to the early symptoms shown by the little animal as I should have been if I had practised this mode of testing before; and, further, I must add that on the Saturday, when my party

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[1] It may also appear surprising that the poisonous gas from the fire should have got back into the downcast shaft. The probable explanation is, that the return air was leaking across into the downcast shaft at various levels. In metalliferous mines the extent of this leakage across into downcast shafts is often very great, unless adequate means are taken to prevent it. To give one instance, I found that in the air near the bottom of a downcast shaft in a badly ventilated tin-mine the oxygen was diminished by 0·43 per cent., as compared with 0·48 per cent. near the top of the upcast shaft. The abundant downward current in the lower part of the downcast shaft was thus mostly made up of return air which had leaked across at various levels.—J. S. H.

suffered from carbonic oxide poisoning, I was using a tame white rat, as my supply of mice had become exhausted. The larger the animal the less speedily does it become affected, and if I had used a mouse on the unlucky Saturday, it is quite possible that I should have had earlier indications of danger. On the whole, I must confess that the test with the mouse does not appear to me to be so delicate as supposed by Dr Haldane, or at all events it is not so delicate in the hand of an unpractised observer.[1]

Finally, I may remark that the Snaefell calamity, like other disasters all over the world, had a sunny side, for it brought out the nobler qualities of many gallant men. Captain Kewley behaved heroically in leading the plucky band of rescuers, and so did my assistant, Mr Williams. Their names will not be forgotten in the Isle of Man in this generation. I was greatly gratified on learning that their noble conduct had been brought by His Excellency the Lieutenant-Governor

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[1] A rat weighs about ten or twenty times as much as a mouse, and would take two or three times as long to react to a given percentage of CO. It is possible, therefore, that the party, when they reached the fifth platform, were from the beginning standing in actually poisonous air on the Saturday, the rat not having been left long enough on that platform to really test the air. A period of fifteen minutes would have been needed for this purpose. It seems more probable, however, that the air down to the fifth platform was at first fairly free from CO, but that the slight rise in temperature due to the presence of the party and their lights produced a current upwards of foul air in the ladderway (the middle compartment) of the shaft. This current probably carried some carbonic oxide up to the 115-fathoms level, to judge by the symptoms of those who were sitting there. Had the air at this point been fairly free from CO, the faintness produced by the exertion of climbing would soon have passed off.

It is undoubtedly the case that a mouse will not indicate by its symptoms such small proportions of CO as were present on the Thursday below the 100-fathoms level. As the mouse test has sometimes been misunderstood, it may perhaps be well to quote the following warning from my description of it in the *Transactions of the Institution of Mining Engineers*, 1896:—"It should be understood that this test cannot be relied on to do more than indicate the presence of actually dangerous proportions of carbon monoxide, for only a practised observer could detect the outward signs of slight symptoms in a mouse, whereas correspondingly slight symptoms in a man might be very distinctly felt. If the mouse merely shows signs of weakness of the legs, there will be danger to a man, though probably not for twenty minutes or half an hour. If the mouse becomes quite helpless and unable to stand, there is danger within a few minutes to a man. If the mouse becomes unconscious and goes into convulsions, there is urgent danger, and not a moment should be lost before retreating."

For detecting very small percentages of CO the mouse must be used in the manner described on page 147. After a recent fire at Dolcoath Mine in Cornwall the whole of the workings were explored by this latter method, and the men allowed to return to work in all parts where an examination of the blood of the dead mice showed that appreciable quantities of CO were absent.—J. S. H.

of the Island to the notice of the Chapter of the Order of St John of Jerusalem, and that the silver medal for saving life on land had been awarded to each of them. Unfortunately, absence in Canada prevented my attending the meeting at which the medals were presented by His Excellency on behalf of His Royal Highness the Prince of Wales, Grand Master of the Order, and I was unable to express publicly my admiration of the gallantry displayed by Captain Kewley and Mr Williams. Captain Kitto and Mr Wynne-Finch, with a party of men from Foxdale, likewise did useful service; and my assistant, Mr Jones, will have the satisfaction for the rest of his days of knowing that he saved a comrade's life under very critical circumstances.

Dr Miller's prompt aid to the injured contributed greatly to their recovery, and must not be forgotten.

In obedience to your Special Instructions, I have penned an account of my sensations under the influence of carbonic oxide, and I have collected statements concerning the effects of the gas from Mr Williams, Mr Jones, Captain Kitto, and Mr Wynne-Finch. These I have placed in an Appendix. I need hardly say that we none of us desire to parade our experiences in public; we relate them at your request, in the hope that the account may be of some service to persons exposed to the risk of carbonic oxide poisoning, or at all events be of scientific interest to physiologists.

## STATEMENTS CONCERNING THE SENSATIONS, SYMPTOMS, AND AFTER-EFFECTS OF CARBON MONOXIDE POISONING.

### Dr C. LE NEVE FOSTER.

On the 13th May I did not notice any unpleasant symptoms while in the mine, but after having been on the surface for a little time I had a decided headache across the forehead. On the following day we did not go down below the 100 level, and felt no inconvenience whatever in any shape or form. On the fifteenth there was certainly a feeling that the air as we descended was less good than on the previous day; but this in no way interfered with my work, such as testing the air from platform to platform below the 115; nor was my power of deciding that it was unsafe to descend to the corpse itself in any way impaired. I cannot recall any symptoms undoubtedly due to carbon monoxide, until I reached the 115 level, after having climbed rapidly up the ladders, when Captain Kewley gave the alarm that he was feeling ill. The poison took effect most suddenly; probably its action was accelerated by the exertion of climbing rapidly. I felt decidedly queer when I reached the level, and thought a drop of brandy might revive me: I took out my little brandy flask, but already my fingers seemed incapable of doing the work properly, and someone unscrewed the stopper for me; I took a small sip and sat down. Everything then seemed in a whirl, and the atmosphere seemed to be a dense white fog. This must have been, as far as I can judge, a little before 1 p.m., for we went down precisely at noon, and allowing full time for the descent and testing the air from platform to platform below the 115, I do not think an hour had elapsed after leaving the surface before we were taken ill.

Sitting next to me was Mr Williams, and within a few feet were Captain Reddicliffe and Henry Clague; the men who had remained all the time at 115 level, or at all events had not descended as low as we did, had started to climb to the surface, but of their starting I have no recollection. A curious fact is that we all sat without moving or trying to escape: the foot of the ladder was close by, yet none of us made any effort to go to it and ascend even a single rung. We none of us tried to walk a dozen steps, which would have led us to the other side of the shaft partition, where we all knew that there was a current of better air. We simply sat on and on; Mr Williams remained motionless like a statue; Captain Reddicliffe, on the other hand, was shouting and groaning nearly all the time, while Clague was moving his arms. Of all this I was perfectly conscious, though rooted to my seat. By my side was one of the pipes conveying compressed air, in which a hole had been punched some days before. I was perfectly conscious that fresh air was a good thing for me, and I frequently leant over and put my mouth to the hole and inhaled a good breath. How soon I realised that we were in what is commonly called "a tight place" I cannot say; but eventually, from long force of habit, I presume, I took out my notebook. At what o'clock I first began to write I do not know, for the few words written on the first page have no hour put to them. They were simply a few words of good-bye to my family, badly scribbled. The next page is headed "2 p.m.," and I perfectly well recollect taking out my watch from time to time. As a rule I do not take a watch underground, but I carried it on this occasion in order to be sure that I left the rat long enough when testing with it. In fact, my note on the day of our misadventure was: "5th ladder. Rat two minutes at man," meaning by the side of the corpse. My notes at 2 p.m. were as follows: "2 p.m., good-bye, we are all dying, your Clement, I fear we are dying, good-bye, all my darlings all, no help coming, good-bye we are dying, good-bye, good-bye we are dying, no help comes, good-bye, good-bye." Then later, partly scribbled over some "good-byes," I find, "We saw body at 130 and then all became affected by the bad air, we have got to the 115 and can go no further, the box does not come in spite of our ringing for help. It does not come, does not come. I wish the box would come. Captain R. is shouting, my legs are bad, and I feel very [1] , my knees are [1] ." The so-called "ringing" was signalling to the surface by striking the air-pipe with a hammer or bar of iron. We had agreed upon signals before we went down. There is writing over other writing, as if I did not see exactly where I placed my pencil, and then: "I feel as if I were dreaming, no real pain, good-bye, good-bye, I feel as if I were sleeping." "2.15, we are all done. No [1] , or scarcely any, we are done, we are done, godo bye my darlings." Here it is rather interesting to note the "godo" instead of "good." Before very long the fresh men who had climbed down to rescue us seem to have arrived, and explained that the "box" was caught in the shaft. Judging by my notes I did not realise thoroughly that we should be rescued. Among them occur the words, "No pain, it is merely like a dream, no pain; no pain, for the benefit of others I say no pain at all, no pain, no pain." I frequently wrote the same sentence over and over again. My last note on reaching the surface tells of that resistance to authority which likewise appears to be a symptom of the poisoning.

These notes afford ample confirmation of the effect produced by carbonic oxide poisoning of causing reiteration. I wrote the same words over and over again unnecessarily. The condition I was in was rather curious. I had absorbed enough of the poison to paralyse me to a certain extent and dull my feelings, but at the same time my reason had not left me.

The general sensation was like a bad dream, and yet I was able to reason properly and write intelligibly, though in a disjointed fashion.

I have been asked whether some of my notes may not have been written automatically or unconsciously. If there had merely been a good-bye to my wife and children I might have been doubtful on the subject, as I find that in my note-book I used some wording identical with that of a letter addressed to my wife which I had written as a matter of prudence before leaving Laxey on the morning of my first descent. After my visit to the mine on the previous afternoon, I knew there was some risk to be encountered, and I simply penned the letter for use in case things should go wrong. Fortunately, the letter was not wanted. Wholly apart from my farewells, it seems to me from my notes that I was recording things correctly, and that my brain was

[1] Word illegible.

reasoning properly ; I do not think I ever lost consciousness in the mine.

Mr Williams, on the other hand, and Captain Reddicliffe, though not absolutely unconscious, did not recognise the lapse of time, for they thought that only about ten minutes passed between my calling out " All up at once " and their arrival at the surface. In reality, nearly two hours had gone by.

That the numbness of the fingers recorded in my notes was no fancy is proved by the fact that I burnt my wrist and hand with my candle while sitting underground, and had no notion that I had done so until a friend in the evening called my attention to a big blister. I daresay this was five hours or more after the burn.

I think there certainly was a feeling of exhilaration on reaching the top of the shaft ; I was quite able to walk and was in full possession of my senses, for I at once asked Dr Miller to take a little of my blood, so that it might be tested spectroscopically. He tied a bandage round my arm, and when one of my veins was well swollen he inserted a hypodermic syringe, but no blood could be drawn. He then tried Mr Williams in the same way, but again without success. That the puncture was deep is proved by the scar which is still apparent. About an hour after I came up I sent off a telegram to my wife, which I reproduce in order to show that the effects of the carbon monoxide in producing unnecessary repetitions had not worn off : " Am perfectly right, do not believe any report to the contrary ; I repeat I am perfectly right.—Clement. Address, Peveril, Douglas."[1]

Though feeling quite able to walk to Laxey, a distance of about four miles, I took the advice of Dr Miller, and went down with some others in a trap. One of the miners who was with us was vomiting from time to time, and by and by I felt a desire to be sick also, and put my finger down my throat with the idea of assisting nature, but without effect. Soon after this I became unconscious for a few minutes ; it was not a true fainting, but something of the nature of epileptiform seizure, as I am told that I was a little convulsed, though I never had anything in the nature of a fit before. Dr Haldane has pointed out that seizures of this description are not uncommon after carbonic oxide poisoning.[2] On getting to the hotel at Laxey I lay down on the sofa with a headache, and Mr Williams suffered from headache and vomiting.

On arriving at Llandudno three days after the accident, I happened to pass our family doctor, and he told me afterwards that he at once noticed that the colour of my face was strange.

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[1] *I.e.*, Peveril Hotel, Douglas.

[2] *On the Causes of Death in Colliery Explosions and Underground Fires*, London, 1896 (C. 8112), p. 18.

A few days after I got back from the island the first time, about the 21st or 22nd of May, I noticed my heart; it could scarcely be called palpitation, as I understand palpitations to be, for there did not seem to be any increased rapidity of its action, but I was conscious of its beating; as a rule, I am not. This passed off, and then on 1st and 2nd of June I noticed it very decidedly again, so much so that I went to my doctor. He sounded me, and said the heart was all right, though there was one sound which was not very distinct. This consciousness of having a heart still returns from time to time, though only to a slight extent. On the 19th May I suffered much from headache, not regularly, but intermittently. The headache lasted for several days, and the feeling in the legs was very apparent; it was an aching in the legs from the knee to the ankles. A coldness from the knees to the soles of the feet was also noticeable; it came on occasionally for a considerable time. The headaches continued at intervals for some time, and lasted certainly for some months after the accident; indeed, I cannot say that they have disappeared altogether. Whether these headaches are still a consequence of the poisoning or not, I am unable to say. I have, at the risk of being wearisome, given the above account of the mental phenomena accompanying partial poisoning by carbonic oxide, because it is possible that they may be of assistance to those who are investigating the subject from a scientific point of view. C. L. N. F.

## Mr GRIFFITH J. WILLIAMS.

On the evening of the 10th May, I descended the Snaefell Mine, accompanied by Captain Kewley and four miners. The Captain and some of the men, who had been down several times during the day, suffered from fatigue and the effects of the poisonous gases, so they descended no lower than the 74-fathoms level; but Frederick Christian, who had a brother among the victims, accompanied me to the platform immediately above the 100-fathoms level. At this point a stiffened corpse blocked the manhole, and we could proceed no farther.

While descending, I had suffered no discomfort except from a burning sensation in the throat and chest, and a perceptible increase in the temperature of the air in the mine as we proceeded.

We then commenced the ascent to return to the surface. This I found to be a very different task from descending, as almost immediately I experienced my strength fail; more particularly did my legs totter; my head also began to ache. We climbed very slowly, and at the 60-fathoms level we came up with our comrades, who had ascended so far and were quite exhausted. After burning about 1¼ lbs. of potassium chlorate and remaining in the gas produced thereby for a while, we continued our ascent. I felt as though a great weight had rolled off me, but the headache continued.

After a short interval at the surface, I descended with a party of men to recover some of the bodies. The lowermost point reached on this occasion was the third platform below the 60-fathoms level. We were down from two to three hours. My headache increased, and a muscular pain began in the region of the heart ; this soon became very severe, but I felt no weakness in my legs, worth speaking of, when climbing up.

As I walked up the mountain side to the "Bungalow," between one and two o'clock in the morning, I felt completely exhausted, and each time I struck my foot against any object in the dark, it seemed as though a knife pierced my forehead ; there was also severe pain at the back of the head. For the few hours I was in bed I lay wide awake ; by morning the headache was better, but I could not bear to touch the left side over the heart ; so bad was the pain that I felt it would be quite impossible for me to descend the mine on the Tuesday. At 7.30 a.m., however, I did descend, and the pain over the heart had completely disappeared before I again reached the surface about 9.30 a.m., and it has not since recurred.

In a quarter of an hour's time I descended again with a fresh party, and felt much stronger than I had done on my first descent the same morning. As time went on, I felt my strength give way ; I was also becoming stupid and sleepy, and at intervals I lost consciousness for short periods, but tried to attend to my work. The men asked me to give the signal to have the "box" raised, but I was unaware of it till Captain Kitto, who had kindly come down the mine to assist, roused me and said, "You are not well, go and sit down." To this I replied that I was all right and could go on. I recollect giving the signal, but nothing more till I found myself sitting in a level with Captain Kitto and Mr Wynne-Finch giving me some brandy. I was informed that I had fallen down insensible by the manhole. After remaining there a short time I could barely stand ; my legs were powerless ; with the aid of men pulling at a rope put around me, and others supporting me behind, I began to ascend, but my legs refused to act. Mr Wynne-Finch asked me if I would not go into the "box" ; I said "box," and right glad was I to find myself in it.

I was quite conscious when I got to the surface, and able to walk without assistance to the mine office. I did not suffer much from headache on this day, and a good night's sleep at Laxey quite cured it.

On Wednesday morning, along with my colleague, Mr Jones, and a party of miners, I descended the mine, feeling quite fresh, and intending not to return till the last body had been recovered. When one of the men, who was on the platform immediately above the 130-fathoms level, called out that his candle was extinguished, I went down to him and put my candle below the platform, when it immediately went out. We climbed up to the 115-fathoms level, and, though the atmosphere immediately below the platform was deadly, that just above it must have been comparatively free from carbonic oxide, as I felt no inconvenience whatever in climbing to the 115-fathoms platform to communicate with the surface by means of the "box." Having all in readiness for bottling the gas, I descended to the same platform, having a rope lashed round me at the arm-pits. William Christian and Robert Cubbon, two strong and willing young men, were on the same platform with me, while my colleague, Mr Jones, and some other men held the rope on the platform above. With my legs through the manhole and my head well above it, I succeeded in filling two bottles with the gas and corking them ; then I discerned a strong disagreeable smell rising from below. I am told that I took a third bottle and put it down through the manhole ; I have no recollection whatever of doing this, though it must have been the case, as I found the bottle, along with my cap, at the 130-fathoms level, five weeks after, close to where Kelly's body had lain. My next sensation was indescribably pleasurable, and one which I wished to last for ever, for, as it passed away, and I recovered consciousness, I ungratefully said to Dr Miller, "Why did not you let me die ?" I then inquired where I was and what the time was. A feeling of sickness followed, which the doctor told me was partly at least due to his treatment of me in bringing me round. I then became somewhat hysterical, but was soon able to get off the sofa on which I had been placed. The characteristic band of headache across the forehead, and the pain at the back of the head, troubled me through the rest of the day, but, thanks to the careful treatment I received from Dr Miller, and the kind nursing of Mrs Hall at Laxey, I got a good sleep and felt quite well by morning.

On Thursday, along with others, I descended under the guidance of my chief, Dr Le Neve Foster, and suffered no inconvenience in any way.

On Friday, the air was so good up to the greatest depth reached by us (though Dr Foster's mice and candle tests indicated that the air was still bad below), that it was, as Dr Foster remarked in ascending, quite a pleasant climb.

On Saturday, I experienced no unusual sensation, nor did I detect any smell similar to that of Wednesday ; in fact, I had no suspicion there was anything whatever wrong, till Dr Foster called out, "Kewley is bad, all up at once to put him in the 'box.'"

I recollect turning round to start climbing, but I have not the faintest idea how I managed to climb up the ladders for 80 feet to the 115-fathoms level, and only know from the testimony of others that I did so. John Kelly tells me that he took hold of me at the top, *i.e.*, just at the 115-fathoms level, to help me. There, I am told, they seated me. How long I remained in a completely unconscious state I know not; but some time before I was removed I felt at intervals a great weight on my head; possibly these sensations occurred at the various times when one of the rescue party poured a hatful of water on to my head. I imagined I was dead, then I thought I was in a horrid dream. I could see a black object pass up and down before my eyes, as one sees an object move between the closed eyes and the light; this I was afterwards told must have been Captain Reddicliffe's arms; he sat close by me, and moved his arms up and down. I had a sense of something revolving inside my head from left to right. Then I could hear the signals being given to communicate with the surface. Giving the signals had been part of my duty all through the sad days of the week: among other signals, three strokes on the compressed-air pipe were meant to tell those at the surface to raise the "box"; six strokes told them that all was right. I was able to count the number of strokes given, and when they passed three I knew there was something wrong, and I wanted to say so; I was struggling inwardly to speak, but could not.

When I recovered consciousness, I was being carried in a horizontal position to be put into the "box," which was only a few yards distant, to be sent to the surface. I could speak and could fully understand what was being told me. I was conscious all the way up the shaft, and I know I shook hands very heartily at the top of the shaft with some of the men who had been repeatedly down the mine with me during the week, but I could not bear to have anyone order or contradict me: I *would* have my own way. I insisted, not with very good grace, I fear, on walking by myself to the office, and Dr Miller, who thought I ought to allow myself to be carried, at last said to me, "Walk, then, you pugnacious little fellow!" When I sat down at the office, I became unconscious again for fifteen or twenty minutes; the first thing I recognised afterwards was Henry Clague, one of the miners, who was moving his limbs convulsively while sitting in a chair in front of me. This must have roused me. I asked if that man was Clague, and if the place we were at was the Snaefell Mine office.

From this time I was fully conscious, and although I felt excruciating pain in the head, I was able to go down to Laxey; the pain continued all the evening, but it had quite left me by Sunday morning.

My face wore a deep red blotchy appearance for some time, and my friends on the mainland remarked upon it repeatedly, even as late as the 23rd of May. I also suffered from weakness.

In my case, any ill defects which I could attribute directly to carbonic oxide poisoning passed quickly away, and I am not aware that the experiences of the week have done me any permanent harm.

G. J. W.

## Mr O. R. JONES.

On Wednesday, the 12th May, at 8 a.m., Mr Williams and I descended the mine. Between that hour and 11 a.m. five dead bodies were recovered. After sending the fifth body to the surface, Mr Williams decided to take some samples of the bad air in the shaft. For this purpose he descended to the platform just above the 130-fathoms level, and, being aware of the risk he was running, he took the precaution of having a rope lashed round him, the tail-end of which was held by me and some miners standing on the platform above. Mr Williams had three bottles with him, and emptied the water from two of them, and recorked his bottles. To all appearances, he was not suffering from the effects of gas up to this moment. He then took the third bottle, and while he was in the act of emptying the water from it he collapsed and fell suddenly, as if he had been shot. As the rope was already round his body, I lost no time in dragging him up, with the aid of some of the miners. While he was being dragged up the first three ladders he was groaning very much, but before he was on the platform at the top of the fourth ladder he had ceased groaning. We had some difficulty in getting him to the top of this ladder, as we felt our own strength going. When we examined him we found that he was not breathing at all, and his eyes were wide open. We poured some brandy into his mouth, but he did not swallow it. We then dragged him up one more ladder to the level. He then appeared to be quite dead. The "box" was already in this level; but we did not send him up at once, as packing him into the "box" and sending him to the surface would have taken a considerable time, and we thought it more prudent to make an effort to revive him on the spot. We carried him to a compressed-air pipe in which a hole had been punched, and I sat down under him and kept his mouth at the hole whilst two of the men were working his arms backwards and forwards. As nearly as I can guess, about ten minutes elapsed before he began breathing again. Brandy was given to him several times, and when his heart began to beat he was put into the "box," though still quite unconscious, and sent to the surface. When I tried to get up to carry Mr Williams to the "box," I discovered that my legs were in a semi-paralysed state, and I had to sit down again by the compressed-air pipe for about half an hour. After this rest I started climbing, and reached the top of the second ladder all right, and then all of a sudden I collapsed. I thought that my heart was stopping, but I soon recovered. The same thing happened three times before I reached the surface, when I vomited and suffered from a very bad headache. I felt the effect of the poisoning in my legs for some weeks, besides suffering from palpitation of the heart on several occasions afterwards, though never troubled by any heart affection previously. O. R. J.

## MR W. H. KITTO.

The effect upon me of the air of Snaefell Mine was peculiar ; physically, I am fairly strong, but in going underground the first time, and before reaching the 115-fathoms level, I felt slight pain and weakness in my knees, and the back of my throat, and my tongue and lips became parched. My eyes felt as if they were too large for their sockets ; there was also a throbbing in my temples and a burning sensation about my heart and throughout my body, but there was no pain worth mentioning, with the exception of that in my knees. This, no doubt, was aggravated by climbing the ladders, as there has scarcely been any of this treadmill work with us at Foxdale for many years past. However, on reaching the 115-fathoms level, and as soon as we had commenced to recover the bodies, I felt better, and able to go about and do anything ; but on starting to climb up the ladders to the surface the peculiar sensation returned, and I feel sure if it had not been for some brandy, a flask of which I had the precaution to take with me, I certainly would have failed on my way up. On reaching *terra firma* I felt very ill and wanted to vomit. When we got down to Laxey Dr Miller gave me a dose of something which did me good, but through the night I had severe palpitation of the heart, a thing I have never felt in my life before or since. On the Wednesday my experience underground was something similar, but I did not feel so ill on reaching the surface. The day following, Thursday, the pain in my knees was so great that I could not stand properly, and for fully a week I had great pain when walking, and still (10th June) feel slight effects of the poisoning. W. H. K.

## MR HENEAGE WYNNE-FINCH.

On Tuesday, May 11th, 1897, at 11.45 a.m. I went down the Snaefell shaft, forming one of a party led by Captain Kitto, of the Foxdale Mine.

I spent three hours below ground at the 100-fathom level, and while at work there felt no symptoms of discomfort with the exception of a slight nausea due to the gases exhaled by the dead bodies.

On starting to return to the surface I found that my legs had partially lost strength and had become heavy and numbed. My arms were not appreciably affected, and the only other symptom I noticed was an unusual shortness of breath. This was, no doubt, due to the fact that the exertion of climbing rendered the badness of the air more distinctly appreciable to the lungs. With the aid of my arms I climbed very slowly and with considerable difficulty to the surface.

On Wednesday, May 12th, I went down shortly after 3 p.m. The party consisted of men from Foxdale Mine led by Captain Kitto. Our object was to find and if possible recover the one remaining body. The air was known to be bad below the 115-fathom level, and my portion of the work consisted in punching holes in the compressed-air pipes to freshen the atmosphere as we went down. This necessitated my descending first with a rope attached to my body to avoid accidents.

While I was striking the punch I noticed once or twice a violent quickening of the heart's action, which, however, passed off again after a few moments in each case. At about 5.15 p.m. I had just climbed back from the open portion of the shaft on to one of the platforms, after making a hole in the air-pipe. The platform in question was, I believe, the fourth below the 115-fathom level. At this point a sudden giddiness seized me, lasting a few seconds only and then passing off. A minute or so later, the same sensation recurred more strongly, together with a pain in the head and an unpleasant feeling of pressure on the chest, almost amounting to pain. As the giddiness continued, and I felt my legs growing weaker, I decided at once to climb to the 115-fathom level, fearing that if I waited longer I might have to be lifted up with ropes. It was necessary to reach this latter point, as it was the lowest point at which the "box" was accessible, the hoisting compartment of the shaft being boarded off from the ladder road except at the different levels. After I had removed the rope from my body I began at once to climb. As I felt the effects of the gas rapidly increasing, I climbed as fast as possible, so as to get to the level above before I was overpowered.

Before I had climbed the first ladder my eyesight began to be impaired, and, though there were men stationed at each landing, I could not see them. On calling out to them as I passed, however, I was able to hear and understand their answers in each case. The position of the ladders rendered it possible for me to climb without the use of my eyesight. The last ladder I was only able to get up with a great effort, and I am not sure whether I climbed or was pulled through the manhole at the top.

On reaching the 115-fathom platform, I lost all physical power, and both my breathing and the action of my heart became much affected. Paroxysms of rapid breathing set in, during which respiration was very laboured.

During the periods of apparent inaction of the lungs between the fits of hurried breathing, I experienced no particular pain or discomfort, feeling only extremely weak. I could still hear and understand all that was said to me, as well as speak intelligibly myself, but had entirely lost physical power, besides being unable to see or recognise faces even when quite close to me and in a tolerably good light. My eyes at this point could only discriminate between light and darkness, and seemed to have entirely lost the power of focussing objects. After I had been lifted into the "box" I remember explaining to the man how to strap me in, etc. I was quite conscious during the time that I was being drawn to the surface, and can remember all that occurred on the way up, including the catching of the box on the timber about half way. On reaching the surface I could see nothing distinctly, though my eyes were conscious of the brightness of the light. I attempted to walk from the shaft top, but had not sufficient strength, and was consequently carried to Captain Kewley's house, where I was immediately attended by Dr Miller, of Laxey.

Paroxysms of difficulty in respiration continued at intervals for between two and three hours from the time that it began in the mine.

I do not think I was ever quite unconscious, but for an hour or so after I came up I could not see properly. About two hours after I reached the surface I was sick, which relieved me considerably.

The sense of weakness was greatest just before the sickness mentioned above, and for about ten minutes at this time I experienced a sensation of complete collapse. I can only describe this by saying that all vital functions appeared to have stopped. After the sickness a severe frontal headache came on, which lasted for nearly four hours, and then wore off gradually.

At about nine o'clock I was lifted into a trap and taken down to Laxey, still having no power to move.

By the following morning the physical effects of the gas had quite passed off, though for several days afterwards I noticed a certain amount of weakness in my legs.

I may add, in reference to my mental condition during the time that I was under the influence of the gas, that, while my head was tolerably clear, there was undoubtedly a certain incompleteness in the action of my memory. The persistence of one or two ideas seems to have been very marked. I repeated five or six times to Captain Kitto my desire that the men should not be allowed to attempt to go any lower that day. This request was dictated by my sense of the suddenness with which the effects of the gas had overtaken me. On each occasion I was assured that nothing more would be attempted that day, and under ordinary conditions one such assurance would certainly have been sufficient for me. This, I think, shows that the action of my brain and my memory were somewhat impaired.

I am informed by a friend of mine who was present at the time that during the few minutes before my sickness, to which I have previously alluded, I appeared to be quite unconscious. He tells me that at this time he spoke to me more than once without receiving any sign of recognition on my part, while all sign of respiration appeared to have ceased. From my own recollection, however, I am sure that I was not entirely unconscious, as I distinctly remember a *consciousness* of the sensation of complete collapse mentioned above. H. W. F.

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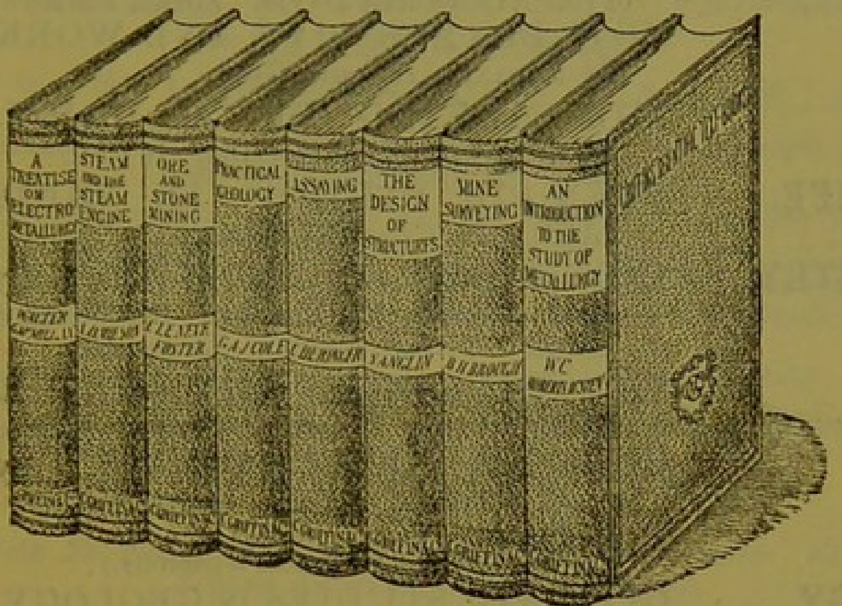

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